Synthesis and characterisation of wide-bandgap semiconductor nanostructures towards opto-electronic applications

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**SYNTHESIS AND CHARACTERISATION OF
WIDE-BANDGAP SEMICONDUCTOR NANOSTRUCTURES
TOWARDS OPTO-ELECTRONIC APPLICATIONS**

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*The knowledge of anything, since all things have causes, is not acquired or
complete unless it is known by its causes.*

Ibn Sīnā

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Abstract

Semiconductor structures offer unique properties at the nanoscale. Mastering the growth of semiconductor crystals and fabrication processes is crucial towards developing better opto-electronic devices. Morphological variations at nanoscale have a direct effect on available electronics states, impacting fundamental electronic properties and photonics capabilities of the material. This thesis focuses on one-dimensional Gallium Nitride (GaN) nanowires, Graphene Quantum Dots (GQDs) and two-dimensional hexagonal-Boron Nitride (hBN).

First, synthesis of semiconductor nanostructures with a focus on nanoparticle mediated growth of one-dimensional Gallium Nitride crystal is developed. Catalyst-assisted growth of GaN nanowires using a Low Pressure Chemical Vapour Deposition (LPCVD) system is shown. The choice of growth catalyst influences directly the GaN crystal and the morphology of nanowires along with growth parameters such as temperature, vacuum pressure, precursor gases or time. An uncommon nanostructure of GaN in the shape of pine trees is introduced.

Next, promising emission from GaN nanowires and hBN monolayers in the visible range is reported. Defects in LPCVD-grown GaN nanowires show yellow and green luminescences. Besides, femto-second pulsed laser is used, on defect-free nanowires grown by molecular beam epitaxy, to intentionally induce optically-active defects. Above a laser threshold power the irradiated GaN nanowires melt, higher power sublimates the crystal. Irradiated GaN is characterised as Wurtzite crystal and show emission in the visible range, additionally to the band-to-band UV luminescence. Similar experiment on hBN monolayers show defect-related visible emission near the irradiated areas. Contrary to GaN nanowires, where a wide emission is observed, hBN defects show strong and sharp emission. Point defects created in hBN - monolayers and flakes - are shown to be single photons emitters.

Finally, fabrication of efficient micro- and nano-scale emitters is of crucial importance for optical nano-devices. In conventional semiconductors, such as Si or GaAs, fabrication processes can involve expensive and time consuming electron beam lithography and etching. Us-

ing femto-second pulsed laser, efficient and cost-effective GaN and hBN-based localised micro and nanometer-size light emitters can be fabricated using optically active defect states. Coupling these nano-emitters with surface plasmons of another nanostructure can improve the emission rate as shown by coupling GQDs to single Bi_2Te_3 nanoplates.

From synthesis by chemical vapour deposition methods to structural and optical characterisation, this thesis will show how emission wavelength can be modulated and localised micro-/nano-emitters be fabricated before coupling them with surface plasmons to improve the emission rate for more efficient and bright emitters.

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Acronyms

Abbreviation	Description
CCD	Charge-Coupled Device
CFD	Constant Function Discriminator
CVD	Chemical Vapour Deposition
CW	Continuous Wave
EBL	Electron-Beam Lithography
EDX	Energy-dispersive X-ray spectroscopy
FIB	Focused Ion Beam
<i>fwhm</i>	Full Width at Half Maximum
GaN	Gallium Nitride
Ge	Germanium
GL	Green Luminescence
hBN	Hexagonal Boron Nitride thin film
HFET	Hetero-junction Field-Effect Transistor
HVPE	Hydride Vapour Phase Epitaxy
IPA	Isopropyl alcohol
LASER	Light Amplification by Stimulated Emission of Radiation
LIDT	Laser-Induced Damage Threshold
LO	Longitudinal Optical
LPCVD	Low Pressure Chemical Vapour Deposition
MOCVD	Metal-Organic Chemical Vapour Deposition
MBE	Molecular-Beam Epitaxy
NME	Near-Band-Edge
N-GQD	Nitrogen-doped Graphene Quantum Dots
Ni	Nickel
NW	Nanowires
PbS	Lead Sulfide
PL	Photoluminescence
PMMA	Polymethyl-Methacrylate
PMT	Photomultiplier tube
RCA	Radio Corporation of America
RHEED	Reflection high-energy electron diffraction
RTA	Rapid Thermal Annealing
sccm	Standard Cubic Centimeters per Minute - $1 \text{ sccm} = 1.7 \times 10^{-8} \text{ m}^3 \cdot \text{s}^{-1}$
TAC	Time-to-Amplitude Converter
TEM	Transmission Electron Microscopy
TMDC	Transition Metal Dichalcogenide
TO	Transverse Optical
TCSPC	Time-Correlated Single Photon Counting
...	

Abbreviation	Description
...	
UHV-TEM	Ultra-High-Vacuum Transmission Electron Microscopy
UV	Ultra Violet
VLS	Vapour-Liquid-Solid
VLSI	Very-large-scale integration
XPS	X-ray Photoelectron Spectroscopy
YL	Yellow Luminescence

CHAPTER 1

Introduction

The microprocessor industry started with the Intel 4004 in 1971 with 2000 transistors at 10 μm , in 2017 the AMD Vega showed twelve billion transistors at 14 nm lithography on similar surface area. The technological prouesse to reduce production cost and energy consumption while increasing the computational power is remarkable. Yet, in the era of information, the demand is increasing more than ever before. Looking at the information and communication technology (ICT) sector only, it represents 4-6% of the global power consumption in 2017 with a predicted increase up to 20% by 2030 [11].

The limitations of the continuous shrinking of electronics are known [12] while these integrated circuits are exclusively using electrons to trigger logical gates. The most viable solution today to reduce the energy consumption at high bit rates resides in dense photonic networks introduced into processor chips, with a large number of ultra-small photonic devices such as light sources, optical memories, and photodetectors.

Photonics is the science to generate, detect and manipulate photons. The word ‘photonics’ is derived from the Greek word ‘phos’, meaning light, and appeared in the 1960s with the discovery of laser (‘light amplification by stimulated emission of radiation’). When photons are used to transport information instead of electrons, it opens opportunities for low energy devices while increasing tremendously the amount of information transferred. This allows an entirely new approach for integrated circuits and allows various applications. Today, photonic-based technologies surround us from LED lights, flatscreen TVs, LIDAR sensors in driverless cars, laser-guided missiles, solar panels or tomographic scans.

The potential of integrated photonics was recognised following the early studies of waveguides in silicon-on-insulator (SOI) wafer structures in 1985 [13]. First commercialisation turned to wavelength-division-multiplexing (WDM) telecommunication products where chips were able to multiplex many channels of high-speed data into one single fibre using complementary metal-oxide-semiconductor (CMOS) fabrication process. This demonstrated the fundamental potential of the technology. Photonic integrated circuits (PICs) have today revolutionised the optical communication market with compact and more complex systems at low cost.

Unlike markets such as chemical, bio-sensing or medical instrumentation also see a great

potential to replace their bulky and costly instrumentation made of lasers, microscopes, discrete modulators, detectors and imagers by small all-in-one photonic-based chip. Indeed, key life science companies see opportunities of integrating and miniaturising their optical instruments and developing sensors to bring personalised diagnostics and therapeutics for more efficient and cost-effective medical procedures [14].

For efficient PICs, it is needed to develop small photon-based power splitters, multiplexers and demultiplexers, modulators, photodetectors, and light emitters. A marriage between physics, material sciences and electronic engineering is crucial to fabricate these components and effectively confine light in nano-structured materials.

Research Problems

The source and detector of light are the building blocks in photonic-based components. Integration of nanoscale light sources is a very challenging task, and at this moment requires laborious and expensive assembly methods such as flip-chip or bonding. The development of integrated hybrid systems based on III-V semiconductor materials on Silicon or a combination of dielectric and plasmonic materials seems to be an unavoidable path towards an ‘all-photonics’ signal processing and communication. Indeed, Silicon-based processes are unavoidable due to their low cost, large scalability and maturity while III-V semiconductors show great optical properties and already commercialised applications such as LEDs.

Low-dimensional semiconductor structures such as thin films (2D), nanowires (1D) and quantum dots (0D) have shown to be good candidates for sub-wavelength lasers and LEDs [15, 16], and fabrication as well as heretogenous integration into mainstream photonic circuit platforms is manageable. However, in light sources with dimensions smaller than the emission wavelength, the confinement of light is weak. Mastering the growth of semiconductor crystals and fabrication processes at the nanoscale has become crucial while morphological variations of the semiconductor crystal have a direct effect on light emission and influences available electronics states, impacting fundamental electronic properties and photonic capabilities of the material.

From synthesis of nanoscale semiconductors to light emission, the following questions rise

and are discussed in this thesis: how to fabricate high-quality III-V semiconductor nanostructures using low-cost, scalable and Silicon-compatible technologies? Can morphological variations in crystal lattice be used as efficient radiative emitters? How to generate or passivate morphological irregularities in crystal lattice to control the emission? How to engineer electronic states to create micro-/nano-emitters in the visible range? How to engineer the electromagnetic environment of a nanoscale light source by nano-structures to enhance the emission?

To meet the answers, this study will focus on Gallium Nitride, Boron Nitride and Graphene materials, in their 1D, 2D and 0D form, respectively. Although very different, III-V materials are already known for their optical properties. GaN is widely known for its use in light-emitting diodes since the 1990s. Graphene quantum dots have shown promising electronic and optical properties, often considered to be the future nano-emitters due to their excellent properties such as resistance to photo-bleaching, low toxicity, bio-compatibility, abundance in nature, and low cost. Hexagonal Boron Nitride, given its wide band gap, presents a Graphene-like structure, high thermal conductivity and chemical stability, show naturally a deep ultra violet photoluminescence.

This thesis investigates three main themes: synthesis of nanostructures, visible emission from defects and emission rate enhancement of emitters. The synthesis of nanostructures is studied mostly on GaN one-dimensional nanowires using a commercial Low-Pressure Chemical Vapour Deposition (LCPVD) system. Influence of growth parameters and nature of catalyst are shown to influence greatly the morphology and crystallinity of the semiconductor, while a novel type of GaN nanostructure is introduced. The visible emission is studied from structural defects in GaN and BN semiconductors. Along with the fundamental band-to-band emission in the ultra-violet (UV) range, GaN and BN are shown to be promising emitters in the visible range owing to defect-related inter-band radiative states. Finally, Graphene quantum dots, emitting in the visible range, are used to show how emission can be enhanced using surface plasmons. Emission rate enhancement from Graphene quantum dots coupled with Bismuth Telluride nano-plates is shown.

Outline

The chapter two will introduce the three different materials studied in this study, GaN, BN and Graphene, by focusing on the basic properties that will be useful for the next chapters. Then the optical characterisation methods such as photoluminescence or Raman spectroscopy will be introduced.

The chapter three will develop the synthesis methods of semiconductor nanostructures with a focus on nanoparticle mediated growth of one-dimensional Gallium Nitride crystal. Catalyst-assisted growth of GaN nanowires will be presented using a Low Pressure Chemical Vapour Deposition (LPCVD) system. We will see how the choice of catalyst influence the GaN crystal and the morphology of nanowires while also studying the influence of growth parameters such as the temperature, pressure, precursor gases or time. Finally, an exotic nanostructure of GaN in the shape of pine trees will be introduced.

In chapter four we will show that GaN one-dimensional structures grown by LPCVD show high concentration of surface states emitting yellow and green luminescence besides the near-band edge emission. This emission can be selectively suppressed by passivating the point defects source of the emission. Then we will study the defect-related emission from the exotic pine tree-like nanostructure of GaN with a structural and optical characterisation.

In chapter five, we will study how it is possible to intentionally induce point defects in GaN standing nanowires and hBN two-dimensional structure to create localised micro- and nano-emitters. A method based on femto-second pulsed laser irradiation shows a cost-effective and scalable method to create energy states below the conduction band that act as effective radiative states in the visible range. We show that a femtosecond laser-assisted ablation of GaN creates nano-emitters that exhibit a strong gaussian photoluminescence localised at the ablated area. The emission peaks at 626, 653 and 680 nm for GaN thin film, intrinsically doped and Mg-doped nanowires, respectively. Laser processed hBN flakes exhibit sharper emission, brighter colour centres and better single photon emission compared to monolayers.

Finally, the chapter six explores a method to improve the emission rate from radiatively active states such as those observed or created in GaN and hBN. To show this method we

couple quantum dots of Graphene with single Bi_2Te_3 nano-plates. Easier to couple than GaN nanowires or hBN thin film or flakes, Graphene quantum dots (GQDs) also show excellent properties for visible emitters. This chapter shows the emission rate enhancements from N-doped GQDs coupled with single Bi_2Te_3 nano-plates. With ~ 500 nm-diameter Bi_2Te_3 nano-plates, we improve the emission rate enhancement by ~ 2.9 . We first show that the quantum yield of the N-GQDs is almost unity, showing a promising active medium for optoelectronic applications. Then, we show that single Bi_2Te_3 nano-plate is an alternative plasmonic antenna for enhancing spontaneous emission rate beside semiconductor and conventional metal antennas.

Semiconductors offer unique properties at the nanoscale. Mastering the growth of semiconductor crystals and fabrication processes is crucial towards developing better opto-electronic devices. Morphological variations at nanoscale have a direct effect on available electronics states, impacting fundamental electronic properties and photonics capabilities of the material. This thesis focuses on one-dimensional Gallium Nitride (GaN) nanowires, Graphene Quantum Dots (GQDs) and two-dimensional hexagonal-Boron Nitride (hBN). From synthesis by chemical vapour deposition methods to structural and optical characterisation, this thesis will show how emission wavelength can be modulated and localised micro-/nano-emitters be fabricated before coupling them with surface plasmons to improve the emission rate.

CHAPTER 2

Introduction to Wide-Bandgap Semiconductors and Optical Characterisation Methods

Chapter two focuses on the basic properties of wide-bandgap materials used in this thesis. Beginning with Gallium Nitride (GaN), Boron Nitride (BN) and Graphene Quantum dots are introduced. Then optical characterisation systems used to characterise these materials are presented, from theoretical point of view to practical limitations.

2.A Introduction to Wide-Bandgap Semiconductors

The best way to understand this section would be to introduce the photoelectric effect that will be, directly or indirectly, at the center of the talks and experiments in this chapter.

The photoelectric effect, observed by H. Hertz in 1887 and described by A. Einstein in 1905 [17], happens when a photon ($h\nu$) interacts with matter, a bound electron in an atomic or molecular orbital or in an energy band of a solid. In an element A it can be described as follow:

$$h\nu + A \rightarrow A^+ + e^- \quad (2.1)$$

The photon interaction with the element A create a free electron that can be collected and transferred for other use. This photon-generated electron, a photoelectron, obtains the kinetic energy E_k :

$$E_k = h\nu - E_b(nl), \quad (2.2)$$

where $E_b(nl)$ is the binding energy of electrons in the atomic orbital with quantum numbers ' nl '. The lowest photon energy needed to create a photoelectron is

$$h\nu_{min} = I(A), \quad (2.3)$$

where $I(A)$ is the ionisation energy (the binding energy of the outmost electron shell) of the element A. It varies significantly, being lowest for the alkali metals and highest for rare gas atoms, as seen in figure 2.1.

In solids, the electrons form bands, seen as the collection of interactions between the discrete energy levels of many individual atoms. The bands can be regarded as distributions of very closely packed quantum states. The overall band structure is characterised by the density of states function $D(E)$, which tells how many electrons can be in an energy range $[E, E + dE]$. The quantum states of the bands are filled up to the Fermi level E_F . The electrical properties of the material are determined by the position of the Fermi level (see figure 2.2, defined simply as the highest energy level occupied by electrons at the temperature 0 K).

Figure 2.1: Periodic trends for ionisation energy vs. atomic number. © Creative Commons

In semiconductors or insulators, the highest band containing electrons is defined as the valence band while the next empty band above is the conduction band. The distinction in metals is more blurry whether the electrons in the uppermost band are in the valence or conduction band. The gap between these two is naturally called the ‘band gap’, characteristic of the semiconductor or insulator.

Figure 2.2: Classification of solids according to their band structure.

In semiconductors, the bandgap is small and mastering the separation between the valence and conduction bands is a challenge that can be overcome by thermal, electrical, or chemical excitations.

In the following, we will present more specifically the properties of the semiconductors studied in this work: Gallium Nitride, Boron Nitride and Graphene. Then we will introduce the optical characterisation methods used during this work.

2.A.1 Gallium Nitride

Like Boron Nitride, Gallium Nitride is a III-V compound semiconductor obtained by combining group III elements with group V elements.

Gallium Nitride (GaN) presents a high Young modulus, thermal conductivity and electron mobility, it has a high melting point (2500 °C) and low chemical reactivity. GaN exhibits great material properties with direct and wide band-gap. It also shows high charge carrier mobility, and excellent thermal stability [18, 19] which allow a wide range of applications from high-speed MOSFETs [20], light-emitting diodes and lasers [21, 22] to micro resonators, chemical sensors, and highly sensitive atomic probe tips.

Gallium Nitride is known to crystallise in two crystallographic structures: Zincblende (cubic) and Wurtzite. A Wurtzite structure is made of two embedded hexagonal close packed (*hcp*) lattices, one is for Ga atoms while another is for nitrogen, as shown in figure 2.3. Both *hcp* lattices are offset by $3/8$ along the *c*-axis of the matrix height. Alternate layers of Gallium and Nitrogen atoms are stacked according to an Ga and N alternation in the (0001) direction.

Figure 2.3: a. Wurtzite structure of GaN - ©Creative Commons. b. Brillouin zone of the *hcp* lattice of Wurtzite GaN structure.

One can notice that the Wurtzite structure does not have an inversion plane perpendicular to the *c*-axis which means that directions (0001) and (000 $\bar{1}$) are not equivalent. Therefore, two polarities can be found: a metal polarity if the Gallium-Nitrogen bond is directed towards the surface or a nitride-polarity in the reverse case.

This absence of centro-symmetry and highly ionic bonds are responsible for intrinsic physical properties of Wurtzite GaN, such as spontaneous electric polarisation and piezoelectricity.

Table T2.1: Basic parameters of GaN Wurtzite crystal. [5]

	GaN	Unit
Crystal Structure	Wurtzite	
Gap	Direct	
Lattice constant, a	3.189	Å
Lattice constant, c	5.185	Å
c/a	1.626	
Bandgap energy, E_g	3.42	eV

Spontaneous polarisation field can be measured along $(000\bar{1})$ direction, whereas piezoelectric polarisation appears along $(000\bar{1})$ and (0001) under tensile and compressive stress respectively. These polarisation properties can induce significant improvements in GaN-based electronic devices. For example, in $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ hetero-junction field-effect transistors (HFETs), positive polarisation charge at the hetero-junction interface contributes to the formation of a two-dimensional electron gas with extremely high carrier concentrations. However polarisation effects are not always desirable for optoelectronic devices as they provoke a red shift of the emission wavelength as well as a decrease of the recombination efficiency.

GaN is also found in the Zinc-Blende crystal structure, hard to obtain, it is usually grown epitaxially on a cubic substrate. The Zinc-Blende is formed by joining two face-centred cubic lattices with a shift of $1/4$ along the longest diagonal of the cube. However the zinc blende structure is less common since it is metastable.

The importance of the GaN for the optoelectronic industry is due to its wide bandgap. The bandgap is direct, which allows for efficient light emission. According to data that adorned the literature for years, the established bandgap values is 3.42 eV at room temperature [5] which correspond to ultra violet light. In the early 1990s, Shuji Nakamura paced the way with highly bright blue LED by growing thin film of GaN on Sapphire substrates. GaN is now a key material for LEDs, laser diodes and photo-detectors operating from visible to deep UV spectral range.

Epitaxial growth techniques allow formation of high quality material with low density of dislocations and low concentration of point defects. GaN was grown on Sapphire substrates by Nakamura for LEDs [23], and even if the cost of these substrates have decreased over the years, Silicon remains the industry standard. The lattice mismatch between GaN and Si is significant

and is the reason why the implementation is limited. The strain induced by the mismatch results in lattice dislocations that further cause the degenerescence of devices if not a failure. A buffer layer between GaN and Si to reduce the mismatch is the key for the recent GaN-on-Si developments.

In this thesis, we counter this issue by working on a one-dimensional structure of GaN. We show a low-cost process to grow GaN nanowires on Silicon substrate. Nanowires are typically free of strain because strain mismatch between the substrate and the growing GaN nanowire can readily be relieved by dislocation formation perpendicular to the (0001) planes. The small diameter of the wire and ease of dislocation glide within the c-plane allow annihilation of the dislocations at the nanowire surface, leaving the crystal to grow defect-free after a few nanometers of axial growth.

If strains dislocations are not preferred for reliable GaN-based components, some point defects in GaN crystal are known to be optically active, emitting red, yellow, green or blue luminescence [24–27]. These type of defects, if used efficiently, can be great emitters at the nanoscale. Indeed, they ideally act as 0D quantum emitters. For example, Nitrogen vacancy (N_V) center is predicted [28] in GaN crystal but the energy states of this type of defects are not always identified accurately [29,30]. Another example of red luminescence, that is observed at 1.8 eV (689 nm) with a zero phonon line at 2.38 eV (at room temperature). This luminescence is attributed to a transition from the conduction band to a deep acceptor, but of unknown origin [31].

Another III-V material showing similar properties as GaN and revealing promising for photonic applications is Boron Nitride.

2.A.2 Boron Nitride

Like Gallium Nitride, Boron Nitride is a III-V compound semiconductor obtained by combining group III elements with group V elements.

Boron Nitride (BN) appears in three major isoelectronic crystallographic structures. The cubic crystal assembly, named cBN is analogous to carbon diamond but softer and presents higher thermal and chemical stability. The Wurtzite structure of BN exists but is very rare,

Table T2.2: Basic parameters of amorphous BN [6] and crystalline BN [7, 8].

Material	a-BN	h-BN	c-BN	w-BN	Unit
Density	2.28	~ 2.1	3.45	3.49	g/cm^3
Knoop hardness	10		45	34	GPa
Bulk modulus	100	36.5	400	400	GPa
Thermal conductivity	3	600 $\parallel$, 30 $\perp$	740		$\text{W.m}^{-1}.\text{K}^{-1}$
Thermal expansion		2.7 $\parallel$, 38 $\perp$	1.2	2.7	$10^{-6}/^\circ\text{C}$
Bandgap	5.05	5.2	6.4	4.55.5	eV
Refractive index	1.7	1.8	2.1	2.05	

it is harder than diamond. The hexagonal form (noted hBN) is the most stable and layered similarly to graphite. Within a single layer of hBN, boron and nitrogen atoms show strong covalent bonds, while two different layers are held together by weak Van der Waals forces. It is worth pointing out that an amorphous form of BN exists, it is non-crystalline and analogous to amorphous carbon. The table T2.2 sums up the main characteristics of these structures such as the density, thermal conductivity and bandgap.

Boron Nitride is known for its thermal and chemical stability. Its thermal conductivity properties make it a perfect candidate for thermal management applications such as heat dissipation. Yet, thanks to its wide bandgap (5.2 eV for hBN at room temperature) fluorescence properties of hBN monolayers naturally show an ultra violet emission. Since the discovery of the deep-ultraviolet luminescence properties of hBN [32], hBN has attracted considerable attention for its applications in photonics.

Further than the band-to-band emission in the deep-ultraviolet, the wide-bandgap opens door for engineering a wide range of possibilities of states below the conduction band to modulated the emission from the ultraviolet to the visible range. Engineering structural or point defects in hBN to create radiative energy states can be achieved by annealing [33, 34], electron [33, 34] or ion beam [35] irradiation, or wrinkle process [36]. The origin of defects is predicted as three stable native point defects defined as a boron vacancy (V_B), a nitride vacancy (V_N) and $N_B V_N$ in which one nitrogen atom is missing and the boron site is occupied by nitrogen [37, 38].

As an example, Toan Trong Tran et al. created atomic point defects in hBN monolayers using annealing and electron beam irradiation, finding a photoluminescence peak around 623

nm that was closely related to $N_B V_N$ point defect with single photon characteristics [33, 34].

Engineering luminescent centres in hBN is an aspiring goal thanks to their excellent stability at room temperature [32]. Localised on-demand defects become very interesting to produce sub-band-gap defect-related sources in hBN monolayers.

2.A.3 Graphene Quantum Dots

Graphene was first produced by exfoliation of graphite consisting in peeling of a piece of graphite using adhesive tape [39]. Its form lies in a sheet of single layered carbon atom arranged in hexagonal lattice. The Oxford dictionary define the word ‘Graphene’ as “the thinnest, strongest material known to science”. It presents a high mobility and optical transparency, in addition to flexibility, robustness and environmental stability. Even though the main focus over the past decade have been on fundamental physics and electronic devices, Graphene shows an increasing interest in photonics and optoelectronics.

We have seen GaN and hBN as wide-bandgap material, Graphene is known as a zero-gap semiconductor. Electrons and holes propagating through the 2D structure of Graphene have a linear relation between energy and momentum, they behave as massless Dirac fermions [40]. This dispersion of electrons enables ultra-wideband tunability for applications ranging from solar cells and light emitting diodes, ultra fast lasers to touch screens [41].

Although it is a single atom thick layer, Graphene is optically visible [42]. Saturable absorption is also observed due to Pauli blocking, showing opportunities for laser cavities [41]. But in order to get luminescence, that is in our interest, chemical or physical treatments are required to reduce the connectivity of the π -electron network [43–45]. Another way to achieve emission is to have nano-ribbon or quantum dot form of Graphene. A particularity of Graphene, where emission can occur broadly in the visible spectrum, for energies both higher and lower than the excitation.

Practically, fabrication methods via electron-beam lithography [46] and ruthenium-catalysed C_{60} transformation [47] are expensive. Recently, hydrothermal [48] and electrochemical [49] strategies were introduced as common fabrication methods for GQDs. Using this hydrothermal reaction, the effects of atom doping on GQDs have been further investigated through the

preparation of various precursors [50].

Nitrogen doped (N-) GQDs showed better photoluminescence (PL) properties, compared to GQDs. They are synthesised from citric acid and urea as precursors [51, 52] and the emission colour can be tailored from green to yellow by simply changing the solvent in the hydrothermal reaction [50]. The shortening of the emission lifetime (τ) from 14 to 10 ns is proportional to the increase in the emission wavelength from blue and yellow, showing that the emission originates from single luminescent species specific to each N-GQD [51]. The quantum yields (QYs) of those N-GQDs were reported to be as high as 0.9 (in particular blue-emitting QDs) due to less hydroxyl and carboxyl groups acting as non-radiative electron-hole recombination centers [51, 52]. Such excellent properties associated to the tunable emission wavelength of N-GQDs are useful for the applications of eco-friendly bio-labelling, bio-imaging, and efficient optoelectronics.

For optoelectronic applications, dense photonic networks require ultra-small light emitting devices modulated at high bit rates and operated at low energy [53]. However, the maximum bit rates of devices are limited to the intrinsic τ of the nano-emitters [54]. For achieving faster τ and brighter emission of N-GQDs, the emission rate enhancements needs to be optimised. Photonic crystal cavities [54, 55], plasmonic antennas [56], and disordered nanostructures [57, 58] are the solutions to engineer nanoscale electromagnetic environments to enhance the spontaneous emission rate through cavity quantum electrodynamics in the Purcell regime [59].

The following section will introduce the optical methods used to characterise and study these materials from their growth process to the applications.

2.B Optical Characterisation Methods: Theory and Practical

2.B.1 Photoluminescence

Luminescence is the emission of photons from electronically excited states. From band theory, a semiconductor is characterised by the small forbidden energy gap between valence and conduction bands. Practically, the energy bands are defined by the energy E and momentum $\hbar k$ of an electron, where $\hbar$ is Planck's constant divided by 2π and k is the wave-vector.

From symmetry properties of crystal lattices, the band diagrams of semiconductors are divided into two categories (see figure 2.4): direct-gap - lowest minimum in the conduction band appears for same k as the highest maximum of valence band - and indirect-gap semiconductors - conduction band minimum happens at different k than valence band maximum. Radiative emission occurs when electrons from the conduction band recombine with holes in the valence band. In practice, it is only possible to pump electrons in the lowest conduction band minimum, that will recombine with holes in the valence band. Thus, this transition is less probable in indirect-gap materials as an additional particle (usually a phonon) is needed for momentum conservation (see figure 2.4).

Figure 2.4: Energy vs. crystal momentum for a semiconductor with an direct and indirect band-gap. Depicted is a transition in which a photon excites an electron from the valence band to the conduction band.

Photoluminescence measurement consists in exciting a material with a laser then observing the spectrum of light emitted from the material. If the excitation laser's energy is higher than

the band-gap, the emitted photons will have an energy equal to the band-gap of the material as they result from the recombination of a photo-electron in the conduction band minimum with a hole in the valence band maximum. As we will see later, in chapter 4 and 5, it is possible to engineer materials (by doping, inducing structural defects,...) to have electronic states in the forbidden band. Photoluminescence will allow to study these states.

Figure 2.5: Schematics of multi-excitation micro-PL system. (Below) Picture of the micro-PL, TCSPC and Single Photon Anti-Bunching systems running in parallel.

As presented in figure 2.5, a photoluminescence system consists in a laser beam focalised on the material to be probed. The reflected light is filtered with a longpass filter to suppress the excitation laser (high energy photons) from the lower energy photons resulted from photoluminescence. This emission, dispersed in a monochromator, is sent to a Photomultiplier tube (PMT) (or CCD) to form a spectrum informing on the excited energy levels of the material. Using several wavelengths to excite (at the same time or independently) the same semiconductor allows to study specifically certain energy states only. We will see how this can be useful with study on GaN and hBN defect-related emissions in chapter 4.

2.B.2 Time-Resolved Photoluminescence

Time-resolved PL gives more information on the recombination process by studying the decay time, defined as the average time that it takes for an electron to recombine with a hole.

The decay time (or lifetime) τ is measured using a Time-Correlated Single Photon Counting (TCSPC) system. The material is excited with a short pulse laser, some pulses result in photons emission from the material. The typical detection rate observed is 1 photon per 100 excitation pulses. The time between the excitation pulse and the observed photon is measured and plot as one count in a histogram, as shown in figure 2.6.

Figure 2.6: Schematics of TCSPC system.

The laser pulse from the laser is synchronised with an electrical output that passes through a constant function discriminator (CFD), which accurately measures the arrival time of the pulse. This signal is then passed to a time-to-amplitude converter (TAC), which generates a voltage ramp that increases linearly with time on the nanosecond timescale. A second channel detects the pulse from the single detected photon collected by a PMT. The arrival time of the signal is determined using another CFD, that sends a signal to stop the voltage ramp. The TAC now contains a voltage proportional to the time delay (Δt) between the excitation and emission

signals (see figure 2.6). The plot on the histogram typically shows an exponential decay, its fitting allows to retrieve the lifetime.

2.B.3 Single Photon Anti-Bunching

Photon anti-bunching reveal the quantum nature of light and have been a topic of strong interest this last decade. The first detection of anti-bunched light was done by Kimble, Dagenais and Mandel [60].

Literally, anti-bunching is the separation of photons in time, following the statistical distribution in time it follows that light is classified in different categories. These categories can be more simply distinguished by the second order correlation function $g^{(2)}(\tau)$:

$$g^{(2)}(\tau) = \frac{\langle n_1(t)n_2(t+\tau) \rangle}{\langle n_1(t) \rangle \langle n_2(t+\tau) \rangle} \quad (2.4)$$

Where $n_i(t)$ represents the number of counts registered by detector i at time t or $t + \tau$. The two detectors in question are part of the Hanbury Brown and Twiss interferometer shown in figure 2.7.

Figure 2.7: Schematics of single photon anti-bunching detection system and an example using CW Laser as excitation source.

From this, if $g^{(2)}(0) = 1$, the light detected is perfectly coherent, the probability of obtaining a stop is equal for any given τ . If $g^{(2)}(0) > 1$, the emission of photons is randomly separated in time, this is commonly found for thermal light sources. If $g^{(2)}(0) < 1$, this means we have emission of photons more equally separated in time, it is impossible to detect two photons at the same time, this is the way towards single-photons sources.

2.B.4 Raman Spectroscopy

Raman spectroscopy is another optical characterisation method that allows to probe basic properties of semiconductor materials. Shortly described, Raman effect is the inelastic scattering of light by matter. From the composition of materials in a device to the strain of the layers or the crystallinity of the material can be efficiently probed.

Raman spectroscopy is used to observe vibrational, rotational, and other low-frequency modes in a material. In a semiconductor, an incident photon with energy lower than the band-gap can interact in three different ways: it can be elastically scattered and retain the incident energy or can be scattered by either giving energy up to the material or by removing energy from it. Photons undergoing inelastic loss of energy give rise to Stokes scattering while photons shifting to higher energy give rise to anti-Stokes scattering. The energy gained by the material in Stokes scattering is transferred into vibrational energy where the material is in a different rotational or vibrational state. It is an equivalent vibrational energy that is lost in the case of anti-Stokes scattered photon.

The figure 2.8 sums up these different states. The Rayleigh scattering is filtered before the scattered light is sent to monochromator and detector.

Figure 2.8: Energy-level diagram showing the states involved in Raman spectra.

Raman scattering occurs essentially as a result of modulation of the electronic polarisability induced by phonons or plasmons. While the literature is extensive and we refer to [61] and [62] for more insights on the study of Raman scattering, in this manuscript Raman scattering is used

to identify phase shift of BN crystal, study GaN nanowires and spatial mapping allows us to probe material properties, along with PL and Scanning Electron Microscopy (SEM).

CHAPTER 3

Synthesis of Multidimensional Nanostructures

This chapter entails a short overview of epitaxial and chemical vapour deposition methods used for growth of nanostructures. A focus is given to the synthesis of Gallium Nitride (GaN) nanowires with an industrial Low Pressure Chemical Vapour Deposition (LPCVD) system. Aim is to show the challenges encountered in synthesising a high-quality semiconductor crystal. Using scanning (SEM) and transmission electron microscopy (TEM) as well as Raman spectroscopy and X-Ray diffraction (XRD) we characterise the growth and show single crystal GaN one-dimensional nanostructures. More widely used Molecular Beam Epitaxy (MBE) and Metal-Organic Chemical Vapour Deposition (MOCVD) systems are also presented.

Part of the work presented in this chapter has been reported in the following research paper:

- Saleem Umar, Hong Wang, David Peyrot, Aurélien Olivier, Jun Zhang, Philippe Coquet, and Serene Lay Geok Ng. 2016. “Germanium-Catalyzed Growth of Single-Crystal GaN Nanowires.” *Journal of Crystal Growth* 439 (April):2832.

3.A Methods for Synthesis of Nanowire

Discovery of nanowires goes back to 1964 when Wagner et al. [63] synthesised Si nanowires using Au nanoparticles as seed. Since then a tremendous amount of time and resources have been devoted to master and understand growth of nanowires at the atomic scale to accurately control its shape, size, pattern, crystal structure or composition.

Gallium Nitride (GaN) nanowires exhibit great material properties with direct and wide band-gap, high charge carrier mobility, and excellent thermal stability [18, 64] which allow a wide range of applications from high-speed MOSFETs [20], light-emitting diodes and lasers [21, 22] to micro resonators, chemical sensors, and highly sensitive atomic probe tips. Growth of GaN nanowires on low-cost large size Silicon wafers has attracted great interest in recent years.

This section gives a general overview of nanowires' growth techniques, then the important new concepts developed in the past decade will be reviewed with a focus on "bottom-up" growth methods for GaN nanowires.

"Top-down" approach is to create nanoscale structures by using external means to break the system and build smaller sub-systems, while "bottom-up" approach seeks molecular level components that build up into more complex assemblies. Our focus here will be on "bottom-up" synthesis methods that allow smaller and smoother nanowires as well as high crystal quality. This section will review the novel techniques and concepts from this decade.

The Table T3.1 outlines current "bottom-up" methods used to synthesis one-dimensional nanostructures.

The method most widely used to grow 1D nanostructures is undoubtedly the VLS nanoparticle-mediated method due to its great flexibility. It is a gas phase synthesis where a metal is used as catalyst to grow nanowires. Many fundamental aspects of VLS mechanisms have been kept unanswered. But a great amount of work has been produced these last decades to better understand the thermodynamics and kinetics of this process.

3.A.1 Nanoparticle-Mediated Growth of Nanowires

The first successful controlled growth of Silicon microwires (whiskers) was described as following a VLS mechanism by Wanger and Ellis in 1964 [63]. Nanometer-size metallic particle form an eutectic alloy with the desired material and acts as recipient for atoms or precursor molecules that decompose and diffuse in the droplet. Generally, these particles collect for the desired nanowires' materials once the chemical potential of the surrounding vapour is higher than the particle. Higher incorporation in the nanoparticle increases its chemical potential until super-saturation where the NW materials precipitates at the bottom of the particle's liquid-solid interface. An atomic layer of the nanowire is formed and the particle is lifted up to continue the process. Recent observations show that the particle can be a solid, thus the process become Vapour-Solid-Solid (VSS).

Aim of this section is to give a theoretical overview of VLS growth process to better understand how nanowires can be synthesised. The model is simplified here for the growth of a single material by a single catalyst (e.g. Au, Ni or Ge). Predictive modelling of III-V nanowires have seen significant work this past decade, applying it to metal-catalysed or self-catalysed MBE-grown nanowires showed matching results [65, 66]. The LPCVD system used in our studies is less accurate than MBE or MOCVD, if the growth of nanowires is highly repeatable, the accuracy and control over the precursors to the sample is much more random that prevents any significant analysis.

Table T3.1: Overview of nanowire synthesis methods mainly used in this last decade

Growth principle	General description	Local mechanism and challenges
Nanoparticle-Mediated Methods	Gas Phase Synthesis	Vapour-Liquid-Solid (VLS)
		Foreign-metal-catalyst loss channels
		Control of crystal structure
		Control of position and orientation
		Nanowires with complex structures
		Continuous nanowire production
		Transition between VLS and VSS growth mode
		Vapour-Solid-Solid (VSS)
	Solution Phase Synthesis	Solution-Liquid-Solid (SLS)
		Supercritical Fluid-Liquid-Solid (SFLS)
		Supercritical Fluid-Solid-Solid (SFSS)
Direct Deposition Methods	Selective-Area Epitaxy (SAE) Method	-
	Seed-Induced Nanowire Growth	
	Screw-Dislocation-Driven Nanowire Growth	
Template-Directed Methods	Soft-Template-Based Methods	-
	Hard-Template-Based Methods	
Oriented-Attachment Method	Shape-Dependent Oriented Attachment	-
	Ultrathin Semiconductor Nanowires	
	Nanowire Length Control by Oriented Attachment of Nanorods	

These mechanisms are still the most widely used method thanks to the great flexibility. Various types of 1D nanostructures are generated using this method: III-V semiconductor (GaAs, InP, GaN, GaP, InAs), II-VI semiconductors (ZnS, ZnSe, CdS, CdSe) and oxides (ZnO, MgO, SiO₂). A metallic catalyst is often used to assist the growth of the nanowire. This mechanism involves three main steps: alloying, nucleation and crystal growth. Figure 3.2 shows the mechanism with more details.

The catalyst is considered stable during the process, thus the diameter and length of the grown nanowires can be directly mastered by focusing on the initial droplet size and growth time. Yet, the reality is not that perfect. Several shapes of nanowires are observed from non-straight to tapered nanowires, and the growth direction is not always the same depending on the substrate and the type of the nanowire. It has been shown that the size of the catalyst droplet changes during growth, in the case of Si nanowires grown on Si (111) assisted by Au catalyst [67]. The gold catalyst diffuses, wetting the nanowire sidewalls or diffusing from smaller droplets to bigger (Ostwald ripening) which leads to tapered nanowires. This diffusion and indirect consumption of the catalyst can terminate the VLS growth limiting radically the growth of the nanowire. Generally, the loss of the catalyst to the nanowire lattice or substrate surface is believed to happen for any foreign nanoparticle mediated nanowire VLS growth [68].

Several models to predict the growth of nanowires have been developed from their morphology, length, diameter to the crystal structure. Givargizov et al. studied the diameter dependence of Au-catalysed Si whiskers grown by CVD and showed a limitations due to Gibbs-Thomson effect: fast growth for large whiskers and limited growth for whiskers below a critical diameter [69]. Givargizov concluded that the rate-limitation of the whisker growth was the contribution of the whisker material at the crystal lattice level. Alternatively, Bootsma and Gassen [70] showed chemical decomposition at the liquid-solid interface to be the rate-controlling process.

Catalyst-assisted growth offers the straight advantage of controlling the position and size of the nanowire by controlling the seed particle and growth parameters. One strong disadvantage is the contamination of the NW material by the catalyst, thus degrading the crystallographic structure of the NW, meaning the electronic and optical properties.

Figure 3.1: Phase diagram of (a) Au-Si for Si nanowires growth catalysed by Au. (b) Au-Ga for Ge nanowires growth catalysed by Au. (c) Ge-Ga for GaN nanowires growth catalysed by Ge (d) Ni-Ga for GaN nanowires growth catalysed by Ni

3.A.1.1 Growth mechanisms

VLS growth mechanism of nanowires is a multifactorial thermodynamic and chemical process. The stability of the nanoparticle seed layer is due to interface tension equilibrium states as presented in figure 3.2. We propose the give an overview of the forces intervening in a VLS growth by studying the growth of a nanowire of element A using a catalyst of element C.

A thin layer of catalyst C is deposited on a substrate. For the following descriptions, we represent the interface tensions solid-vapour, liquid-vapour and solid-liquid by σ_{sv} , σ_{lv} and σ_{ls} , respectively. The growth of a new face is always followed by a minimisation the Gibbs free energy and the condition for the growth to pursue is for the droplet to dewet on the newly created layer. A symmetrical droplet produces cylindrical or conical nanowires. Any asymmetry of the catalyst droplet from the growth direction can be explained by non-uniform interface energies.

Most of the time, during a VLS mechanism growth, the catalyst radius (R) is bigger than the radius of the nanowire (r). It can be defined by the stability criteria of Nebo'sin [71, 72]:

$$R = r \sqrt{\frac{1}{1 - \left(\frac{\sigma_{ls}}{\sigma_{lv}}\right)^2}} \quad (3.1)$$

The stability of the droplet depends on its supersaturation. [73]. The minimum of the droplet size, e.g. of Au-Ga liquid, is only dependent on the pressure of the vapour phase of Au and Ga. The minimum diameter of the nanowire depends on the composition of the liquid droplet and its size. As mentioned earlier, independently from the growth limitations by a minimum size of droplet, nanowires can grow for smaller and smaller droplet diameters before reaching a kinetic limit.

As the size of this droplet determines the diameter of the nanowires, a particular care needs to be done to control these droplets size and distribution over the surface of the substrate. To ensure cleanness of the substrates and avoid potential surface contamination, a thorough cleaning is done before the growth process. The cleaning process inspired from the commonly used RCA cleaning is given in Annex table T7.1.

When a uniform thin film of a material is deposited on a substrate and the equilibrium contact angle θ is ranged between 0 and 180° then the film is in a metastable state that will break up the thin layer into a multitude of spherical particles, this is called a dewetting. For an isotropic material, if $\theta = 180^\circ$, there is no wetting at all, the material deposited is a thin film on the substrate. If $\theta = 0^\circ$, the film wets completely the surface of the substrate. For intermediate angle the substrate-Vapour interfacial energy is smaller than the sum of the two others.

Independently from the nucleation type and growth mechanism, the grow kinetic and morphology of nanowires is directly related to the kinetic of dissolution at the vapour-liquid interface, crystallisation at liquid-solid interface and diffusion process of adatoms on the substrate and nanowires sides (see figure 3.2).

After decomposition of molecules of the precursor gas, an adatom diffuses until reaching the crystal lattice, this is characteristic of a CVD process. In this case of nanowires, the incoming material is given by the flux of material adsorbed at the surface of catalyst droplet added

Figure 3.2: Schematic of faceting of nanowires during a typical nanoparticle-mediated growth. (a) Equilibrium state of a catalyst droplet on substrate surface and on top of a nanowire. (b) Faceting of lateral sides of a nanowire. (c) Schematic of the processes involved. (1) Adsorption on the NW tip. (2) Incorporation. (3) Diffusion through the particle. (4) Precipitation. (5) Adsorption on the substrate. (6) Film growth. (7) Surface diffusion. (8) Adsorption on the NW side facets. (9) Desorption from the different surfaces.

to the number of atoms reaching the surface of the droplet by diffusion, minus the desorbed molecules. Considering a fast diffusion in the droplet, the net flux Φ_{net} feeding the growth of nanowire per surface and time unit at the solid-liquid interface can be simply described as follow: $\Phi_{net} = \Phi_{ads} - \Phi_{des} + \Phi_{diff}$. With Φ_{ads} , Φ_{des} and Φ_{diff} being the atom flux adsorbed at the surface, desorbed from the surface and from diffusion at the surface of the droplet.

Thus, the growth speed $\frac{dL}{dt}$ is defined as:

$$\frac{dL}{dt} = \frac{S}{s} \Omega_s \Phi_{net} \quad (3.2)$$

With Ω_s being the volume of a solid phase atom, S the surface of the catalyst droplet and s the relative surface of the section of nanowire.

With this basics, the following development will focus on defining with more details the flux involved in the growth of a nanowire.

Adsorption is the adhesion of molecules of gas, liquid, or dissolved solids to a surface.

The adsorption coefficient is defined as the number of adsorbed molecules (physisorbed or chemisorbed) over the incident molecules. The adsorbed flux is described as any kinetic process where a surface is in contact with gas molecules under a certain pressure. It is equal to the flux of molecules reaching the surface of the catalyst droplet described by Hertz-Knudsen:

$$\Phi_{ads} = \alpha \frac{P_g}{\sqrt{2\pi m_g k_B T_{vap}}} \quad (3.3)$$

With P_g the partial pressure of precursor gas, T_{vap} the temperature of vapour phase, m_g the mass of precursor gas molecule, k_B the Boltzmann constant and α the effective adsorption coefficient.

Adatoms diffusing on the surface of the nanowire of the substrate can evaporate. The desorption process depends the surface structure and the type of adatom but especially on the temperature, it happens only over a given activation energy.

If the droplet is at equilibrium with a vapour phase at a saturating pressure $P(r)$, the flux of desorption is equal to adsorption. Yet, for the growth to happen, a supersaturation is needed. This thermodynamic parameter masters the growth of nanowires. When supersaturation in the gaseous phase is higher than the supersaturation in the liquid droplet alloy then adsorption at the surface dominated over the desorption.

The pressure $P(r)$ above the catalyst droplet at the growth temperature is given by the Gibbs-Thomson equations:

$$P(r) = P_\infty \exp\left(\frac{2\Omega_l \sigma_{lv}}{r k_B T_G}\right) \quad (3.4)$$

With Ω_l the volume of an atom in the droplet, σ_{lv} the surface tension of the droplet at the liquid-vapour interface, T_G the growth temperature and P_∞ the vapour tension for an infinite diameter drop.

The flux of desorbed atoms at the droplet surface can be written as:

$$\Phi_{des} = \frac{P(r)}{\sqrt{2\pi m k_B T_G}} \quad (3.5)$$

Equaling the adsorbed and desorbed flux, the critical radius r_c for growth is defined as:

$$r_c = \frac{2\Omega\sigma}{k_B T \ln\left(\frac{P}{P_\infty}\right)} \quad (3.6)$$

In this case, adatoms diffused from the surface have a strong impact on the growth. The flux through the metal-semiconductor interface is insignificant over the diffusion flux. This case is particularly relevant for growth with MOCVD, MBE and especially LPCVD where growth speed is relatively high.

Adatoms density at the substrate surface is given by:

$$D_s \nabla^2 n_s - \frac{n_s}{\tau_s} + J_s = \frac{\partial n_s}{\partial t} \quad (3.7)$$

The density of adatoms at the lateral surface of nanowire is given by:

$$D_w \frac{\partial^2 n_w}{\partial z^2} - \frac{n_w}{\tau_w} + J_w = \frac{\partial n_w}{\partial t} \quad (3.8)$$

With D_i the surface diffusion coefficient of adatoms on the substrat, n_i the density of adatoms, τ_i the average time of diffusion and J_i the incorporation ratio. Where 's' and 'w' denominates the substrate and nanowire, respectively.

Atoms diffusion flux reaching the top of the wire can be given by [74]:

$$\Phi_{diff}(L) = -D_w 2\pi r \left. \frac{dn_w}{dz} \right|_{z=L} \quad (3.9)$$

Although simplistic, the feeding of the droplet can be qualitatively accurately understood by this definition of Φ_{net} where diffusion, adsorption and desorption are the main flux involved in the growth process.

The overall treatment can be used to analyse and model the dynamics of axial III-V nanowire growth via the vapour/liquid/solid mechanism as a function of the basic growth parameters such as partial pressures and substrate temperature. However, it would be too ambitious to pretend studying quantitatively the growth of GaN nanowires using these models. Especially because of the limitations of the growth system we use: the LPCVD. Most models are developed and applied to MBE-grown III-V nanowires where the flux of each element can be accurately con-

trolled, as we will present in the following, the LPCVD system, in the configuration we use it in, allows only N element control over the Ammonia gas flux. Understanding qualitatively the growth is feasible but the growth is engineered by empirical research. Establishing a quantitative model and predict the growth through simulation-assisted work would be too ambitious and unrealistic. What is important to note is that the formalism relies on transition state kinetics driven by minimisation of free energy of the total system. To have an accurate quantitative picture of the mechanism, all chemical potentials need to be measured with respect to a common equilibrium reference state where the total system is in a thermodynamical equilibrium. The formalism makes it possible to understand the complex mechanisms of NW growth dynamics in greater detail and can serve as strong analysing tool when optimising VLS growth of III-V nanowires [66] . MBE-assisted growth leads the way for accurately controlled III-V nanowires growth, LPCVD-assisted growth follows similar VLS mechanisms, as we will see.

3.A.1.2 Control of crystal structure

The crystal structure quality has a direct impact on nanowires electrical and photonic properties, it is crucial to precisely master the crystallographic properties of the nanowire during its growth: direction of growth, phase and defect levels. The growth of nanowires here is entirely based on a chemical and thermodynamic process. Nanowires should grow along the direction minimising the total free energy of the system, for VLS mechanism it accounts the liquid/solid interfacial and the nanowire surface energy, which directly depend on the diameter and surface properties of the nanowire. A recent study have showed that phase pure Zinc-Blend and Wurtzite InAs nanowire can be grown in a wide range of diameter by simply tuning the growth temperature and III/V ratio [75].

The growth speed and sometimes the shape of the nanowire depend on the pressure and the temperature of growth. The nanoparticle seed (a metal or a semiconductor) allows the nucleation and growth of the nanowire while the precursor gases determine the type of nanowire to be grown. The precursor gas can be changed during the growth to incorporate a 0D structure in the 1D nanowire, such hetero-structures present very interesting properties that can be used for sensor applications.

Our own studies conducted on GaN nanowires growth, in Low Pressure Chemical Vapour Deposition (LPCVD) system, have shown the impact of temperature and pressure on the form and crystallinity of the nanowires. As our Gallium source was a liquid source, the distance of the sample from this source was also important to take into account as it determines the quantity of Ga provided and the III/V ratio. But the main factor we observed is the catalyst used. Indeed, between Au, Ni and Ge the GaN nanowires show very different shapes and crystallinity keeping the same growth parameter. We will discuss in more detail of GaN nanowires later in this report.

3.A.1.3 Challenges for VLS process

The control of position and orientation is crucial for device fabrication. Lithographic techniques or template-directed methods are generally used to position accurately the catalyst nanoparticles. The direction of growth depends on the substrate where epitaxial relationship with the nanowire determines the growth direction. For example, Ni catalysed GaN nanowires on Sapphire substrate can be grown up to millimetre long horizontal nanowires due to hetero-epitaxial relationship between the nanowire and the substrate.

The localised growth of III-N NWs is an important issue of the project. The main objective is not to control the position over the surface of the NWs but to control precisely their dimensions in order to grow very uniform nanowire arrays.

We have seen that the VLS growth method is widely used, as it is simple to implement using a heated chamber and the appropriate gases under a reasonable vacuum while using a catalyst (such as Au as we have seen). Yet, choosing the appropriate catalyst is quite important and difficult. Important because metal catalysts, such as Au or Ni, are a serious source of contamination and can significantly change the nanowire properties, which is disastrous to its electronic and photonic properties. Difficult because all metals do not work as catalyst with every semiconductor, the right couples need to be found.

Therefore, to avoid contamination and defects, self-catalysed or catalyst-free growth could solve this issue but are not applicable to many semiconductors. We will show later a metal-free Germanium catalysed growth of GaN nanowires that show very interesting results and great crystal quality.

3.A.2 Synthesis systems

Based on the knowledge of the Vapour-Liquid-Solid (VLS) growth, several processes have been investigated for the production of nanowires. This chapter describes common methods employed for the synthesis of GaN nanowires. The main features and advantages of each method are highlighted throughout this section.

3.A.2.1 Molecular-Beam Epitaxy (MBE)

A Molecular beam Epitaxy is a system used for thin-film depositions. The method consists in several effusion cells providing the precursors with heating coils towards the substrate position near the center of the chamber. The absence of interaction between evaporated atoms until reaching the substrate is the key of the system, allowing a deposition with individual ‘beam’ of atoms. The process operated under highly controlled environment and high vacuum (from 10^{-8} to 10^{-10} Torr). The deposition rate is usually very low (few $\mu\text{m/h}$). Although the system shows similarities with MOCVD method, the use of reflection high energy electron diffraction (RHEED) make the MBE system very accurate in the crystal growth allowing development of hetero-structures with precise control over thickness of each layer. Another characterisation can be performed adding mass spectroscopy to the system.

Despite these qualities, MBE systems are often limited to laboratories only as they require particular care and each growth presents a high financial cost and are time consuming. The high vacuum and preparation of chamber are also very limiting for futur scalability.

3.A.2.2 Metal-Organic Chemical Vapour Deposition (MOCVD)

MOCVD is the method of choice in the industry for the epitaxy of III-V semiconductor materials involved in the fabrication of LEDs, laser diodes and more general transistors. It belongs to the vast family of Vapour phase deposition techniques and its distinctive feature is to enable the deposition of very thin crystalline layers on a substrate.

MOCVD reactors can be divided in three main parts: gas distribution system, deposition chamber and exhaust. A wafer is put in the chamber on a graphite-made crucible. The precursors used are organo-metallic compounds. For GaN thin films or nanowires, trimethylgallium

Figure 3.3: A layout of a Molecular Beam Epitaxy system - © Creative Commons, source: Wikimedia

molecules (TMGa: $\text{Ga}(\text{CH}_3)_3$) are used as the gallium source and ammonia as nitrogen source. A carrier gas (H_2 or N_2) goes through a bubbler containing the liquid organometallic source before going to the chamber where the molecules decompose on the heated substrate. Growth is usually performed between 400 and 700 °C at pressure from 100 to 700 Torr.

Kuykendall et al. [18] made the first report on the successful synthesis of GaN nanowires by MOCVD. The growth, based on a catalyst-assisted reaction, was performed at atmospheric pressure between 800 and 1000 °C on c-plane sapphire substrates. The nanowires exhibited a triangular cross section and showed two preferential growth directions: along the m-axis when Ni or Au catalyst were used and along the a-axis when Fe particles were used.

MOCVD growth of nanowires was also performed without catalysts that could potentially be a source of contamination. Usually, a GaN film is grown first on the substrate to serve as a buffer layer. SiO_2 or Si_3N_4 thin films are then deposited and patterned to defined regular array of holes from which the nanowires will emerge. The use of growth masks enables to precisely

Figure 3.4: MOCVD apparatus - © Public Domain

control the nanowire position and diameter.

MOCVD is an attractive technique for the synthesis of nanowires as it offers the possibility to obtain vertical nanowires with control over their location and dimension. The flexibility of this technique enables to rapidly switch the precursors making possible to fabricate heterostructures and to dope the material in order to fabricate p-n junctions. MOCVD is also compatible with current CMOS technology and has the ability to perform thin film deposition with excellent uniformity on large area wafers with a high throughput.

3.A.2.3 Low-Pressure Chemical Vapour Deposition (LPCVD) system

LPCVD is a chemical Vapour Deposition technique already widespread in the semiconductor industry, it is used to deposit thin films. A common CVD system is made of a furnace (oriented vertically or horizontally) where the desired gas are incorporated while heating the chamber, the reaction produces the film on the substrate. CVD is the general method, it induces several other techniques from the simplest one operating at atmospheric pressure (APCVD) to more sophisticated ones as PECVD (Plasma Enhanced Chemical Vapour Deposition) or MOCVD.

The LPCVD system (SEMCO UPSYS) consists in an external heater that heats a primary

cylindrical quartz tube (Length: 1200 mm - $\varnothing_{in}$: 230 mm) then another cylindrical quartz tube (Length: 1050 mm - $\varnothing_{in}$: 210 mm) placed inside. A thermocouple, protected from toxic gases inside a thin quartz tube (Length: 900 mm - $\varnothing_{in}$: 8 mm - $\varnothing_{out}$: 10 mm), is positioned at the bottom-middle of the cylindrical reaction chamber at the bottom. The samples and the solid Ga source are placed on a platform at the centre of the chamber. During a typical process, a Si (100) substrate is coated with a thin layer of Ge using an electron-beam evaporation system (Edwards). The sample is then placed near a solid source of Ga (a half-filled $20 \times 30 \times 10$ mm Al_2O_3 crucible). The chamber is purged and relevant gases are introduced in the chamber as detailed in Table T3.2.

Figure 3.5: Industrial LPCVD-system used for GaN nanowires growth. The mark ‘-1-’ indicates the entrance of reaction chamber and orientation of the images.

Precursors for growth of GaN nanowires are ammonia gas (Nitrogen source) and the gallium solid source is deposited in a small crucible near the sample. A carrier gas, argon or d’hydrogen, is injected in the furnace along with the ammonia to transport the reacting species inside the tube. The substrates are placed downstream to the ammonia flow and in close proximity to the Gallium source. The layout of a typical CVD experiment is presented in figure 3.5. Growth of nanowires in such a system is highly dependent on the distance between Ga source and the substrates (as it indirectly determines the III/V ratio), the temperature, the gases ratio

and the pressure within the furnace tube.

Nanowires made by thermal evaporation grow in a disordered fashion and form a tangle of filament-like products. Often, the lattice mismatch and surface tensions between the substrate and the nanowires prevents a vertical growth. In consequence, nanowires exhibit random directions and defects are often incorporated in the structure to accommodate the lattice mismatch. Yet we have seen that the substrate type and crystal direction can influence the direction of growth of the nanowire. But the cross-section of CVD grown nanowires is also quite variable: triangular, hexagonal, prism cross sections have been reported. These observations point out the lack of order and non-homogeneity of CVD grown nanowires.

Parameter	Range
Max. temperature	1 000 °C
Temperature ramp	19-22 °C/min
Pressure	750 Torr to ~10 mTorr
Gas flow	from 10 to 4999 sccm
Gases available	N ₂ : pure
	H ₂ : pure
	NH ₃ : pure
	SiH ₄ : 5 % diluted in H ₂
	GeH ₄ : 1 % diluted in H ₂

Table T3.2: Characteristics of the LPCVD system.

3.A.2.4 Comparative summary

The techniques previously described can be summed up as presented in table T3.3. CVD synthesis is attractive because of its lower cost and high growth rate. However, nanowires grown by vapour phase deposition are randomly oriented. More refined and complex techniques such as MBE and MOCVD are preferred to control the diameter and precise location of the nanowires by using growth masks or localised catalyst deposition. The table T3.3 also summarises the advantages and drawbacks of each technique presented here.

Table T3.3: Brief comparison between LPCVD, MOCVD and MBE system to grow nanowires

Technique	Pros	Cons
LPCVD	<ul style="list-style-type: none">- Low cost- Not a complex system- High growth rate: $\sim 20 \mu\text{m/h}$- Relatively low growth temperatures: $\sim 700^\circ\text{C}$	<ul style="list-style-type: none">- No control of position and direction of nanowire's growth- Initial catalyst layer determines the diameter and distribution of the nanowires
MOCVD	<ul style="list-style-type: none">- Deposition of epitaxial layers- Controlled growth of nanowires using masks	<ul style="list-style-type: none">- Complex and expensive process- High growth temperature: $\sim 1000^\circ\text{C}$- Low growth rate: $\sim \text{few } \mu\text{m/h}$
MBE	<ul style="list-style-type: none">- Catalyst free growth- High crystalline quality- <i>In situ</i> characterisation- Vertical growth- Relatively low growth temperatures: $\sim 700^\circ\text{C}$	<ul style="list-style-type: none">- Very expensive- High complexity system- Very low growth rate: $\sim 500 \text{ nm/h}$

3.B Experimental: catalyst-assisted growth of GaN nanowire by LPCVD

Both metal and semiconductor catalysts (e.g. Ni, Au or Ge) were used for the growth of the nanowires. Prior to the LPCVD growth, a thin layer (a few nanometers) of the catalyst was deposited by electron-beam evaporation on a substrate (e.g. Si, SiO₂ or Al₂O₃). During LPCVD process, the substrates were heated up to the desired temperature, the thin catalyst layer tends to melt and form small droplets at the surface of the substrate due to surface tensions, and serve as the seeds for the 1D growth of nanowires.

3.B.1 Growth Process of Nanowires with LPCVD System

The nanowires shape, density, quality and growth efficiency differ depending on the growth parameters such as the temperature, the gas mixture or vacuum. A typical GaN nanowire growth process with the LPCVD system lasts about 2 to 5 hours, from the sample loading, chamber heating, introduction of gas mixture to the cooling.

Figure 3.6: Typical LPCVD process for GaN nanowire growth.

Figure 3.6 shows a typical growth process of GaN catalysed nanowires by the LPCVD system. The growth starts by setting the samples inside the chamber near the Gallium solid

source as shown in figure 3.5.b. The chamber is closed and the vacuum stabilised at minimum value possible in neutral N₂-rich environment(10-50 mTorr). The temperature is raised up to a primary value (500-600 °C), for about 5 mins, to dewet the thin layer of catalyst into nanoparticles. Then the chamber's temperature is raised up to the desired one, and H₂ and NH₃ mixture is introduced in the chamber to start the growth. The table T3.4 details the process step by step.

Table T3.4: Growth process for GaN nanowires with LPCVD system.

Step	Name	t (mins)	t _{Process} (mins)	T (°C)	P (mTorr)	N ₂ (sccm)	H ₂ (sccm)	NH ₃ (sccm)
0	Start	0	0	25	0	500	0	0
1	Load	5	0	25	0	100	0	0
2	Slowpump 1	2	5	25	0	0	0	0
3	Slowpump 2	2	7	25	0	0	0	0
4	Fastpump	2	9	25	0	0	0	0
5	Leakcheck	1	11	25	0	0	0	0
6	Heating	15	12	600	0	0	50	0
7	Dewetting	5	27	600	0	0	50	0
8	Heating	10	32	750	0	0	50	0
9	H ₂ -NH ₃ on	2	42	750	500	0	50	20
10	H ₂ -NH ₃ on	2	44	750	500	0	150	150
11	Process	30	46	750	500	0	150	150
12	Gas off	1	76	750	0	0	0	0
13	Cool-down	150	77	25	0	0	0	0
14	Purge	5	227	25	0	500	0	0
15	Pump	5	232	25	0	0	0	0
16	Backfill	10	242	25	0	4500	0	0
17	End	0	252	25	0	500	0	0

3.B.2 Catalysts for GaN nanowires: Au, Ni, Ge

The figure 3.7 gives a qualitative comparison of nanowires obtained with three different catalysts: Au, Ni and Ge.

Figure 3.7: GaN nanowires obtained with various catalysts: Au, Ni and Ge.

Au has been reported [76] and experimented as catalyst for GaN nanowire's growth. Yet,

the LPCVD system showed a poor growth efficiency, the wires are very small and tapered, as seen in figure 3.7. The average length is up to 200 nm while the diameter is around 20 to 50 nm at the bottom of the wires. The growth mechanism is seen to be VLS. Comparatively, Ni-catalysed nanowires are long, twisted and polycrystalline. The growth is very efficient and highly repetitive. Ge-catalyst gives straight and c-axis oriented nanowires.

A VLS mechanism is observed in all three cases. Criteria for a metal to be a catalyst can be described as follow:

1. The catalyst must form a liquid solution
2. The solubility limit of the liquid phase must be higher than the solid phase.
3. The vapour pressure over the liquid alloy must be small for it not to evaporate during growth, thus stopping nucleation process.
4. The catalyst must not react with the crystal components or form any intermediate solid.

A phase diagram can help to predict how a catalyst will behave during crystallisation process. Describing the behaviour of elementary nanowires (e.g. Si, Ge, B,...) with an elementary catalyst is less complex than dealing with multi-elementary structure.

As an example, let's consider the phase diagram in figure 3.1.a of the Au-Si system for the growth of an Si nanowire catalysed by Au nanoparticle. The diagram indicates that the growth occurs only if the temperature is higher than the eutectic point at 364 °C. It also suggests that the composition of the liquid alloy droplet will follow the equilibrium liquidus line. At a given temperature, qualitatively speaking, fluctuations of the vapour pressure over the liquid alloy will incorporate more Si in the droplet than the equilibrium ratio thus triggering a supersaturation - moving vertically on the diagram phase to the right. Supersaturation is a non-equilibrium state resulting in the formation of the Si nanowire crystal. Thus, consuming 'Si' component in the liquid alloy that relaxes back to the equilibrium state - move vertically back to the left to the equilibrium line. Continuous feeding of the alloy droplet will allow synthesis of the nanowire.

Phase diagrams are good for a qualitative approach towards studying the growth steps of nanowires. But the current available phase diagrams are obtained from bulk systems. Thermodynamic properties of a system at the nanoscale changes significantly. Eli et al. showed that the

phase diagram of the Au-Ge system changes significantly at the nanoscale from the bulk system by studying various sizes of Au-Ge alloy at the tip of a Germanium nanowire. The surface energy at the nanoscale influences significantly the phase diagram at the nanoscale [77–80].

In the following we show practical experiments to study how these observations can be qualitatively confirmed and help to improve the growth process for high-quality GaN crystal while using scalable systems. The following sections will discuss the use of nickel and germanium as catalysts for GaN nanowires.

Figure 3.8: Distribution of size of nanoparticles after dewetting a 5 nm thin layer of Ge at various temperatures

3.B.3 Formation of nanoparticles

The formation of catalyst nanoparticles in our case is done by dewetting a thin layer on a substrate. In this section, we discuss the influence of the temperature and annealing atmosphere on the density, shape or size of the nanoparticles.

The first crucial step in the growth of nanowires is the preparation of the substrate. Before dewetting, samples are cleaned following the RCA cleaning process, as detailed in Appendix A, to eliminate any foreign residue from the surface of the sample.

Then a thin layer of catalyst is deposited on the Substrate by electron-beam evaporation

followed by annealing.

3.B.3.1 Effect of temperature

We processed nine Si samples by depositing 5 nm thin layer of Ge by e-beam evaporator. Then we annealed each sample at different temperature, from 400 to 800 °C with a step of 50 °C. Characterisation has then been done using an optical microscope in Dark Field mode. Here the limit of diffraction of light must be took into account. Considering the resolution of the CCD camera, used to take pictures of the samples, we do not take into account small areas. Aim is to get a trend of the particles' size variation.

The figure 3.8 shows the distribution of the area of nanoparticles after dewetting a 5 nm thin Ge layer on a Si (100) substrate at various temperatures. We observe the average area remains around $2.5 \mu\text{m}^2$ for temperatures below 650 °C and a sudden drop at 700 °C and above. The size of nanoparticles lowers with a higher temperature as stated in previous literature.

3.B.3.2 Effect of atmosphere

Figure 3.9: Annealing of Ni 5 nm thin layer on Si (100) substrate under various conditions.

Figure 3.9 shows annealing of Nickel thin layer at different temperatures with a focus on the influence of H_2 on the dewetting process. It is important to note that to grow GaN nanowires we provide Ga atom source and due to practical limitations, this source can only be provided by a crucible positioned next to the samples. Thus, during annealing, the environment is composed of Nickel deposited on Si substrate and Ga atoms provided by a source close to the sample.

Figure 3.10: Energy-dispersive X-ray spectroscopy (EDX) mapping of a) the tip of a Ni-catalysed and b) Ge-catalysed GaN nanowire.

Figure 3.9 shows that annealing in an atmosphere void of H_2 forms random puddle-like particles. In a H_2 -rich atmosphere, we observe the formation of separate nanoparticles.

In terms of composition of the nanoparticle, figure 3.10 shows an EDX mapping of the tip of a Ni-catalysed GaN nanowire. We observe that the core is filled with Nickel and is void of Ga while it is surrounded with Ga. As the growth follows a VLS mechanism, the Ni filled tip of the nanowire results from supersaturation then nucleation in a nanoparticle after annealing. Thus, we may presume a similar distribution here and after annealing, except the presence of nitrogen. The nanoparticle is made of a Nickel-core surrounded with Gallium.

Growth of nanowire is achieved through cycles of supersaturation of the catalyst nanoparticle and crystallisation at liquid-solid interface and is driven by the chemical potentials at vapour, liquid and solid interfaces. Understanding and accurately quantifying the growth process has proven difficult due to several factors involved in supersaturation such as growth kinetics, catalyst stability or crystal phase. Thus, rationally engineering growth by controlling composition, size, crystal structure or growth directions is laborious.

Factors involved in a vapour-liquid-solid growth are highly coupled. The inability to selec-

tively check a single growth factor such as supersaturation or a specific surface energy, limits a majority of nanowire research to empirical efforts. This is particularly the case with our chemical vapour deposition system where the high volume of the reaction chamber associated to a solid/liquid source of gallium limits a high rate of repeatable experiments without unintentionally influencing the growth environment. This has often triggered unintended or unexpected results.

In the following, we present GaN nanowires growth using Nickel and Germanium as catalysts. The study involves engineering work to improve nanowire growth yield with LPCVD system by investigating the influence of growth parameters such as the temperature, H_2 -atmosphere, $NH_3:H_2$ ratio or thickness of catalyst thin layer.

3.B.4 GaN nanowire growth assisted by Ni catalyst

GaN nanowires have been grown by depositing 3 to 10 nm thin layer of Ni on a Si (100) substrate. The growth was performed at different temperatures, pressures and precursor gas ratios to study their influence and optimise the growth. The formation of GaN nanowires was inspected mostly by using SEM, Raman spectroscopy and PL characterisation.

Figure 3.11 shows the influence on growth of preliminary annealing with and without H_2 -rich environment. As seen previously, the impact on the droplet shape was significant. Yet, the result on the growth nanowires is less binary, we observe a better growth efficiency by dewetting in H_2 -rich environment. Growth at 700 °C gives thin wires, annealing without H_2 did not show long wires. The observations are similar for growth at 750 °C, dewetting in H_2 -rich environment gives higher growth yield.

The PL characterisation in figure 3.12 shows a weak near-band-edge peak for growth without H_2 dewetting while annealing in H_2 -rich environment gives a strong and distinct near-band-edge peak characteristic of GaN crystal suggesting low density of defect in the crystal, especially for nanowires grown at 700 °C.

The growth of GaN crystal is *in fine* controlled by the Gallium and Nitrogen atoms supersaturating in the catalyst droplet. The reactants at our disposal are gaseous Ammonia and solid Gallium.

Figure 3.11: Ni-catalysed GaN nanowires growth under various temperatures with preliminary annealing at the same temperature to form seed nanoparticle under neutral and H₂ environment.

Due to the configuration of the LPCVD system, Gallium is constantly present in the chamber and is abundantly available, it is the reagent in excess. Nitrogen is controlled indirectly as the flow of Ammonia in the reaction chamber, it the reactant that limits the reaction. It is worth noticing that considering the consequent volume of the reaction chamber (see 3.5), the reaction does not begin and stop synchronously with the injection of Ammonia. H₂ is used as carrier gas. The figure 3.13 shows some engineering work using various NH₃ flows (under constant H₂ flow of 150 sccm) at different temperatures. For a low NH₃:H₂ ratio, no growth is observed, increasing the ratio to 1 : 3 (50 sccm of NH₃) allows growth of nanowires. For ratio of 1:1 the growth is the most efficient, with thin and dense GaN nanowires are observed.

The average diameter of the nanowires ranges from 50 to 300 nm while their length reaches several micrometers, depending on the growth time. The nanowires exhibit different shapes: some of them grow straight with a relative smooth surface; others present a rough surface with

Figure 3.12: Photoluminescence of Ni-catalysed GaN nanowires growth under various temperatures with preliminary annealing at the same temperature to form seed nanoparticle under neutral and H_2 environment.

ramifications perpendicular to the main growth direction. The smooth nanowires also exhibit a tapered shape as they grow thinner towards their termination. Moreover, some nanowires are interconnected to each other: they share the same root and then expand in different directions. In general, grown nanowires catalysed by Ni are very disordered and non-straight. The TEM characterisation (see figure 3.14) shows polycrystalline nanowires. The crystal growth direction is different from the growth direction of the nanowire.

Growth temperatures were evaluated from 700 to 850 °C as shown in figure 3.15, the pressure and gases flow are kept invariant. Growth temperature influences significantly the shape of nanowires. At 850 °C, Ni-catalysed growth results in heterogeneous shape. The yield of nanowires growth is low, the rare nanowires that are observed have a short length of a few hundreds of nanometer. However their diameter is quite small in the range of 20 and 50 nm. Most of the substrate is covered with 3D nanostructures exhibiting triangular faceting as shown in figure 3.15.d. It appears that the edges and corners of these irregular islands serve as nucleation sites for the growth of the few nanowires observed: the nanowires emerged laterally from the already grown nanostructures.

From the analysis of the nanowire dimensions for the different temperatures tested it seemed that the best compromise between length, density and diameter was realised at 750 °C with nanowires exhibiting the highest density (~ 8 nanowires/ μm^2) and diameters in the 30-50 nm range.

Figure 3.13: Ni-catalysed GaN nanowires growth under various temperatures and NH₃ flow. Growth time 5 mins, pressure 250 mTorr, H₂ flow at 150 sccm.

Overall, for a growth duration of 30 minutes, the length of the nanowires increased slightly with temperature but did not exceed 2 μm . The length of the nanowires is essentially a function of growth time. Longer nanowires could have been produced by increasing the duration of the process to reach several tens of micrometers as commonly reported in the literature.

3.B.5 GaN nanowire growth assisted by Ge catalyst

In this section, we use the conventional CVD method but demonstrate for the first time that Ge can be used as an efficient catalyst to assist growth of high quality single-crystal GaN nanowires using a Low Pressure Chemical Vapour Deposition (LPCVD) industrial system [81]. This CMOS compatible process provides a new possibility for the integration of GaN NW devices with Si CMOS circuits.

As with Ni-catalysed growth, a solid form of Gallium (Ga) (99.99% purity) was used as Ga source. High purity gaseous Ammonia (NH₃) was used as Nitrogen source and gaseous

Figure 3.14: (left) TEM image of Ni-catalysed GaN nanowires. (right) High-resolution TEM with electron diffraction characterisation.

di-hydrogen (H_2) was used as carrier gas. High purity Germanium (Ge) was deposited under high vacuum (0.75 mTorr) by electron beam evaporation on n-doped Silicon (100) substrate.

The influence of growth parameters such as temperature, pressure, and catalyst thickness on the formation of GaN nanowires is detailed in the following. The growth of GaN nanowires was observed from 600 to 950 °C, keeping a constant pressure and other parameters such as Ge layer thickness and gas flow in the chamber.

As shown in figure 3.16, the optimal condition that gives high growth yield is observed at a temperature of 750 °C and a pressure of 500 mTorr. In fact, the highest solubility of Ga in $(\text{Ge})_s$ (of 1.1 at.%) is found at 750 °C in the equilibrium phase diagram of Gallium-Germanium system [82], that is a relevant condition required for VLS growth, as seen previously. It was found that lowering the pressure might enhance the growth rate resulting in longer nanowires but playing with the growth time is the best way to obtain longer nanowires.

SEM images on figure 3.16 show GaN nanowires grown on Si substrate at 750 °C under 500 mTorr pressure, NH_3 and H_2 flows set at 100 sccm and 150 sccm, respectively. Different thicknesses of Ge thin layer catalyst (3, 5 and 10 nm) have been tested and show different shapes of GaN NWs. For a Ge thin layer thickness of 3 nm and 5 nm, straight and uniform NWs are obtained whereas they are tapered for Ge layer of 10 nm as shown in figures 3.16.a, b and c, respectively.

Figure 3.15: SEM of GaN nanowires by Ni catalyst at different temperatures.

A droplet is seen at the tip of most of the nanowires, this is the signature of a VLS growth mechanism [19, 63, 69]. If the droplets are clearly seen for nanowires grown with 3 and 5 nm thin layer of Ge, they are sometimes smaller at the tip of the nanowires grown with 10 nm thin layer of Ge. This could be due to the surface migration of catalyst, which induces tapering of the nanowires and interacts with VLS growth by reducing the catalyst supply [67]. If precursor adatoms can migrate along the nanowire to feed the growth, Germanium from the droplet can also diffuse along the nanowire towards the surface, thus reducing the size of the droplet and resulting in tapered wires or stopping the growth. Hannon et al. show that the diffusion from smaller droplets to bigger ones can also lead to change in size of the droplet during growth thus leading to nanowires' diameter change.

In general, we observe that the diameter of the nanowires decreases as the thickness of Ge thin layer decreases (figure 3.17), this is directly due to the conversion of Ge thin layer into nano-liquid droplets at a high temperature thanks to surface tensions. The thinner the layer, the smaller and spaced out are the droplets as seen previously. In a VLS growth mechanism, the size of the nanowire is partly related to the diameter of the catalyst droplet, this results in the decrease of the nanowire diameter with the reduction of Ge layer thickness.

Figure 3.16: SEM images showing high-density GaN nanowires grown on Si (100) substrate at 700 °C under 500 mTorr pressure, H₂ flow set at 150 sccm and NH₃ flow set at 100 sccm with Ge thin film of (a) 3 nm, (b) 5 nm and (c) 10 nm. (d) SEM image showing high-density GaN nanowires grown on Si (100) substrate at 750 °C under 500 mTorr pressure, H₂ flow set at 150 sccm and NH₃ flow set at 100 sccm with Ni thin film of 3 nm. - Scale bar: 500 nm.

A relatively large growth process window was obtained for Ge catalysed GaN NWs. Compared to conventional CVD systems, LPCVD system reduces drastically the thermal budget of the growth which could be important for the process integration of GaN nanowire devices on Si substrates.

Crystalline structure of our GaN nanowires was verified using High Resolution Transmission Electron Microscopy (HRTEM) and Electron Diffraction (ED). Figure 3.18.a shows the hexagonal GaN nanowires as a single crystal growing along the c-axis axis, which is usually commonly observed for Wurtzite GaN nanowires [89]. Room-temperature photoluminescence (PL) of these Ge catalysed GaN nanowires shows a strong emission at around 3.58 eV (346

Figure 3.17: Density (left-Y) and diameter (right-Y) of nanowires from figure 3.16.a, b and c in function of Ge layer thickness.

Table T3.5: Comparison of GaN material's fundamental band gap at room temperature.

Wurtzite GaN (eV)	Zinc-Blende GaN (eV)	Method [ref]
3.44	3.17	Ellipsometry [83]
-	3.23	Modulated Photo-reflectance [84]
3.54	3.37	Reflection [85]
3.45	3.21	Cathodoluminescence [86]
3.44	3.28	Photoluminescence [87]
-	3.45	Cathodoluminescence [88]
3.58	-	Photoluminescence [Ge-catalysed GaN NWs]
3.50	-	Photoluminescence [Ni-catalysed GaN NWs]

nm), which is very close to the band-edge emission of a Wurtzite GaN nanowire.

Energy-dispersive X-ray spectroscopy (EDX) in figure 3.19.a shows elementary composition of a GaN nanowire tip. We can see the tip of the nanowire is composed of a Ge-enriched core and its size is close to the diameter of the nanowire, another characteristic of VLS mechanism. The phenomenon has not been reported on metal catalysed VLS-based nanowires growth so far. Around the Ge core, a thin layer deposition composed of Gallium and Nitrogen is observed. The composition along one GaN nanowire is shown in figure 3.19.b. Still, EDX analysis is sometimes not sufficient to entirely conclude on the contamination or not with Ge of the

Figure 3.18: (a) Lattice-resolved TEM image taken at the bottom of a single-crystal GaN nanowire. Scale bar: 5 nm - Inset: The corresponding electron diffraction pattern (ED). - (b) Photoluminescence spectra of single-crystal GaN nanowires grown by Ge-assisted catalysis. The circled peak is a known artefact due to our system that we observe in different other samples.

GaN nanowires. Indeed, group IV atoms can be amphoteric dopants for GaN. Yet we observe here a high Ge content only at the tip of the GaN NWs, confirming the growth follows a VLS mechanism. Furthermore, the low detection of Ge along the nanowires (figure 3.19.b) allows us to affirm that there are no Ge particles present along the nanowire, or at least, we can say that the intrinsic Ge doping of GaN is low.

In conclusion, the use of Germanium as a catalyst to grow high quality single crystal Wurtzite GaN nanowires on Si substrate by LPCVD is demonstrated. Unlike the previously reported VLS grown GaN NWs, the metal-free Ge catalytic growth of GaN nanowires on Si offers a fully CMOS compatible approach for the integration of GaN nanowires on Si platform.

Figure 3.19: (a) Low resolution Transmission Electron Microscopy (TEM) image of a single-crystal GaN nanowire grown by Ge-catalysed VLS (top) and the corresponding EDX elementary mapping showing spatial distribution of Ga (green), Ge (blue) and N (red). Scale bar: 200 nm. (b) Low resolution TEM image of another GaN nanowire (top) and its quantised compositional EDX line scan along the nanowire from the middle to its tip (bottom). Scale bar: 200 nm.

3.C Hybrid Catalyst for Synthesis of Unconventional GaN Nanostructures

The use of Germanium opens interesting window for growth of high-quality GaN crystal by an industrial LPCVD system. We have shown that by playing with the growth parameters the shape and crystal quality of GaN can be tuned before and during the growth, the parameters are the following: substrate, catalyst, catalyst layer thickness, growth temperature, pressure, $\text{NH}_3:\text{H}_2$ gas ratio, growth time.

The table T3.6 gives an overview of the relevant values these parameters can take considering the limitations of the heater, the gas sensors, the MFCs as well as the vacuum pumps of the LPCVD system.

Table T3.6: Growth parameters variations.

Parameter	Variations possible
Substrate	Si (100), Si (111), SiO_2 , Al_2O_3
Catalyst	Au, Ni, Ge - Ge/Ni, Ni/Ge
Thickness (nm)	1, 3, 5, 10 - 1/5, 1/1
Temperature ($^\circ\text{C}$)	500 to 950
Pressure (mTorr)	250, 350, 500, 700
$\text{NH}_3:\text{H}_2$ (sccm:sccm)	50:500, 50:200, 25:150, 50:150, 150:150, 200:150
Time (mins)	5 to 160

Testing all possible variants would take an unthinkable amount of time and resources and would not be relevant. As we have seen with Au, Ge and Ni catalysts, the quality and shape of GaN nanowires depends on these criteria. The growth similarities before precursor flux or time between Ni and Ge catalysts present a common behaviour following the model VLS mechanism initially introduced.

In this section we present a new way to use catalysts that have already demonstrated efficient growth. Aim is to take advantage of the high growth efficiency, density and long nanowires resulted from Ni-catalyst and the high quality single-crystal and straight nanowires resulted from Ge-catalyst into one single growth process. We present the growth of ‘Pine Tree’ GaN nanostructures obtained by using Ge and Ni as catalyst.

3.C.1 Structural Characterisation

The experimental protocol is similar to previous growths. Pine tree-like GaN nanostructures are obtained with hybrid Ge and Ni catalyst. On a Si substrate, a thin layer of Ge (1 to 5 nm) is deposited before a Ni (1 to 5 nm) thin layer. The process is then run as usual.

The particular shape of pine tree GaN nanostructure is observed in figure 3.20. The SEM images exhibits a very dense growth with quite long structures (up to 20 μm) with a very thin and sharp tip (~ 50 nm). The structure presents a central spine similar with a straight and thin shape. This central spine presents a bulky lateral growth. Clearly visible on the higher magnification SEM image in the insert of figure 3.20.b at the tip of one pine tree, the bulky lateral growth seems to use the irregularities on the surface of the the central spine as preferential growth site, as seen on figure 3.21.

Figure 3.20: Pine tree-like GaN nanostructures obtained with hybrid Ge/Ni catalyst.

We have seen from the previous chapter that several catalysts can be used for the growth of GaN nanowires, Ni-catalyst results in very dense and polycrystalline 1D nanostructures while Ge allows single-crystal straight nanowires.

From the shape of the pine trees in figure 3.20, the central spine shows a straight and thin structure suggesting a Ge-catalysed growth while the bulky side-growth suggests a Ni-catalysed synthesis. In order to confirm this observation, the best proof would be an XRD mapping as previously shown, but the limitations of access to such a system made the characterisation difficult. Indeed, the pine trees are very fragile structures, isolating one structure and transferring it to a TEM grid turns out to be a difficult task where we damaged the structure all the time.

Preparing and cutting a part of the sample with Focused Ion Beam (FIB) was the best way but residual deposition from evaporated material added to a poor understanding by the operator made the task difficult to achieve. Thus, observations by SEM will be our best tool to investigate the structure of these pine trees.

Figure 3.21 gives more insights on the shape of tip and the behaviour of the growth. The growth lasted 60 mins and was stopped after cutting the $\text{NH}_3:\text{H}_2$ gas flux in the chamber. As we have seen previously with the VLS growth mechanism, a nanowire grows by adding layer and layer of crystal on its top, the catalyst droplet allows the nucleation and moves up as the nanowire grows. Thus, considering simply, the bottom a nanowire is ‘older’ than its tip. In other terms, observing the tip of a nanowire after a time t gives a snapshot of the growth process.

Figure 3.21: SEM images of pine tree-like GaN nanostructures obtained with hybrid Ge/Ni catalyst with high magnification on the tip.

The high magnification images on figure 3.21.a allow us to observe how the growth mechanism with Ge/Ni hybrid catalyst happens. It seems clear that the central spine grows first, it is straight, thin and pristine at the tip, reminding Ge-catalysed GaN nanowire (see figure 3.16). Yet, this straight nanostructure shows an irregular surface pointing to structural dislocations. Going down along the spine, near the area labeled ‘2’, we observe sidelong bulky structure. Raman spectroscopy in figure 3.22 confirms this bulky structure to be GaN as the E_2^H mode, characteristic of GaN Wurtzite crystal, is clearly observed. The area near label ‘3’ shows even more lateral growth, the conic shape of the pine tree suggest that the more the growth goes further the wider the bulk GaN structures expands. This is particularly well visible in the figure 3.20 where the bottom of the wires is much wider than the top. Just taking the width ratio

top/bottom, we obtain a rough average of 1/100.

We observe that some shorter nanostructures do not show a sharp tip but rather a flat tip with short conic slope. This is probably due to a shorter VLS growth for these wires that stopped earlier (e.g. diffusion of catalyst droplet), thus inducing a wider lateral growth at the tip. Another exception is from the very thin nanowires without any lateral growth. As seen in figure 3.20.b near the white arrow, a very thin nanowire about 50 nm wide growth more than 25 μm . This size has never been observed in any previous growth and remains particular.

Figure 3.22: Raman spectroscopy mapping of a single pine tree-like GaN nanostructure obtained with hybrid Ge/Ni catalyst. The SEM image is giving as reference showing that sample preparation damages the nanostructures.

Raman spectroscopy mapping in figure 3.22 allow to investigate the GaN crystal structure along the wire. The preparation for this measurement consisted in cutting a small part of the as-grown pine tree sample. Inside a small glass tube, insert this sample and ~ 1 mL of VLSI-grade IPA then sonicate for 10 to 20 s. Using a micropipette, drop ~ 10 μL of the solution on a clean substrate (preferably SiO_2 on Si sample). Use N_2 gun to accelerate the drop evaporation. Check on the optical microscope if single pine tree can be seen in a good density, it is best to have them as isolated as possible for better measurements.

Once one single pine tree can be isolated, a Raman mapping is performed with a low power CW laser at 532 nm. We observed that the laser can damage the pine tree as it seems to absorb

a lot, thus keeping a low power is important. Group theory predicts four pairs of Raman active modes for hexagonal structure of GaN: A_1 and E_1 (Raman and infrared active), B_1 (silent mode) and E_2 (only Raman active) [9]. One set of A_1 and E_1 modes are acoustic while all others are optical modes. The A_1 and B_1 modes result from atomic displacement along the c-axis while E_1 and E_2 inform on displacement perpendicular to that axis. The curve in figure 3.22 shows the Raman spectra of pristine GaN pine tree, as measured during the mapping. The peak E_2^H , most easily observed, is identified around 578 cm^{-1} , characteristic of Wurtzite structure of GaN. The peak E_1^L is also observed in the broad peak at 558 cm^{-1} . The A_1 (LO) phonon mode, observed at 727 cm^{-1} , has atomic displacement along the c-axis and x- and y-directions perpendicular to the c-axis.

All these peaks are observed in a Wurtzite structure of GaN, the mapping locates them along the whole pine tree, from the center to the lateral bulky crystal. Although a rigorous characterisation is required to identify the crystalline direction, from the previous observations with isolated Ni- and Ge-catalysed growths, the straight central spine evinces a single-crystal GaN growing along the c-axis while the bulky lateral growth suggests a polycrystalline GaN crystal.

3.C.2 Growth parameters: a multi-factorial impact on nanowires' morphology

In this section we will present the effect of growth parameters on the synthesis of GaN nanostructure using Ge/Ni hybrid catalyst. Indeed, obtaining GaN pine tree is not as straight forward as previous single element catalyst growth.

Coming back to the figure 3.6, it is important to take into account every step in order to have a relevant and repeatable growth. One crucial step is the preliminary annealing at $600\text{ }^\circ\text{C}$ in H_2 -rich environment that prepares the Ge/Ni catalyst. Why $600\text{ }^\circ\text{C}$? Considering the size of the LPCVD chamber, the proximity of the Ga-solid source and the position of the sample in the chamber, this value results from an empirical engineering work. The flux of the precursor gas and the temperature is studied below. But it is worth noticing that this particular growth of pine tree happens only in a Ga-rich environment. The Ga-solid source is not only positioned

control on.

Figure 3.24: $\text{NH}_3:\text{H}_2$ gas flux ratio variation study on GaN nanowires grown by LPCVD system with Ge/Ni - 5 nm/1 nm catalyst. Growth parameters are as follow: 750 °C, 250 mTorr, 60 mins.

A first study started by using the temperature, pressure and time that gave relevant nanowires with Ni and Ge taken separately: 750 °C, 250 mTorr for a 60 mins growth. A Silicon substrate was used for growth, a thin layer of Ge (5 nm) was deposited by e-beam evaporator, followed by a layer of Ni (1 nm). The sample was loaded in the chamber to follow a growth as described in figure 3.6. The $\text{NH}_3:\text{H}_2$ gas flux ratio was tested from 0.14 to 2.0, as shown in figure 3.24. As previously observed with Ni (see figure 3.13), the Ammonia precursor flow ratio, mixed with H_2 , needs to be low in order to have an efficient growth, if it is in excess we observe that the growth does not happen. Growth is driven by supersaturation resulted from the feeding of the droplet by precursor molecules. The adsorbed flux is equal to the flux of molecules reaching the surface of the catalyst droplet described by Hertz-Knudsen, as defined in section 3.A. A high $\text{NH}_3:\text{H}_2$ gas ratio gives a high NH_3 partial pressure. For nucleation of GaN crystal, Ga and N molecules must be present in a stoichiometric ratio. Keeping a low $\text{NH}_3:\text{H}_2$ ratio of gas gives enough partial pressure of NH_3 to allow supersaturation then nucleation of GaN. For further growth, the $\text{NH}_3:\text{H}_2$ ratio was kept to 0.25.

Compared to previous growths, the temperature seems to be determinant in shaping the pine trees. As seen in figure 3.25, the influence of the temperature is crucial in structuring the nanos-

Figure 3.25: Temperature variation study on GaN nanowires grown by LPCVD system with Ge/Ni - 5 nm/1 nm catalyst. Growth parameters are as follow: $\text{NH}_3:\text{H}_2$ - 50 sccm/200 sccm, 250 mTorr, 60 mins.

structure as it directly influence the various surface energies involved in the growth process, as described in section 3.A.1.1. From very random growths below 600 °C, straight structures appear from 730 °C, very similar to what has been observed with Ge-catalysed GaN nanowires. Increasing the temperature to 780 °C results in stacked cone nanowires with stacked-shaped wires, the density of growth is very high compared to the previous lower temperatures.

As the temperature increases to 880 °C, pine tree-like structure are observed. The growth is described in the previous section with a stacked cone central spine nanowire and lateral bulk growth that seems to use the surface dislocations as preferential sites for nucleation. Raising the temperature even more, pine tree are not observed anymore, neither any nanowire-like structure. At 930 °C a 2D foam structure of GaN is obtained as seen in figure 3.25. The foam-like layer is approximately 1 μm thick with very rugous surface.

One last parameter was tested, the thickness of Ge was changed to 1 nm. The figure 3.26 shows the growth for Ge/Ni - 1 nm/1 nm catalyst thickness. The central spine nanowire is thinner as well as the bulky lateral growth. Our initial hypothesis claiming that the bulk lateral growth may be only Ni-catalyst dependant turns out to be false as reducing Ge in the hybrid

Figure 3.26: Temperature variation study on GaN nanowires grown by LPCVD system with Ge/Ni - 1 nm/1 nm catalyst. Growth parameters are as follow: $\text{NH}_3:\text{H}_2$ - 50 sccm/200 sccm, 250 mTorr, 60 mins.

catalyst composition changes the thickness of the central spine and the slope and width of the pine tree. It is worth noticing that the overall shape of the trees is flat. The lateral growth happens in one plane only, not all around the central spin nanowire. From higher magnification images in figure 3.21.a we observe that growth happens all around the nanowire, but as the lateral growth gets wider, one 2D plane growth is preferred.

From literature, we do not find any similar GaN nanostructure reported, either in the GaN pine trees or the GaN 2D foam-like layer. Structures being close are the dislocation driven nanowires, following the Eshelby twist [92] or the hyper-branched PbS and PbSe trees driven by screw dislocation [93,94]. In both cases the branches are single nanowires growing through a self-catalytic VLS mechanism and using the dislocation along the surface of a central spine nanowire as preferential site for growth initiation. The central spine nanowire presents a screw dislocation allowing an overall growth following the consecutive dislocations from bottom to the top of the central nanowire, resulting in a tree with separated nanowire-made branches. In Ge/Ni-catalysed GaN pine trees, no distinct branches are observed, only a large random GaN structure surrounds the centre spine nanowire.

This unconventional morphologie of GaN micro-/nano-structure opens way for various ap-

plications. The pine-tree-like structure could show interest in micro-sized directive antenna for example. In the next chapter we study the optical properties of these structures and discuss applications for photonics.

CHAPTER 4

Visible Emission from Optically Active Defect-States

The previous chapter has shown how low dimensional nanostructures can be synthesised using chemical vapour deposition methods. Gallium Nitride nanowire have been grown using an industrial CVD system. We show different morphologies and crystal qualities depending on the catalyst used. Nickel shows randomly oriented and very dense ensemble of GaN nanowires while Germanium catalyst allows a CMOS-compatible synthesis process for high-quality GaN crystal on Si substrate, the nanowires are shown to be straight growing along the c-axis. Finally, we have shown that combining Nickel and Germanium together allows a particular pine-tree-like structure that shows a straight spine with bulk Wurtzite GaN growing laterally.

This chapter focuses on the optical properties of these structures with a an emphasis on visible emission capabilities. We first present yellow and green luminescence from defects in GaN nanowires and methods to selectively suppress the green emission by passivating the structural defect it is related to. Then we focus on optical properties of the exotic pine tree-like GaN structures.

Part of the work presented in this chapter has been published in the following research papers:

- Saleem Umar, Muhammad Danang Birowosuto, Noelle Gogneau, Philippe Coquet, Maria Tchernycheva, and Hong Wang. 2017. “Yellow and Green Luminescence in Single-Crystal Ge-Catalyzed GaN Nanowires Grown by Low Pressure Chemical Vapor Deposition.” *Optical Materials Express* 7 (6):1995.

4.A Yellow and Green Luminescence from LPCVD-grown GaN nanowires

The defect-related yellow (YL) and green (GL) luminescences are often observed in GaN, the formation and transition energies of these defects in GaN is a topic of intense research. Yet, the precise origin of these luminescences remains under debate [25, 95–98]. In 2-dimensional layers, etching experiments demonstrated a near independence of the visible intensity with the etch depth supporting the bulk nature of the defects [99], whereas other experiments using photo-voltage spectroscopy argued in favor of surface defects being responsible for the visible band [100, 101]. From literature, the main candidates for YL band are defects, either isolated carbon in a nitrogen site (C_N) [96], carbon-oxygen complexes (C_NO_N) [25], or other complexes such as $V_{Ga}-3H$ or $V_{Ga}O_N-2H$ [26]. The GL band, observed in high-purity GaN, is most recently [102] associated with transitions from different charge levels of the same C_N defect responsible for YL band.

Changing from the 2D film to the nanowire morphology provides an elegant solution to the dislocation problem. Indeed, thanks to the efficient strain relaxation by the free lateral surface, dislocation-free nanowires (NWs) can be grown on highly mismatched substrates [103]. GaN NWs open a new window of applications presenting a number of potential advantages for nanophotonics and nanoelectronics. In particular, nitride NWs have been proposed as an active medium for high-efficiency 3D LEDs [104, 105] and high sensitivity photodetectors [106].

The most widespread way to fabricate GaN NWs relies on epitaxial techniques such as Molecular Beam Epitaxy (MBE) or Metalorganic Vapor Phase Epitaxy (MOVPE) using catalytic, self-catalysed or selective area growth modes [107, 108]. Although these techniques provide the best control over the wire morphology and composition, they are expensive and present difficulties for up-scaling the sample size. For a large number of applications (e.g. light sensors for UV exposure monitoring) the development of a low cost synthesis technique is desirable. The Low Pressure Chemical Vapor Deposition (LPCVD) method, which allows a significant cost reduction due to a lower vacuum and a lower thermal budget, can also be used for GaN NW growth [81].

Figure 4.1: (a) SEM image of Ge-catalysed GaN nanowires. (b) Same NWs after coating with 5 nm Al₂O₃. (Inset) higher magnification images of individual nanowires showing the Ge rich tip. Scale bars in (a, b) and insets indicate 500 nm and 100 nm, respectively.

In this section, we quickly summarise the synthesis and characterisation of GaN NWs grown by catalyst-assisted LPCVD. YL and GL bands are observed and are similar to the ones reported from bulk and thin film GaN samples. Thanks to their large surface to volume ratio, LPCVD-grown GaN NWs appear as excellent candidates to investigate the origin of YL and GL bands. The presence of high density of surface states tends to pin the Fermi level near the surface and bends the electronic bands that affects the recombination process [109]. Structural defects, such as dangling bonds or point defects, charge the surface states and are reported to influence the optical and transport properties of nanowires [110, 111]. By passivating the surface of LPCVD-grown GaN NWs with a thin layer of Al₂O₃, we demonstrate a drastic reduction of the defect-related YL band while maintaining the GL band and the NBE emission unchanged. The defect responsible for the YL band is believed to be localised near the surface of GaN nanowires. The GL not being affected by NW passivation, it could be attributed to defects with bulk nature.

Figure 4.2: a) High resolution TEM image taken at the bottom of a non-passivated single-crystal GaN nanowire. Inset: The corresponding electron diffraction pattern (ED). b), c) and d) High Resolution TEM images of non-passivated single-crystal GaN nanowires.

4.A.1 Structural characterisation

Figure 4.1.a shows scanning electron microscope (SEM) images of GaN NWs grown by LPCVD. Nanowires grow in random directions following a Vapor-Liquid-Solid (VLS) mechanism catalysed with Ge. It is worth noticing that the background is composed of Germanium seeds that have not resulted in NW growth. Most likely, the supersaturation was not reached for these droplets explaining the absence of the VLS growth. GaN NWs present a straight shape and show a single-crystal Wurtzite structure growing along the c-axis, as previously reported [81], see also the transmission electron microscope images (see figure 4.2). As-grown nanowires are characterised by a spatial distribution of $\sim 10^8$ NWs/cm², an average length of 3.4 ± 0.9 μ m and a diameter of 34 ± 7 nm, determined from SEM images. figure 4.1.b shows the GaN

NWs after passivation with Alumina Oxide deposition. The NWs remain straight. The SEM charging effects confirm the successful deposition of alumina oxide around the GaN nanowires. Moreover, the average diameter after passivation is 41 ± 6 nm. This thickening indicates that the GaN core is embedded into a ~ 3.5 nm thick Al_2O_3 shell.

Ge-assisted catalytic growth by LPCVD method leads to the synthesis of GaN NWs with high crystalline structure as demonstrated by High Resolution Transmission Electron Microscopy (HRTEM) and Electron Diffraction (ED) characterisation (figure 4.2). The as-grown GaN NWs exhibit a single crystal structure growing along the c-axis, atomic planes are separated by 2.52 Å. The single-crystal structure and the [0001] growth direction are confirmed by the ED image in the inset of figure 4.2. TEM images of single nanowires in figures 4.2.b, 4.2.c and 4.2.d give insights on the morphology of Ge-catalysed GaN nanowires. The surface of as-grown GaN NWs is atomically sharp with uniform lattice and no amorphous phase is observed.

4.A.2 Time-resolved PL and Raman spectroscopy

Figure 4.3 presents the PL characterisation, at room temperature, of an ensemble of single-crystal GaN nanowires before (figure 4.3.a) and after (figure 4.3.b) passivation. Both nanowire ensembles were analysed under the same excitation and detection conditions so that the emission intensities can be compared. PL emission of Ge (contained inside the droplet on top of nanowires) is localised from 0.6 to 0.9 eV and the Al_2O_3 shell (a wide band gap material with $E_g = 6.6$ eV) surrounding the core-GaN NWs, is transparent. The PL spectra of non-passivated GaN nanowires shows a NBE emission at 3.58 eV, characterised by a full width at half maximum (*fwhm*) of 450 meV. The spectrum is slightly asymmetric with a higher broadening at lower energies. A wide emission in the visible range, centred around 2.09 eV with a *fwhm* equal to 588 meV, is also observed. The BOE cleaning before passivation had no effect on the PL. And similar peaks are present in passivated GaN NWs. The NBE peak of GaN is observed at 3.58 eV with a sharper *fwhm* of 305 meV and a decrease by 3 % in intensity compared to non-passivated nanowires. We associate this slight decrease to a spatial variability of the nanowire ensemble since different areas were probed before and after passivation. The cleaning with BOE, before Al_2O_3 deposition, had no effect on the PL emission.

Figure 4.3: Photoluminescence spectra of a forest of GaN nanowires before (left) and after (right) passivation excited with HeCd laser at 325 nm. The discontinued lines are Gaussian fits showing YL and GL band. (insets) Mapping of YL band emission from single nanowire excited with a continuous diode laser at 532 nm.

Gaussian fitting of the asymmetric visible PL peak of passivated GaN NWs resulted in two distinct contributions: one centered at 2.09 eV and another at 2.40 eV (figure 4.3.b). The peak at 2.09 eV is commonly identified as a Yellow Luminescence, the one at 2.40 eV is associated to Green Luminescence. By considering the combination of these two peaks, the visible luminescence of as-grown nanowires can be attributed to a strong YL band emission ($I_{YL}/I_{NBE} = 4.63$), dominating a weak contribution of GL emission. By contrast, the visible luminescence of passivated NWs can be described as a combination of YL band (with a drastic decrease in its intensity $I_{YL}/I_{NBE} = 0.60$) and a GL band. The insets in figure 4.3 show the mapping of PL emission from single nanowire while excited with a laser diode at 532 nm (see Appendix A3 for more data). Thus, only the YL defect state is excited showing a strong and uniform distribution along the as-grown nanowire (figure 4.3.a) while there is almost no YL emission from Al_2O_3 coated nanowire (figure 4.3.b).

For the PL mapping, GaN NWs samples were sonicated in a pure Isopropanol Alcohol (IPA) then dispersed on Si substrate. Figure 4.4.a shows one single as-grown GaN nanowire with another smaller one, probably broken during sonication. The associated PL mapping (figure 4.4.b) matches exactly with the GaN nanowire position, the emission seems uniformly

distributed along the wire showing a similar distribution for the related defect. The comparison with Al_2O_3 coated NWs (figure 4.4.e) shows the effect of passivation on YL band, the emission is drastically suppressed. We see an emission only at the bottom of two bonded wires (figure 4.4.e, marker '2') while the nanowire near the marker '3' doesn't show any emission.

The NBE peak is quite broad and strongly blue-shifted (for both as-grown and passivated NWs) compared to bulk undoped GaN. This shift is associated to the heavy n-doping of these nanowires (above 10^{19} cm^{-3}). This high level doping most probably originates from the incorporation of Ge from the catalyst as Ge appears to be an efficient donor for GaN [112]. The second peak in the visible range, is slightly shifted to higher energies (centred around 2.15 eV). We remark that its intensity decreases by 88 %, after passivation. The visible luminescence of these LPCVD-grown GaN nanowires is wide and higher in intensity than the NBE emission. Few reports show this PL signature in GaN NWs grown by the classical techniques, such as MOCVD [113] or Plasma-assisted MBE. By contrast it is more commonly observed in thin film GaN [29].

Figure 4.4: Optical microscope image of dispersed nanowires on Si substrate of as-grown (a) and Al_2O_3 coated (d) NWs. Associated mapping of YL band emission from as-grown (b) and Al_2O_3 coated (e) NWs. Brightest emission from points 1 and 2 for single as-grown (c) and Al_2O_3 coated (f) nanowire, respectively. Excited with a continuous diode laser at 532 nm

In both as-grown and passivated NWs, we observe that the band-edge peak is quite broad

and largely shifted compared to bulk undoped GaN. Indeed, the photoluminescence (3.58 eV) is shifted by 140 meV compared to the bulk GaN at 300K (3.42 eV [5]). This shift could have been attributed to the quantum confinement effects. However, both SEM and TEM characterisations confirmed the diameter of core-GaN nanowires (around 34 nm) to be much larger than the Bohr radius of GaN bulk exciton which has been reported to be 2.8 nm [114]. This Bohr radius value thus excludes the hypothesis that the shift is originated from quantum confinement effects.

By contrast, the shift could be attributed to the high level of doping of our GaN NWs. Significant band-edge peak blue shift for heavily Si-doped Gallium Nitride layers [115], and nanowires [116, 117] has been reported. In our case, GaN NWs were grown on Silicon substrate using Germanium as a catalyst. Since both Germanium and Silicon appear to be electron donors for GaN, the blue shift observed in our GaN NWs can be explained by the band filling effect. In fact, due to the high doping element concentration, electrons populate states inside the conduction band, pushing the Fermi level higher in energy and giving rise to indirect optical transitions (with non-conservation of k-vector allowed by many-body interactions). This band-filling hypothesis is supported by the observed high broadening and asymmetry of the PL peak, with a higher broadening on the low energy side, which is typical for momentum non-conserving transitions [118]. For bulk n-doped GaN, the emission first shifts to longer wavelengths, which is attributed to band gap renormalization due to Coulomb effects (up to approx. 10^{19} cm^{-3}), and then blue-shifts due to band filling [115, 119]. Therefore, the strong blue-shift of the NBE emission suggests that the nanowires are heavily n-doped. This high level doping most probably originates from the incorporation of Ge from the catalyst, Ge appearing as more efficient donors for GaN than Si [112].

Time-resolved emission measurements show that after passivating the surface of the GaN NWs, the lifetime decay varies significantly for the YL-band (figure 4.5.a). For analysis, we fit the decay curves in figure 4.6 with a single or double exponential using the following equation:

$$N(t) = N_1(0) \exp\left(\frac{-t}{\tau_1}\right) + N_2(0) \exp\left(\frac{-t}{\tau_2}\right) \quad (4.1)$$

Where $N(t)$ is the total number of population from all emission channels after t time. $N_1(0)$ and $N_2(0)$ are the initial population at $t = 0$, which have emission lifetimes for fast and slow

Figure 4.5: Lifetime decay curves of YL (564 nm) and GL (489 nm) emission from quasi-resonant excited with a pulsed laser at $371 \text{ nm} \pm 5 \text{ nm}$. The Instrument Response Function (IRF) is 0.35 ns. The time constants are obtained after deconvolution with the Instrument Response. The exponential decay fitting is shown with full lines.

emission channels of τ_1 and τ_2 , respectively.

A $371 \pm 5 \text{ nm}$ pulsed laser was used to excite the defect-related states only. YL lifetime decay is observed as a single exponential decay before Al_2O_3 deposition ($\tau_1 = 0.23 \pm 0.01 \text{ ns}$) while a slower component appears after passivation ($\tau_1 = 0.18 \pm 0.01 \text{ ns}$ and $\tau_2 = 5.90 \pm 0.17 \text{ ns}$). τ_1 and τ_2 are the characteristic times of the bi-exponential decay (as defined in equation 4.1). The fast component in YL remains almost constant after passivating the surface, suggesting an emission from similar recombination state, but its contribution decreases, which concurs with the weakened YL emission observed earlier (figure 4.3), with Al_2O_3 layer most surface states have been suppressed. However, after passivation the YL emission includes an additional slower component that originates either from a volume recombination or a new defect could have been created by the Al_2O_3 deposition (interfacial defect states). From PL observations, this overall defect emission is still much weaker than before passivation.

Figure 4.6 show the lifetime decay curves for several wavelengths from as-grown (figure 4.6.a) and Al_2O_3 coated GaN nanowires (figure 4.6.b). The qualitative observation when comparing these decays confirms the initial conclusion on the selectivity of passivation on the YL band. Indeed, for lifetime decay curves at 620, 564 and 557 nm (close to YL band) we see a strong effect of passivation on the nature of surface charges. The higher the detection energy we observe at (toward GL), the lesser is the effect of the passivation.

By comparison with the YL band, where the intensity of PL and decay curves are strongly

Figure 4.6: Lifetime decay curves from quasi-resonant excitation of a forest of as-grown (a) and Al_2O_3 coated (b) GaN NWs. Excited with a pulsed laser at $371 \text{ nm} \pm 5 \text{ nm}$.

affected by the passivation of NWs, the GL band is almost unchanged. The presence of high density of surface states tends to pin the Fermi level near the surface and bends the electronic bands which affects the recombination process. Growth of alumina oxide layer on the surface of core-GaN NWs induces a modification of the nature of surface charges, such as active defects. The poor effect of this passivation on GL decay curves is in favour of the selectivity of the process to YL related-defects. Thus, the selective suppression of the YL emission suggests YL peak is mostly related to structural defects located at or near the surface while GL-related defects are more uniformly distributed in the NW volume. This observation is consistent to the earlier photo-voltage spectroscopy [100] and temperature and excitation dependence experiments [101] on GaN layers.

4.A.3 Conclusion

The optical properties of as-grown and aluminum-oxide passivated GaN nanowires synthesised by LPCVD have been analysed. As-grown nanowires exhibit a strong visible luminescence. By analysing the optical properties of the as-grown NWs and passivated with a thin Al_2O_3 shell, we observed that the visible luminescence results from two contributions: a yellow (2.09 eV) and green (2.40 eV) band. The passivation of NWs drastically reduces the yellow band while maintaining the green band and NBE emission. The results suggest the defects responsible for the YL band could be localised near the surface of the GaN nanowires and can be easily passivated by Al_2O_3 ALD while the defects causing GL are of bulk nature. GaN nanowires are

grown using cost-effective LPCVD-system and Ge as catalyst.

Defect-related emission is shown to be selectively modulated by passivating the surface with a thin layer of Al_2O_3 . Here we show a method to utilize the defect at our advantage by selecting the emission wavelength.

4.B Defect-related emission from exotic GaN nanowires

4.B.1 Introduction

GaN nanowires can be typically grown following a CVD method with or without catalyst. It has been shown previously that GaN nanowires can be grown efficiently using Gold (Au), Nickel (Ni) or even Germanium (Ge) as catalysts [81,120–122]. Experiments with an industrial LPCVD system showed high-quality single-crystal GaN nanowires using Ge as seed catalyst. Resulted nanowires were straight, growing along the c-axis with an atomically sharp surface exhibiting a uniform lattice without amorphous phase. Whereas, Ni-catalysed growth resulted in twisted nanostructures as observed in previous sections.

Pine trees-like GaN nanostructures are obtained with hybrid Ge and Ni catalyst as presented in section 3.C. The structure varies significantly from conventional nanowires observed with MBE- or MOCVD-assisted synthesis. Similar structures of GaN have not been reported in literature before to the best of our knowledge. Dislocation driven growth of hierarchical lead sulfide (PbS) pine tree structures have been reported by Bierman et al. in Science in 2008 [92]. Yet, the morphology differs significantly from GaN pine trees presented in figure 4.7.

Bierman et al. show their nanostructures as a demonstration and validation of Eshelbys theory on dislocations. This theory predicts that lattice distortions in nanowires containing an axial screw dislocation should show a crystal rotation due to the dislocation induced torque. A spine nanowire of PbS is grown following a VLS mechanism with screw dislocations, the dislocations allow sites for concentration of adatoms and a self-sustained growth of PbS nanowires. Following the dislocations, the lateral growth of individual nanowires results in a macro morphology similar to a pine tree. Screw dislocation-driven growth resulting in similar nanostructures have been reported several times [93, 94, 123]. Wurtzite III-nitrides nanostructures, have also shown screw dislocations. Hollow structures have been reported in GaN [124], AlN and InN [123].

Nothing like the GaN pine-trees observed here have been reported so far. Surface dislocations being the cause of the lateral growth seems to be the best explanation here, yet in the following discussion, the absence of proper TEM characterisation keeps us from an accurate

Figure 4.7: Pine tree-like GaN nanostructures obtained with hybrid Ge/Ni catalyst.

answer. Yet, the lateral growth's width compared to the very small diameter of the central spine is very curious. Also, as observed previously, the pine trees are flat, the growth seems to be anisotropic around the central spine.

In this section we focus on the optical capabilities of these pine trees.

4.B.2 Methods

The synthesis of GaN nanowires was carried out as described in previous section 3.C using an industrial Low Pressure Chemical Vapour Deposition (LPCVD) system (from SEMCO UP-SYS). The following paragraphs sum up the growth methodology to focus later on the study of the defect-related emission observed from these structures.

Synthesis: The synthesis of GaN nanowires was carried out as described in previous sections.

The temperature is raised to the desired growth temperature in approximately 30 mins (heating speed of 22 °C/min) and stabilised for 15 mins. The GaN nanowires were successfully grown in the temperature range of 580 to 930 °C. The thin layer of catalyst on the substrate tends to dewet at high temperature and forms nanoparticles that will be the seeds for the growth, as for a typical VLS growth mechanism. The growth starts as a flow of 50 sccm of NH_3 , diluted in 200 sccm of H_2 , is introduced in the chamber through a long tube to a position right below the growth zone to feed the growth. The pressure in the reaction chamber is kept at 250 mTorr and the growth lasts 30 mins to 1 hour. Once the process is over, the chamber is cooled down passively to room temperature. The figure 3.6 helps to better understand the system.

RGaN Pine Tree nanostructures are specifically obtained for Ge/Ni catalyst at a temperature near 880 °C, with a pressure set to 250 mTorr and NH₃:H₂ ratio of 1:4.

Optical characterisation: The Raman and PL mappings were performed using a 532 nm CW laser at 37 μ W. Coupled to a WITec focus innovations microscope, the beam is focused on the sample with a $\times 100$ Olympus objective with 0.8 NA. The scanning is done using a computer-controlled piezoelectric stage with a resolution of 0.5 μ m/step. The emission is filtered at 570 nm with a long-pass filter and the data is processed with the associated WITec Project software.

The time-resolved photoluminescence set-up consisted on a Picosecond Pulsed laser VisUV based on master oscillator fibre amplifier system from PicoQuant. This excitation source emits at 355 nm. The decay is measured using a Hamamatsu H7422-40 photo-sensor associated with a single-grating emission monochromator of 1200 grooves/mm density. The signal is analysed using single photon counting card.

4.B.3 Structural characterisation

As we have seen in section 3.C, pine tree-like GaN nanostructures are obtained with hybrid Ge and Ni catalyst. On a Si substrate, a thin layer of Ge is deposited before another Ni thin layer. From the growth main parameters, such as chamber vacuum, NH₃:H₂ ratio and temperature, the latter is observed to be most critical in the synthesis of pine trees. Figure 3.25 from previous chapter exhibits the effect of temperature on nanostructures obtained with Ge/Ni (5 nm/1 nm). From twisted and randomly grown structures, the pine trees appear at 880 °C showing a straight and flat shape with length exceeding 15 μ m.

The side wall is due to dislocations at the surface of central spine nanowire. Diffusivity of adatoms on the surface allows the formation of nanostructures: self-perpetuated or Ni/Ge-catalysed growth ensure the development of the pine tree. We explain this due to surface orientation. At the tip of the pine trees (e.g. inset of figure 3.20.b), the bulk structure tends to grow all around the wire, as the growth progresses (e.g. middle of nanostructure in figure 3.21) and the bulk expands, it promotes only on crystallographical orientation: the same opposite the hexagone of GaN. TEM images may inform on which sides are promoted but sample prepa-

Figure 4.8: Raman spectrum and spatial mapping of one single GaN Pine Tree nanostructure on Si substrate. Excitation source: CW Laser at 532 nm.

ration tend to break the pine trees. After several failures with FIB and drop-casting, the TEM characterisation could not have been performed. Better sample preparation protocol is needed to prepare such structures for TEM (e.g. nano-manipulators).

4.B.4 Optical characterisation

Group theory predicts four pairs of Raman active modes for hexagonal structure of GaN: A_1 and E_1 (Raman and infrared active), B_1 (silent mode) and E_2 (only Raman active). One set of A_1 and E_1 modes are acoustic while all others are optical modes. The A_1 and B_1 modes result from atomic displacement along the c -axis while E_1 and E_2 inform on displacement perpendicular to that axis [9].

Additionally to the previous figure 3.22 in section 3.C, the figure 4.8.a shows the Raman

spectra of another single GaN pine tree with a spatial mapping showing E_1 (TO) and E_2 (high) Raman modes and the shift from Si substrate. It is worth noticing the small focus range of the objective of the Raman system. As the GaN structure is not completely flat, the sides of the structure are out of focus during the mapping, resulting in lower intensity Raman scattering.

The peak E_2^H , identified at 573 cm^{-1} on figure 4.8.a, is correlated to the stress within the c-plane and is characteristic of hexagonal (Wurtzite) phase of GaN. The mapping reveals a strong E_2^H (and E_1) along all the pine tree structure with low intensity at the edges, this may be due to the sharp depth of field of the microscope objective, the pine tree not being totally flat, the edges are out of focus, thus exhibiting a lower intensity Raman signal.

Figure 4.9.c shows the PL emission spectra after exciting the structure with a CW diode laser at 532 nm. Only defect-related states are excited. As-grown pine trees structures exhibit a yellow-red photoluminescence from 580 to 620 nm and the spatial PL mapping (figure 4.9.b) localises the highest emission close to the central area of the structure. It is worth noticing the GaN in this form is sensitive to the power of excitation source, the structure absorbs strongly and can be damaged during optical measurements.

Figure 4.9: PL spatial mapping of a single pine tree. a) Single pine tree structure observed with optical microscope. b) Mapping of PL intensity. c) Spectrum of PL emission. Excitation source: CW diode laser at 532 nm.

Reshchikov et al. may be the most active group reporting on defect-related luminescence in GaN. In 2006, they reported [24] in high-purity freestanding GaN templates, the YL band is attributed to $V_{Ga}O_N$ complex. Yet, in less pure GaN layers, similar emission can be caused by V_{Ga} -related defects (isolated complexes and defects trapped at dislocations and other structural imperfections). Whether carbon could be responsible for a similar PL also remains to be answered. In 2014, they report for a majority of GaN samples, carbon impurities to form

complexes with oxygen and induce the YL band at 2.2 eV. Only in HVPE-grown GaN film, with low concentration of carbon and oxygen defects, they observe luminescence from isolated C_N defects as source of the YL band at 2.1 eV. In 2017, the YL band is confirmed to be related to carbon as majority of GaN samples show C_NO_N complex with a transition level at 0.85 eV above the valence band with Deep-Level Transient Spectroscopy (DLTS) studies.

We understand from literature [24, 26, 97, 125–127] that the source of the energy level equal to the YL or GL may not be due to one particular structural defect of impurity. Various impurities seem to result in similar luminescence bands. The characterisation methods available to us do not give enough information to investigate precisely the origin of the defect. PL characterisation gives us the energy levels at which the defects allow energy states, but as we have seen before, several defects can be related to these energy levels, from isolated nitrogen site or carbon-oxygen complexes.

4.B.5 Conclusion

We have shown in this section the Wurtzite nature of GaN pine trees, with a shape very different from conventional one-dimensional nanostructures observed in literature. PL mapping, with emission ranging from 580 to 620 nm, shows defect-related emission distributed along the pine tree structure. This strong defect-related emission opens door for emitters based on defect-related states.

CHAPTER 5

Intentionally induced Point Defects for Localised Micro- and Nano-Emitters

Previous chapter developed the optical properties of GaN nanowires with a focus on visible emission capabilities. Yellow and green luminescence from defects in GaN nanowires have been presented as well as defect-related visible emission from exotic pine-tree-like GaN structures.

This chapter shows how to intentionally induce defects in GaN and hBN crystals to engineer localised emitters. A method based on femto-second pulsed laser irradiation shows a cost-effective and scalable method to create energy states below the conduction band that act as effective radiative states in the visible range.

We show that femto-second laser-assisted ablation of GaN creates micro-/nano-emitters that exhibit a strong gaussian photoluminescence. The emission ranges from 620 to 680 nm for GaN thin film, unintentionally doped and Mg-doped nanowires, respectively. Similarly laser-processed hBN flakes exhibit sharp emission, bright colour centres and single photons. Our results offer a new approach to engineer defects in hBN and opens way to explore further the optical properties of 1D and 2D materials in the application of nano-photonics and quantum technology using laser irradiation induced defects.

Part of the work presented in this chapter has been published in the following research papers:

- Saleem Umar, Muhammad Danang Birowosuto, Hou Songyan, Anicet Maurice Ange, Beng Kang Tay, Hong Wang, et al. 2017. “Light emission from localised point defects induced in GaN crystal by femto-second-pulsed laser.” *Under review*.
- Hou Songyan, Muhammad Danang Birowosuto, Saleem Umar, Anicet Maurice Ange, Tay Roland Yingjie, Coquet Philippe, Beng Kang Tay, Hong Wang, et al. 2017. “Localized Emission from Laser-Irradiated Defects in 2D Hexagonal Boron Nitride.” *2D Materials* 5 (1):15010.

5.A Intentionally induced point defects in GaN by femto-second-laser

Nanometer-sized light emitters can be obtained from molecules, nanoparticles or nanowires [128]. As we have already seen, Gallium nitride (GaN), a wide bandgap semiconductor, is a key material for LEDs, laser diodes and photo-detectors operating from visible to deep UV spectral range [129–131]. Epitaxial growth techniques allow a high quality material with low density of dislocations and low concentration of point defects. Some point defects in GaN crystal are known to be optically active, emitting red, yellow, green or blue luminescence [24–26], Nitrogen vacancy (NV) center is also predicted [28] but the energy states of defects are not always identified [29, 30]. The red luminescence is observed at 1.8 eV (689 nm) and the zero phonon line at 2.38 eV (at room temperature) is attributed to a transition from the conduction band to a deep acceptor of unknown origin [31].

Fabrication of efficient micro- and nano-meter scale GaN emitters is of crucial importance for optical nanodevices. In conventional semiconductors, such as Si or GaAs, fabrication processes involve expensive and time consuming electron beam lithography and etching. We propose using femto-second laser-based process, already widely used for micro-fabrication [132–134], as an alternative technique to fabricate efficient GaN-based micro- and nano-meter-size light emitters. Such technique is already demonstrated in the fabrication of NV center in diamond [135].

We show robust light emitters from localised point defects induced in GaN crystal by femto-second laser (fs-laser). Three different configurations of GaN have been studied: MOCVD-grown thin film, intrinsically doped and Mg-doped nanowires (NWs). In each case we show a localised ablation and melting of the GaN structure by fs-laser irradiation. Characterisation by scanning electron microscope (SEM) exhibits sharp holes (see figure 5.1, the laser-induced damage threshold is reached at a fluence of 130 ± 10 mJ/cm² for all samples. Raman spectroscopy mapping allows a characterisation of the GaN crystal while quasi-resonant photoluminescence (PL) mapping shows a red emission superimposed with fs-laser irradiated area. From all three different configurations, the emission from defects can be tuned. The emission peaks

Figure 5.1: SEM images of localised irradiations by femto-second pulsed laser at 800 nm of a) MOCVD-grown GaN thin film, b) MBE intrinsically doped GaN nanowires and c) MBE-grown Mg-doped GaN nanowires. and a magnification of irradiation ‘9’ is shown in e), f) and g), respectively.

vary from 626, 653 and 680 nm-wavelength while the emission lifetimes are 0.81, 1.37 and 1.19 ns for thin film, MBE intrinsically doped and Mg-doped NWs of GaN, respectively.

Three structures of high quality GaN crystal have been considered in this study: GaN thin film, MBE intrinsically doped and Mg-doped NWs of GaN.

The thin layer of GaN, commercially available, is 1 μm thin and grown by Metal-Organic Chemical Vapour Deposition (MOCVD) method on a Sapphire substrate. Two variations of GaN NWs have been grown using a Molecular-Beam Epitaxy (MBE) system: intrinsically doped and Mg-doped NWs. Both samples are doped p-type and the substrate used is Si [111] with a thin layer of AlN. In both cases, NWs show a diameter of 40-50 nm, grow along the [0001] axis and are N-polar [136, 137]. Scanning Electron Microscope images give more insights in figure 5.2.

A Mode-locked Ti:Sapphire Chameleon Ultra II laser with a repetition rate of 80 MHz, pulse of 140 ± 20 fs and output power of 4.13 W at 800 nm is used for irradiating the samples. To attenuate and tune this high laser power, a cross polarisation set-up is used by inserting a half wave plate (HWP) between two linear polarisers. Depending on the angle θ of the HWP, the laser power can be adjusted following Malus law ($I_{out} = I_{in} \cos(2\theta)$). Two lenses forming a telescope allow to broaden the beam width and optimise the coupling with a $\times 40$ Olympus objective, with 0.65 NA and 0.6 mm WD. Computer-controlled piezoelectric stage and a beam shutter fulfil a single-shot irradiation.

Figure 5.2: Top-view SEM images of irradiated area ‘7’ for a) MOCVD-grown GaN thin film, b) MBE intrinsically doped GaN nanowires and c) MBE Mg-doped GaN nanowires. d) and e) are side-view SEM images of intrinsically doped and Mg-doped GaN nanowires, respectively.

The Raman and PL mappings were performed using a 532 nm CW laser at 37 μ W. Coupled to a WITec focus innovations microscope, the beam is focused on the sample with a $\times 100$ Olympus objective with 0.8 NA. The scanning is done using a computer-controlled piezoelectric stage with a resolution of 0.5 μ m/step. The emission is filtered at 570 nm with a longpass filter and the data is processed with the associated WITec Project software.

The time-resolved photoluminescence set-up consists in a Picosecond Pulsed laser VisUV

based on a master oscillator fibre amplifier system from PicoQuant. This excitation source emits at 355 nm. The decay is measured using a Hamamatsu H7422-40 photo-sensor associated with a single-grating emission monochromator of 1200 grooves/mm density. The signal is analysed using single photon counting card.

On each sample, defects are induced by focusing the fs-laser beam at the surface. The focusing on the surface of the sample is determined as a position where the smallest energy is necessary for introducing the damage (with a laser power high enough), fs-laser irradiation is *in situ* monitored on a CCD camera. Any deviations from the focusing point (to the air or substrate side) requires a higher energy for damage since the laser-induced damage threshold (LIDT) inside bulk is larger than that at surface. Following this protocol, nine areas are irradiated one by one on each sample. Starting from area labeled ‘1’ in figure 5.1, the HWP is set to 144° , equivalent to 460 ± 30 mW laser power, the shutter is then opened for 2 s exposure. A computer-controlled piezoelectric stage allows to move ~ 5 μm then a new area at decreasing energy is irradiated. One last spot (label ‘9’), similar to the first one, marks the end of irradiations. The specificities of irradiations are given in table T5.1. It is worth noticing that the fs-laser focusing, added to slight misalignments of the beam, result in asymmetric damaged areas, as seen in figure 5.1.a for thin film GaN.

5.A.1 Structural Characterisation

LIDT is a physical characteristic of optical components which defines a critical power or peak fluence of laser irradiation causing irreversible changes in the structure of the material. LIDT is the minimal pulse energy measured corresponding to an appearance of surface damage, as observed on SEM images in figure 5.1.

It is worth noticing the magnification on irradiated area ‘7’ in figure 5.2, where no laser-induced damage is observed. Mg-doped GaN NWs sample shows an anomaly that appears to be a bundle of nanowires detached from somewhere else. LIDT is achieved only from area ‘6’ with fluence 130 ± 10 mJ/cm² with a pulse energy of 2.3 nJ.

LIDT is a physical characteristic of optical component which defines a critical power or peak fluence of laser irradiation causing irreversible changes in materials structure. For the

Table T5.1: Pulse energy, fluence and intensity of irradiation by fs-laser of each sample.

Label	HWP (°)	Pulse energy (nJ)	Fluence (mJ/cm ²)	Intensity (TW/cm ²)
1	144	5.74	325.00	2.32
2	145	5.01	283.63	2.03
3	146	4.10	232.22	1.66
4	147	3.46	195.67	1.40
5	148	2.86	162.12	1.16
6	149	2.31	130.77	0.93
7	150	1.91	108.08	0.77
8	151	1.60	90.56	0.65
9	144	5.74	325.00	2.32

three samples we observe LIDT as the minimal pulse energy measured corresponding to an appearance of surface damage, as observed on SEM images in figure 5.1. We achieve LIDT at fluence equal to $130 \pm 10 \text{ mJ/cm}^2$ with a pulse energy of 2.3 nJ. It is worth noticing that LIDT is the same for thin film and 1D nanostructures of GaN, the threshold energy is only dependent on the nature of GaN crystal. At 800 nm, GaN is transparent to the excitation. For transparent materials, the absorption of light from femtosecond laser is described to be nonlinear as no electronic transitions at the energy of the incident photon are allowed. When a femtosecond laser pulse is focused into a material, the pulse energy is described to partially transfer to electrons in the short duration of the pulse. The highly excited electrons thermalize with the ions and alter the material permanently [138]. Table T5.2 shows parameters and energy details for fs-laser induced defects in various structures of GaN.

The figure 5.3 shows AFM mapping of GaN thin film after irradiation by fs-laser to study the structural shape and depth of the structures defects induced. Due to the fragile structure of standing NWs, AFM image from GaN NW samples was not successful.

Figure 5.3.a shows a general view of the defects with height levelled to non-irradiated area of the thin film. The craters are distinctly visible with darker (deeper) areas as the fluence increases. Figure 5.3.b focuses on area ‘9’ and the marked section is integrated and plot in figure 5.3.c. The crater is $\sim 350 \text{ nm}$ deep while the peak-to-valley height at $\sim 450 \text{ nm}$ shows the melting effect of fs-laser above LIDT.

The laser irradiations in all three cases result in structural deterioration of the GaN crys-

Figure 5.3: AFM characterization of fs-laser irradiation for MOCVD-grown GaN thin film

tal. The laser-induced damage morphology is a good indicator of the nature linked to damage initiation mechanism. SEM images (figure 5.1) show ablation in the center of irradiated areas, the edges of crater become blurred with melted crystal and residual debris. This matches a thermally induced laser damage followed by localised melting, then boiling, evaporation and plasma formation. The high pressure of melted gas results in blurred patterns redeposited on the nearby surface, clearly observed in figure 5.1.a and 5.1.e on GaN thin film sample. These results are reported as irradiation above ablation threshold in the center of the crater and a dissociation of Ga-N bonds on the edges where laser intensity is below ablation threshold resulting in a formation of Ga-rich phase [139].

5.A.2 Optical characterisation: spacial mapping

These fs-laser induced craters are optically active. Figure 5.4 shows irradiation ‘9’ observed under a conventional optical microscope, a mapping of the GaN E_2^H Raman mode and a PL emission intensity map. For thin film sample, we observe from the Raman mapping (figure

5.4.a) that the irradiation at $325 \pm 20 \text{ mJ/cm}^2$ fluence removes the fundamental E_2^H resonant mode of GaN Wurtzite structure. The associated SEM image (figure 5.1.e) distinguishes a central crater surrounded by melted area. The E_2^H Raman mode of GaN does not appear neither in the crater nor the surrounding melted area. An excitation with a 532 nm CW laser however reveals a strong photoluminescence from this surrounding melted area, the emission is centred at 626 nm. The central crater does not emit light while the top melted area is the strongest emitter.

Figure 5.4: Comparative study on irradiation ‘9’ showing an optical image, a mapping of the GaN E_2^H Raman peak and a PL mapping of defect related emission of a) MOCVD-grown GaN thin film, b) MBE intrinsically doped GaN nanowires and c) MBE-grown Mg-doped GaN nanowires..

The observations are quite similar for irradiation of NWs. For intrinsically doped GaN NWs, the SEM (figure 5.1.f) shows a crater, void of GaN surrounded by melted NWs collapsing towards the center. The Raman mapping of the GaN E_2^H Raman mode (figure 5.4.b) confirms

the ablation of NWs in the crater as no scattering is observed. The surrounding pristine NWs show a relative uniform E_2^H peak centered at 567.4 cm^{-1} . The associated PL mapping shows a dim center while the emission from surroundings is bright, uniform and superimposed to the melted area of NWs. The emission is Gaussian and centred at 653 nm. Non-irradiated NWs do not show any emission. Irradiation of Mg-doped NWs results in an area of $\sim 3 \mu\text{m}$ wide with melted nanowires (see figure 5.1.c) only. The associated Raman mapping (figure 5.4.c) does not show the GaN E_2^H mode in the center of irradiation whereas PL mapping exhibits a strong emission well distributed along the melted area. The emission is centred at 680 nm.

Figure 5.5: a) Comparative Raman spectra of pristine GaN thin film, un-doped and Mg-doped GaN nanowires, b) comparative PL spectra of defect-related emission, as measured during the mapping and c) lifetime decay curves of defect-related emission excited with a pulsed laser at 355 nm at 300 K. The Instrument Response Function (IRF) is 0.39 ns. The time constants are obtained after deconvolution with the instrument response. The exponential decay fitting is shown with full line.

Group theory predicts four pairs of Raman active modes for hexagonal structure of GaN: A_1 and E_1 (Raman and infrared active), B_1 (silent mode) and E_2 (only Raman active). One set of A_1 and E_1 modes are acoustic while all others are optical modes. The A_1 and B_1 modes result

Table T5.2: Phonon frequencies observed at 300 K for GaN thin film, Mg-doped and un-doped nanowires [9, 10]

MOCVD thin film (cm ⁻¹)	MBE NWs (cm ⁻¹)	MBE Mg-doped NWs (cm ⁻¹)	Peak identification
		557.7	E ₁ (TO)
577.6	567.4	568	E ₂ (High)
317	307	307	Acoustic overtone (2 nd order)
	434	432	Acoustic overtone (2 nd order)
	620	619	Overtone (2 nd order)
	665	668	Overtone (2 nd order)
	520	521	Silicon substrate
424			Sapphire substrate

from atomic displacement along the c-axis while E₁ and E₂ inform on displacement perpendicular to that axis [9]. Figure 5.5.a shows the Raman spectra of pristine GaN, as measured during the mapping. Table T5.2 identifies all peaks observed. The peak E₂^H, most easily observed, is identified around 568 cm⁻¹ characteristic of Wurtzite GaN for MBE-grown nanowires on silicon, Mg-doped and intrinsically doped [10]. This peak is shifted at 577.6 cm⁻¹ for MOCVD-grown GaN thin film on sapphire. This shift is correlated to the stress within the c-plane. The strain coefficients of phonon modes vary according to GaN/Si and GaN/sapphire systems, E₂^H varies with substrate material [140]. Table 5.3 lists and identifies the Raman spectroscopy peaks as observed in figure 5.5.a.

The PL mappings in figure 5.4.a, 5.4.b and 5.4.c show a spatial distribution of the emission intensity from defects induced by fs-laser, and figure 5.5.e shows the normalised PL spectra from respective samples. We notice a distinct shift in the emission. For MOCVD-grown GaN thin layer, MBE intrinsically doped and Mg-doped GaN NWs, the emission peak modulates from 626, 653 and 680 nm, respectively. The emission is gaussian and spatially matches the irradiated area for each sample.

It has been reported that individual nanowire exhibits single decay while an ensemble of nanowires exhibits different decay times [141]. In this case, two exponential decays from the ensemble of nanowires are probed as one fast and one slow component as superposition of multiple decay times of individual nanowires from the ensemble. For planar layer, the decay is single exponential decay as the structure is less heterogeneous than an ensemble of nanowires.

Time-resolved PL measurements shows a fast lifetime decay for thin film GaN and a slower

Figure 5.6: Comparative study of femto-second laser irradiation showing an optical image, a mapping of the GaN E_2^H Raman mode and a PL mapping of defect-related emission of a) MOCVD-grown GaN thin film, b) MBE intrinsically doped GaN nanowires and c) MBE-grown Mg-doped GaN nanowires.

recombination for NW samples. The samples were excited with a 355 nm pulsed laser associated to a microscope to probe the irradiated area. Qualitatively, lifetime decay increases with distance between states. The fast decay of GaN thin film emission ($\tau_1 = 0.81 \pm 0.01$ ns) compared to intrinsically doped NWs ($\tau_1 = 1.37 \pm 0.04$ ns - 50% contribution) and Mg-doped GaN NWs ($\tau_1 = 1.19 \pm 0.05$ ns - 45% contribution) suggests defects of different nature. Furthermore, the decay of un-doped and Mg-doped GaN NWs is bi-exponential, indicating an additional recombination state with characteristic times of $\tau_2 = 22.73 \pm 2.53$ ns (50% contribution) and $\tau_2 = 19.92 \pm 2.10$ ns (55% contribution), respectively.

The effect of fs-laser irradiation on a larger scale is analysed by scanning all irradiated

areas, as shown in figure 5.6. It is clear from the PL mappings that the centers of emissions are localised precisely at the fs-laser irradiated areas. Only the areas ‘7’ and ‘8’ do not show neither a structural defect nor any effect on the E_2^H Raman mode nor any PL defect-related emission. Defect-related emission only appears above the LIDT for fluence above 130 ± 10 mJ/cm² with structural deterioration.

Red luminescence bands have been reported at various energy positions and several defects may contribute to emission in this range. Red band in GaN grown by Hydride vapour phase epitaxy (HVPE) has been observed at 1.85 eV (670 nm) and Optically Detected Magnetic Resonance (ODMR) characterization reveal a transition from shallow donors to deep level defects (at low temperature) [142]. Undoped GaN sample grown by MBE show red emission ranging from 1.8 to 2.0 eV (620 to 690 nm) while the band transition and related defect are unclear [143]. From literature, in Mg-doped GaN grown by MBE, the red band is located near 1.7-1.8 eV, and ODMR characterization indicated a transition from a deep donor to a shallow acceptor [144]. While in other reports, this transition is attributed to deep donor-deep acceptor transitions [145, 146]. Red luminescence band is more specifically observed in Ga-rich MBE-grown GaN [29].

5.A.3 Conclusion

We show that a femto-second laser-assisted ablation of GaN creates nano-emitters that exhibit a strong gaussian photoluminescence localised at the ablation area. The emission peaks at 626, 653 and 680 nm for GaN thin film, intrinsically doped and Mg-doped nanowires, respectively. The ablation fluence threshold for a 140 fs pulse is about 131 mJ/cm². From Raman observations, GaN is removed on the thin film sample for fluence above the threshold, for samples of GaN nanowires, fluence above threshold tends to melt the targeted area, incorporating defect in the structure. These defects are source of the visible luminescence, located at 626, 653 and 680 nm-wavelength for thin film, MBE intrinsically doped and Mg-doped NWs of GaN, respectively. Such tunable emission from defects in GaN are suitable nano-sized light source. For further applications, engineering nano-meter-sized craters can be achieved using the second harmonic of fs-laser (at 387 nm) [139]. To enhance this emission, light-matter interaction

using photonic crystals can be explored [27, 147].

5.B Localised Emission from Laser-Irradiated Defects in 2D Hexagonal Boron Nitride

In this section, we show colour centres in hBN monolayers and hBN flakes induced with similar laser irradiation technology. As we have seen in the previous section, the laser irradiation method seems quite effective and repeatable owing to the flexibility to tune the irradiation energy and accurate positioning of the laser beam. Creating localised structural defects has been achieved with GaN material. This section explores the effects on hBN, another wide bandgap semiconductor.

We have pointed out in the introductory chapter the benefits and interest in hBN material. Laser irradiation of hBN material results in a crater similarly to the GaN material. Using Raman spectroscopy we see in figure 5.7 a transition from hBN-to-cBN around the laser irradiated region in monolayers. A defect related emission is also found around the crater. The emission is sharp with *fwhm* of 4.5 nm and 1.4 nm in hBN monolayer domains and flakes, respectively. Emission centres are brighter in hBN flakes than in hBN monolayers and even single photon emission is found in irradiated hBN monolayers while bright narrowband emissions with $g^{(2)}(0)$ as low as 0.20 is detected for flakes. The results here show the optical properties of laser irradiated regions in hBN, and confirm the previously demonstrated method of generating localised emitters with laser irradiation.

5.B.1 Characterisation

Hexagonal Boron Nitride (hBN) monolayers are synthesised using a classical CVD method and transferred to SiO₂ on Si substrate. Similarly to previous experiments, fs-laser is used to irradiate hBN monolayer to induce defect and generate localised emitters. It has been reported that such high energy irradiation can trigger a phase transition to cBN [148, 149].

Figure 5.7.a exhibits Raman scattering probed at various locations near one laser irradiation. Each curve is associated to the label in figure 5.7.c. The Raman modes observed around 1460 and 1370 cm⁻¹ correspond to the Si substrate and hBN, respectively [150].

Figure 5.7: Raman spectra of hBN monolayers. (a-b) Raman spectra corresponding to the points on line (a) and curve (b) marked in (c). (c) The microscope of void in hBN with points L1, L2, ..., L7 on the line and points C1, C2, C3 on the curve. The arrows show the order of these points and L2, L5 are the intersectional points of curve and line. Excitation wavelength of Raman is 532 nm. The scale bar of microscope image is 5 μm . The crater is created by a laser irradiation at 1.93 W

Laser ablation results in a crater as previously observed. The center is void of hBN, as suggest the absence of the Raman peak at 1370 cm^{-1} . Instead, the observations suggest the presence of cBN crystal, characterised with two isolated modes: one transverse optical (TO) at 1056 cm^{-1} and one longitudinal optical (LO) vibrational mode at 1305 cm^{-1} [150]. From literature, the changes of the TO and LO modes occur as function of cBN crystal size [150]. In a nano-crystal structure of cBN, TO mode disappears while the LO mode is slightly shifted and broadened. This trend is observed in our case. Indeed, the mode at 1295 cm^{-1} from locations L2 and L5 (see figure 5.7.a and c) is characteristic of the nano-crystal cBN.

The small G band around 1600 cm^{-1} localized at labels L2 and L5 is characteristic of carbon contamination, that could be due to hydrocarbons incorporated during laser processing or polymethyl-methacrylate (PMMA) residues left during sample preparation. The low intensity of the G band suggests a low content of carbon, it will be ignored in the following discussions.

The Raman spectra around the crater does not change much, as seen in figure 5.7.b. This suggests that the phase components in transition region are homogeneous hBN-to-cBN transitions. This transformation is observed in literature for hBN crystal irradiated with high energy. Raman modes are also similar to the transformation from hBN-to-cBN from He⁺ ion implantation [35].

Compared to large monolayers, domains in hBN monolayer show sharper emission peaks when irradiated with fs-laser. This suggests a relationship between optical properties and the

Figure 5.8: (a-c) Localised emission centres in hBN monolayers induced by fs-laser irradiation. (d-g) and flakes. (a,b) PL mapping irradiated regions in hBN monolayers. Inset: PL spectrum. (c) Microscope image of areas shown in (a,b), the laser powers are: 1.25 W, 0.89 W, 0.53 W, 0.27 W and 0.10 W from right to left. (d,e,f) PL mapping of laser irradiated regions in hBN flakes. Inset: PL spectrum. (g) Microscope image of areas shown in (d,e,f), the implemented laser powers are: 1.60 W, 1.25 W, 0.89 W, 0.53 W, 0.27 W and 0.10 W from left to right. Scale bar: 10 μm .

size of hBN and hBN flakes. To stress this observation, hBN monolayers and flakes are irradiated with fs-laser at different laser powers. Figure 5.8 shows optical properties of hBN monolayers and flakes after fs-laser irradiation. Bright luminescence is observed at irradiated regions, indicating the formation of optically active defects. The created defects in hBN monolayers show an emission very close to the one observed in smaller hBN flakes, suggesting a similar type of defect induced by the irradiation (figure 5.8.a and f).

The figure 5.8.f shows a feature not observed in our previous experiments. A narrow emission ($fwhm$ of 1.4 nm) appears in hBN flakes irradiated with laser energy below LIDT. While in hBN monolayers, no luminescence is observed after similar irradiation below the LIDT, no defect is induced. Above LIDT, defect-related emission is observed for both monolayer and flakes, yet hBN flakes show stronger fluorescence than monolayers (see figure 5.8.a, b, d, e and f).

Figure 5.9: Single photon emitters in hBN flakes. (a-b) Second order autocorrelation functions curves from individual colour centres in hBN flakes (red and blue open circles). Solid red and blue lines are fits using equation. (c-d) PL images corresponding to (a) and (b). Scale bar: 1 μm .

From figure 5.8.d, e and f, plenty of separated bright emitter spots are created with fs-laser irradiation. The majority is attributed to single point defects in hBN flakes. Figure 5.9 presents the lowest and highest $g^{(2)}(0)$ among all measured single photon emitters in hBN flakes with corresponding PL mapping. Each spot is measured at room temperature with 40 μW excitation laser and acquisition time of 20 s. The data is normalised without background correction. The fitting shows $g^{(2)}(0)$ ranging from 0.20 to 0.42 among all single photon sources as observed in hBN flakes in figure 5.8.g. The fitted values of τ_{tot} in figure 5.9.a and b are 3.4 ns and 3.2 ns, respectively. Figure 5.9.c and d show a diameter of bright spot of ~ 650 nm which is the diffraction limitation of CCD camera, indicating diffraction limited optical centre is successfully induced. The bright spot in figure 5.8.f also demonstrates single photon emission with $g^{(2)}(0) = 0.25$, suggesting a single photon emitter can be deterministically engineered by laser processing without damaging the substrate.

5.B.2 Conclusion

We successfully create emission centres in hBN monolayers and flakes via fs-laser irradiation and show a phase transition from hBN to cBN crystal in large hBN monolayer regions. The strong and sharp emission matches well with $N_B V_N$ -like point defects in hBN. Laser processed hBN flakes exhibit sharper and brighter emission centres compared to monolayers and also appear as great single photon emitters. These results confirm the methods used with Gallium Nitride material in the previous chapter and confirm this interesting approach to engineer localised defects in hBN and motivate for further exploration of optical properties of 1D and 2D materials in the application of nano-photonics and quantum technology using laser irradiation-induced point defects.

CHAPTER 6

Photonic Structures towards Enhanced Wide-Bandgap Emitters

The previous chapter showed how it is possible to intentionally induce defects in GaN and hBN crystals to engineer localised micro- and nano-emitters. A method based on femto-second pulsed laser irradiation shows a cost-effective and scalable method to create energy states below the conduction band that act as effective radiative states in the visible range.

This chapter explores a method to improve the emission rate from radiatively active states such as those observed and created in GaN or hBN. To show this method we couple quantum dots of graphene with single Bi_2Te_3 nano-plates. Easier to couple than GaN nanowires or hBN thin film or flakes, graphene quantum dots (GQDs) also show excellent properties for visible emitters. In this chapter we show the emission rate enhancements from N-doped GQDs coupled with single Bi_2Te_3 nano-plates. With ~ 500 nm-diameter Bi_2Te_3 nano-plates, we improve the emission rate enhancement by ~ 2.9 . We first show that the quantum yield (QY) of the N-GQDs is almost unity, showing a promising active medium for optoelectronic applications. Then, we show that single Bi_2Te_3 nano-plate is an alternative plasmonic antenna for enhancing spontaneous emission rate beside semiconductor and conventional metal antennas.

Part of the work presented in this chapter has been published in the following research papers:

- Saleem Umar, Fitri A. Permatasari, Ferry Iskandar, Takashi Ogi, Kikuo Okuyama, Yudi Darma, Meng Zhao, et al. 2017. “Surface Plasmon Enhanced Nitrogen-Doped Graphene Quantum Dot Emission by Single Bismuth Telluride Nanoplates.” *Advanced Optical Materials* 5 (17):1700176.

6.A Surface Plasmon Enhanced Nitrogen-Doped Graphene Quantum Dot Emission by Single Bismuth Telluride nano-plates

6.A.1 Context

Graphene quantum dots (GQDs) are considered to be the future nano-emitters due to their excellent properties, such as resistance to photo-bleaching, low toxicity, excellent bio-compatibility, abundance in nature, and low cost. Fabrication methods via electron-beam lithography [46] and ruthenium-catalysed C₆₀ transformation [47] are expensive. Recently, hydrothermal [48] and electrochemical [49] strategies were introduced as common fabrication methods for GQDs. Using this hydrothermal reaction, the effects of atom doping on GQDs have been further investigated through the preparation of various precursors [50].

Nitrogen doped (N-) GQDs showed better photoluminescence (PL) properties, compared to GQDs, as they were synthesised from citric acid and urea as precursors [51, 52]. In addition, the emission colour can be tailored from green to yellow by simply changing the solvent in the hydrothermal reaction [50]. The shortening of the emission lifetime (τ) from 14 to 10 ns is proportional to the increase in the emission wavelength from blue and yellow, showing that the emission originates from single luminescent species specific to each N-GQD [51]. The quantum yields (QYs) of those N-GQDs were reported to be as high as 0.9 (in particular blue-emitting QDs) due to less hydroxyl and carboxyl groups acting as non-radiative electron-hole recombination centers [51, 52]. Such excellent properties associated to the tunable emission wavelength of N-GQDs are useful for the applications of eco-friendly bio-labelling, bio-imaging, and efficient optoelectronics.

For optoelectronic applications, dense photonic networks require ultra-small light emitting devices modulated at high bit rates and operated at low energy [53]. However, the maximum bit rates of devices are limited to the intrinsic τ of the nanoemitters [54]. For achieving faster τ and brighter emission of N-GQDs, the emission rate enhancements need to be optimised. Photonic

Figure 6.1: (a) Three-dimensional representation of a single Nitrogen (N-) doped Graphene quantum dots (GQDs) coupled with Bi₂Te₃ nano-plates. (b) Scanning electron microscope (SEM) image showing individual hexagonal Bi₂Te₃ nano-plates. (c) Transmission electron microscope (TEM) image showing N-GQDs.

crystal cavities [54, 55], plasmonic antennas [56], and disordered nanostructures [57, 58] are the solutions to engineer nanoscale electromagnetic environments to enhance the spontaneous emission rate through cavity quantum electrodynamics in the Purcell regime [59]. Usually, emission rate enhancements are followed by the those of the intensity but the intensity also can be improved by light extraction due to the photonic crystal cavities [55] or plasmonic antennas [56]. By definition, the emission rate and intensity enhancements are respectively proportional to the inverse of τ ratio and the intensity ratio of the nano-emitters after and before the nanoscale photonic engineering.

Not so many reports on the emission rate enhancement of all types of GQDs are observed [151–153]. Few reports show emission rate enhancement with undoped-GQDs [152, 153]. The enhancement of N-GQDs was observed from an ensemble of silver nanoparticles (Ag NPs) inside solution but this coupling between N-GQD and Ag NP can not be directly implemented

for the photonic devices [151]. The decay curves of GQDs in the coupled Ag NPs have double-exponential components showing the complex mechanisms involved, either due to the intrinsic GQDs process [154] or to the distribution of photonic local density of states from the random ensemble of Ag NPs [57, 58, 155].

Here we present the spontaneous emission rate enhancements of high-QY N-GQDs coupled to single hexagonal Bismuth Telluride (Bi_2Te_3) nano-plates. Although Bi_2Te_3 has slightly larger plasmonic loss in comparison to Ag, it can offer multiple functionalities from excellent thermoelectric properties [156] to tunable plasmonic metamaterial based on topological insulators [157]. The emission rate and the intensity enhancements at 620 nm from colloidal QDs coupled to Bi_2Te_3 nano-plates were previously reported [157]. The maximum emission rate enhancement was about 1.3 folds the emission rate from decoupled QDs while the maximum emission intensity enhancement was 3.8. The intensity enhancements were mainly due to the improvement of extraction efficiency or light collection. The low Purcell enhancements were expected as the emission spectra did not match with localised plasmon resonance [157].

In this section, we observe the largest emission rate enhancement of 2.9 ± 0.3 folds from N-GQDs coupled to localised plasmon resonance of Bi_2Te_3 . We observe this enhancement for N-GQDs with 497 ± 151 nm-diameter Bi_2Te_3 . However, N-GQDs coupled with large-diameter Bi_2Te_3 (795 ± 135 nm) show only 1.5 ± 0.3 fold maximum enhancement. Furthermore, the emission rate enhancements from different sizes of Bi_2Te_3 and emission wavelengths match well with the calculations based on full-wave electromagnetic simulations in which QY is assumed close to unity $\text{QY} \sim 1$. This QY is consistent with the blue emitting N-GQDs as previously reported [51, 52].

6.A.2 Methods

We present here the methodology of the growth of GQDs and experiments, some information may already have been specified in previous sections, such as the characterisation systems. In order to help better understand and contextualise the experiments, we synthesise here the fabrication process of N-GQDs and the characterisation methods.

Materials Fabrication: Bi_2Te_3 nano-plates were synthesised following the solvothermal

method using Bi_2O_3 and TeO_2 as precursors, ethylene glycol as the major solvent and reducing agent, and polyvinylpyrrolidone (PVP) as the surfactants [157, 158]. The resulting precursor suspension was stirred vigorously for 30 min, and then sealed in the autoclave. For the samples with large-diameter Bi_2Te_3 nano-plates, the solution was heated to 210 °C during 4 h. For the small-diameter nano-plates, the solution was also heated for the same duration but at higher temperature of 230 °C. The products were washed several times with distilled water and absolute ethanol, and then collected by centrifugation at 1000 rpm for 5 mins. For the emitter, N-GQDs were fabricated using a hydrothermal method [159, 160]. The precursor solution for GQD was prepared by dissolving 9 g urea and 6 g citric acid in 100 ml pure water at room temperature, then stirred for 5 mins under room temperature. The precursor solution was then transferred to a stainless-steel autoclave and heated at 160 °C during 4 hours, while being stirred.

Figure 6.2: Distribution of the diameter of Bi_2Te_3 nano-plates from sample A (a) and B (b). The scanning electron micrographs of sample A and B are shown in (c) and (d), respectively.

Characterisation: The dark-field scattering measurements of single hexagonal Bi_2Te_3 nano-plates were performed with a commercial spectrometer, Cytoviva, using $40\times$ microscope objective with numerical aperture of 0.75. The spectra were integrated for 0.25 s and corrected with the silver mirror spectrum. The microPL setup is based on free space excitation technique with the excitation path and the emission collection from the side using a visible microscope objective ($\times 80$, $\text{NA} = 0.90$). The samples were excited with a 10 MHz pico-second laser pulses at 371 ± 5 and 405 ± 5 nm with a beam-spot size of $\sim 2 \mu\text{m}$. The imaging part includes a CCD camera sensitive from visible to near infrared. The PL spectra was measured by subsequently directing the emission to a grating spectrometer with a peltier-cooled photodetector (Edinburgh Instruments) and an acquisition card. For time-resolved PL measurements, the emission was filtered with the same grating while the slit set for a 20-nm bandwidth resolution. Finally, the detector was connected to time-correlated single photon counting card. The instrument response function of the time-resolved system is 0.35 ns, which is appropriate for our measurements.

Figure 6.3: (a,b) Transmission electron microscope images of N-GQDs with different magnifications. (c) Electron diffraction pattern of the QDs.

6.A.3 Results

Figure 6.1.a shows the sketch of the sample containing Bi_2Te_3 nano-plates and N-GQDs. Bi_2Te_3 nano-plates have two different group sizes, A and B. The size distributions of Bi_2Te_3 nano-plates are shown in figure 6.2. Samples A and B of Bi_2Te_3 nano-plates have diameters of 795 ± 135 and 497 ± 151 nm respectively, while the thicknesses range from 15 to 20 nm [157]. The image of Bi_2Te_3 nano-plates from sample A is presented figure 6.1.b. Then, a SiO_2 thin

layer of 5 nm was deposited on top of Bi_2Te_3 via thermal evaporation [161]. Finally, N-GQDs were dispersed on top of the layer as shown in figure 6.1.a. Figure 6.1.c exhibits the transmission electron microscope (TEM) image from N-GQDs. The average diameter of N-GQD is 28 ± 10 nm, see also the figure 6.3.

Figure 6.4: Calculated scattering (solid lines) and absorption (dashed lines) cross section spectra for Bi_2Te_3 single nano-plates (a) and nanospheres (b) with a diameter of 400 nm inside SiO_2 medium. The inset in (a) exhibit the spectra of nano-plates for different diameters.

Figure 6.2 summarises the diameters of two samples of hexagonal Bi_2Te_3 nano-plates, prepared with different methods. Sample A presents the large-diameter nano-plates and Sample B the small-diameter nano-plates. Bi_2Te_3 nano-plates were obtained through 4 h heating process of the precursor solutions to 210 °C and 230 °C for samples A and B, respectively. From analysis of the scanning electron micrographs (figure 6.2.c and d), we determine the diameter distribution from 48 nano-plates. The averages diameter for sample A and B is 795 ± 135 and 497 ± 151 nm, respectively. It is worth noticing the diameter mentioned here refers to the measurement of the diagonal of a hexagon.

To determine the size of N-GQDs, we used transmission electron microscope images. For the samples, we diluted 1 μl of sample into 10 ml of ultra pure water, then filtered using a regenerated cellulose filter (0.22 μm). The samples were dried overnight at room temperature on ultrahigh resolution carbon grid, Okenshoji Co., Ltd. The morphology of samples were obtained using a JEM-3000F system operated at 200 kV.

From the images in figure 6.3.a and b, we measure the average diameter of N-GQDs to be 28

± 10 nm. The electron diffraction measurement (figure 6.3.c) shows the QDs are amorphous.

Figure 6.5: Dark-field scattering spectra of single hexagonal Bi_2Te_3 nano-plates of (a) sample A with large-diameter nano-plates of 795 ± 135 nm and (b) sample B with small-diameter nano-plates of 497 ± 151 nm. The insets show dark field microscope images.

Dark-field scattering spectra of single hexagonal Bi_2Te_3 nano-plates are shown in figure 6.5. For sample A with large-diameter nano-plates of 795 ± 135 nm, we observe two bands peaked between 455-465 nm and 665-700 nm. Both scattering wavelengths correspond with the colour observed in the microscope images (figure 6.5). For sample B with small-diameter nano-plates of 497 ± 151 nm, two distinguished bands at 490 and 590 nm tend to merge into broader emission. We also observe the same trend in the simulation using Nanoparticle Boundary Element Method (NPBEM) [162] shown in figure 6.4. In previous report [158], those two bands are shown to be related with two modes. One mode at long wavelength of ~ 600 -700 nm is induced by charge oscillations between the nano-plate center and the edges.

The $\sim 450\text{-}500$ nm short-wavelength mode is a breathing mode of surface plasmon, a two-dimensional standing wave with an antinode at the center of the nano-plate [158]. This dark mode is important because of its capability to store electromagnetic energy more efficiently than the bright mode, due to the suppression of the radiative decay channel. It originates from their low dipole moments results in narrower spectral bands. This characteristic is attractive for creating high-quality factor optical nanocavities, opening the possibility to demonstrate strong coupling between the emitter and localised plasmon resonators [163]. Based on our choice for the emitters, N-GQDs with emission around 450-500 nm can be efficiently coupled with this mode.

We performed simulation (see figure 6.4) for scattering and absorption cross section spectra using Nanoparticles Boundary Element Method (NPBEM) developed by Garcia de Abajo and Howie [162, 164]. Here we solve full Maxwell's equations for a dielectric environment where bodies with homogeneous and isotropic dielectric functions are separated by abrupt boundaries. The only difference between experiment and simulation is that the single nano-plate lays on the SiO_2 substrate in the experiments while it is inside the SiO_2 medium in the simulation model. Yet, we presume that the effect on scattering spectra is minor. In experiment, air is surrounding the SiO_2 boundary layer, but this effect can be neglected by the simulation model as the same approach has already been demonstrated by analytical calculation for a scattering of a sphere in the influence of multiple spheres [57]. It is very difficult to get the emission if they are touching each other since Bi_2Te_3 is a plasmonic material.

Figure 6.8.a shows the emission rate enhancement calculated from the dipole radiation power from simulations described by Xu et al. [165]. These simulations are compared to experimental data where two samples with Bi_2Te_3 nanoplates, 400 and 800 nm diameter respectively, and two excitation wavelengths are considered. The emission rate enhancements from the experiments results as the ratio between the reference emission lifetime of GQDs and the emission lifetime of GQD coupled with Bi_2Te_3 nanoplate. The next contour plot in figure 6.8.b shows the enhancements as functions of Bi_2Te_3 nano-plate diameter and GQD emission wavelength. The maximum peak shifts and the intensity decreases from wavelengths ranging from 400 to 800 nm and diameters ranging from 200 to 700 nm. The small diameter Bi_2Te_3

nano-plates have a stronger maximum enhancement compared to large ones due to the stronger coupling with the breathing mode. The mode involved in the enhancement process is shown in figures 6.8.c and 6.8.d. It is observed as the simulated field and the energy distribution for point dipole located 5 nm above an 800 nm diameter Bi_2Te_3 nano-plate. The confined field in figure 6.8.c is about two times relative to incident $|E|^2$ and is delocalised over the entire Bi_2Te_3 nano-plate except the edge. The latter is already classified as characteristic for the breathing mode of the surface plasmon [158, 163]. The figure 6.10 shows similar simulation with spherical particle of Bi_2Te_3 . We observe a diameter-dependence peak shift of the calculated emission rate enhancement, similarly to Bi_2Te_3 nanoplates.

Figure 6.4 shows the calculated cross section spectra for both single Bi_2Te_3 nano-plates and nanospheres. For scattering cross section spectrum of 400 nm diameter nano-plates in figure 6.4.a, we observe a peak at 496 nm, which well corresponds the scattering spectrum peak of figure 6.5.b. We note the average diameter of the single Bi_2Te_3 nano-plates of 497 ± 151 nm, is very close to the one used in simulations. The absorption cross section is four times smaller than the scattering cross section.

The inset of figure 6.4.a shows the spectra for different diameters of single Bi_2Te_3 nano-plates, we do not only observe the peak at 496 nm wavelength (peak 1), but also around 600 nm (peak 2). When the Bi_2Te_3 nano-plates get a diameter above 700 nm, another peak around 400 nm wavelength (peak 3) appears. For single Bi_2Te_3 nanospheres in figure 6.4.b, the scattering cross section is much larger than that in single nano-plates.

PL spectra of the N-GQDs are shown in figure 6.6.a. The spectrum of the N-GQDs reference (without Bi_2Te_3) consists of a broadband emission from 400 to 600 nm with a maximum at 450 nm. This emission spectrum from microPL measurements is similar to that obtained with commercial spectrofluorometer when exciting the N-GQDs ensemble with large excitation spot at several excitation wavelengths. We show in figure 6.7 that the emission from N-GQDs is only shifted by 9 nm with increasing excitation wavelength. When the N-GQDs are coupled with large-diameter Bi_2Te_3 nano-plates (sample A), the emission spectrum shows two bands peaked at 450 and 650 nm similar to the dark scattering spectrum of the corresponding-size Bi_2Te_3 nano-plates. For the integrated intensity of the whole emission spectrum, the yield of

the N-GQDs coupled to the large-diameter Bi_2Te_3 nano-plates is 1.2 times larger than that of N-GQDs reference. For the N-GQDs coupled with small-diameter Bi_2Te_3 nano-plates (sample B), the integrated intensity from the emission spectrum is 1.8 times larger that of reference.

Figure 6.6: (a) PL spectra and (b,c) PL decay curves from N-GQDs without and with large- (A) and small- (B) diameter Bi_2Te_3 nano-plates. Black, red empty-square, and blue empty-circle lines are attributed to the measurements at room temperature for reference, sample A, and sample B, respectively. Red and blue dashed lines in (a) show scattering spectra of samples A and B, respectively. Decay curves in (b) and (c) were measured at 460 and 480 nm emission, respectively.

Figures 6.6.b and c exhibit the PL decay curves from N-GQDs in samples A and B, respectively. The samples A and B were recorded at 460 and 480 nm, respectively. For all emission wavelengths, the decay curves for reference are single exponential while those for samples A and B are non-exponential. For analysis, we fit the decay curves of samples A and B with a double exponential using the following equation:

$$N(t) = N_1(0) \exp\left(\frac{-t}{\tau_1}\right) + N_2(0) \exp\left(\frac{-t}{\tau_2}\right) \quad (6.1)$$

where $N(t)$ is the total number of population from all emission channels after t time. $N_1(0)$ and $N_2(0)$ are the initial population at $t = 0$, which have emission lifetimes for fast and slow emission channels of τ_1 and τ_2 , respectively. The emission lifetime average $\langle\tau\rangle$ derived from the fast and the slow parameters in Eq. 6.1 is given by

$$\langle\tau\rangle = \tau_1 \cdot \frac{N_1 \tau_1}{N_1 \tau_1 + N_2 \tau_2} + \tau_2 \cdot \frac{N_2 \tau_2}{N_1 \tau_1 + N_2 \tau_2}. \quad (6.2)$$

We attribute the emission lifetimes for sample A (τ_A) and sample B (τ_B) as the average emission lifetimes $\langle\tau\rangle$ from the fits.

We may attribute the non-exponential decay curves to a distribution of radiative decay

rates as a result of spatial and dipole orientational non-uniformity of the local density of states probed by ensemble finite N-GQDs [166]. For further analysis, we fit the curves with a double-exponential function and calculate the average τ from two decay components, see Eqs. 6.1, 6.2, and Ref. [161]. Obtained τ from all measurements can be seen in figure 6.9. For figure 6.6.b and c, τ values of N-GQDs in sample A (τ_A) and sample B (τ_B) are 8.6 and 4.3 ns, respectively. Those are faster than N-GQDs reference values (τ_{Ref}) of 12.9 and 12.5 ns monitoring 460 and 480 nm, respectively.

Figure 6.7: PLE and PL spectra of N-GQDs at room temperature. The PLE spectrum was measured by monitoring 456-nm emission while the PL spectra were obtained using excitation wavelengths between 275 and 400 nm.

In figure 6.7, we present the Photoluminescence excitation (PLE) and photoluminescence (PL) spectra of ensembles of N-GQDs measured using a standard-commercial spectrofluorophotometer (RF 5300PC, Shimadzu Corp., Kyoto, Japan) equipped with a xenon lamp and wavelength resolution of 0.2 nm. The PLE spectrum shows a single excitation band peaked at 382 nm. This band may be attributed to the transition from the highest occupied molecular orbitals (HOMO) to the lowest unoccupied molecular orbitals (LUMO) of N state from

conjugated pyrrole or pyrrolidone group. This group replaces transition of C=O with that of conjugated C-N/C=N as N source was added in the urea precursor [51]. At excitation of 375 nm, the PL spectrum is similar with that of reference measured with microPL for $\sim 2 \mu\text{m}$ beam-spot size. Both have a full width of half maximum (FWHM) of 85 nm and PL peak at 459 nm. With different excitation, all PL spectra of the N-GQDs display slight shift PL emission spectra (about 9 nm along the increase of the excitation wavelength), implying that both the size and the surface state of transition in N-GQDs should be uniform.

Figure 6.8: (a) Emission rate enhancement comparison between measurements and calculations. The red and blue lines represent the calculations for 800- and 400-nm diameter single Bi₂Te₃ nano-plates, respectively. Excitation wavelengths and sample types are shown in the legend. (b) Calculations of emission rate enhancement from the electromagnetic simulations varying single Bi₂Te₃ nano-plates diameter and N-GQDs emission wavelength. Qualitative plot of electric field (c) and energy (d) distribution resulted from the dipole placed 5 nm above the 800-nm-diameter Bi₂Te₃ nano-plate. The thickness of nano-plate is 20 nm while the emission wavelength of N-GQDs is 455 nm.

Figure 6.8 summarises the analysis of emission rate enhancements for wavelengths ranging from 400 to 600 nm. The emission rate enhancements from the experiments results simply as τ_{Ref}/τ_A or τ_{Ref}/τ_B . τ_{Ref} is independent from the emission wavelength, see figure 6.9. In figure

6.8.a the emission rate enhancement is obtained for different emission wavelengths with a 20 nm bandwidth resolution for two excitation wavelengths of 371 ± 5 and 405 ± 5 nm. Then, the enhancement is averaged over the excitation beam of 2,000 nm diameter [167]. For sample A, denoted with red squares, there is no strong emission rate enhancements for both excitation wavelengths as the maximum is only about 1.5 folds. For small diameter Bi_2Te_3 nano-plates (sample B), we observed much large emission rate enhancements of 2.9 ± 0.3 and 2.2 ± 0.3 folds for 371 ± 5 and 405 ± 5 nm excitation, respectively. The excitation at 405 ± 5 nm is still far from Bi_2Te_3 plasmonic resonance peaked at 480 nm. Therefore, we did not observe additional enhancements due to the coupling with the absorption/excitation.

Figure 6.9: Emission lifetimes collected from the N-GQDs as reference, coupled with large-diameter (sample A), and coupled with small-diameter (sample B) single Bi_2Te_3 nano-plates with two different laser excitations; a) 371 ± 5 and b) 405 ± 5 nm.

Figure 6.9 shows the emission lifetimes as function of wavelengths for two different excitation wavelengths of 371 ± 5 and 405 ± 5 nm. The lifetimes were obtained from the average

of the two exponential components resulted from bi-exponential fits. For the reference sample of N-GQDs, the emission lifetimes are 12.9 ± 0.4 and 14.5 ± 0.5 ns were recorded at excitation wavelengths of 371 ± 5 and 405 ± 5 , respectively. They are almost constant for the whole range of the emission wavelengths. For N-GQDs in sample A and sample B, most of the emission lifetimes are faster compared to those of references. The fastest emission lifetime of 4.3 ns was recorded for sample B under excitation of 371 nm. With 405-nm excitation, the second fastest emission lifetime of 6.5 ns was recorded also for sample B. Both lifetimes were recorded at 480-nm emission and they are close to the resonance peaks of Bi_2Te_3 from sample B. Unfortunately, we did not observed much faster emission lifetime at 405-nm excitation due to additional emission enhancement from the coupling with the absorption or excitation since there is no strong plasmonic resonance from Bi_2Te_3 around 400 nm.

6.A.4 Discussion

For understanding the emission rate enhancements, we performed calculations based on the dipole radiation power from electromagnetic simulations [168, 169] as shown in figure 6.8a and b. The emission-rate calculations based on the Purcell factor [170, 171] are more complex as single Bi_2Te_3 nano-plates may have more than one quality factor resulting from multiple modes, see figure 6.5 and 6.4. To investigate further, we performed in parallel the calculation comparisons among the dipole radiation power method, NPBEM [162], and scattering method [172] (see figure 6.10). For dipole radiation power method, the emission rate enhancements (F) derived from τ via classical dipole radiation power (P) can be written as following [168, 169]:

$$F = \frac{\tau_{Ref}}{\tau_{Np}} = \left[\frac{P^{Np}}{P^{Ref}} \right]_{quantum} = \left[\frac{P^{Np}}{P^{Ref}} \right]_{classical} \quad (6.3)$$

where Np denotes values for the dipoles in single Bi_2Te_3 nano-plates of samples A and B. We use a fully vectorial three-dimensional calculation with dipoles located 5 nm above the center of nano-plates. We set the emission polarisation perpendicular to the surface of the nano-plates while the QY is unity. We use the refractive index $n_{\text{Bi}_2\text{Te}_3}$ of Bi_2Te_3 from Ref. [158] while we model the nano-plates inside homogeneous medium of SiO_2 with an index $n_{\text{SiO}_2} = 1.5$, which can be slightly different from the actual sample. The red and blue solid lines in figure

6.8.a show calculations for single Bi_2Te_3 nano-plates of 800 and 400 nm diameter, respectively.

Both calculations with $QY \sim 1$ well agree with experimental results confirming especially the observed-maximum enhancement of 2.9 ± 0.3 folds. The slight differences in the spectral width of the calculations and the experiments in 6.8.a can be related to the emission line-width of the N-GQDs, the difference in refractive index between the experiment and the simulation or the approximation of the nano-plate structure in the calculation, i.e. edges of the hexagonal plate [173]. Unlike the previous emission enhancement in Bi_2Te_3 nano-plate at 620 nm [157], our emission rate enhancement at 480 nm is almost three times larger while the loss is smaller. The imaginary part of dielectric function at 480 nm is almost two times smaller than that at 620 nm [158]. In our experiment, the coupling between the N-GQDs emission and the breathing mode of surface plasmon in Bi_2Te_3 nano-plates can be stronger than that at 620 nm. We may observe such evidence in the contour plot of figure 6.8.b. This plot exhibits the emission rate enhancements as functions of single-nano-plate diameter and wavelength. The maximum enhancement derived from calculation is 2.8 folds. In figure 6.8.b, the maximum peak shifts and the intensity decreases from wavelengths ranging from 400 to 800 nm and diameters ranging from 200 to 700 nm. The other peak starts to appear for 700 nm diameter Bi_2Te_3 nano-plates. The small diameter Bi_2Te_3 nano-plates have a stronger maximum enhancement compared to large ones due to the stronger coupling with the breathing mode. However, in the nano-sphere, the effect of the diameter is more important than for the nano-plates.

In figure 6.10 we compare the emission rate enhancement using three methods, classical dipole radiation power of finite-element method [168, 169], solution of full Maxwell's equation of NPBEM [162], and Mie scattering [172]. We used single spherical particles for the simulations as these three methods can be successfully employed for these particles. To compare these results with figure 6.8, the medium of the single sphere is Bi_2Te_3 (refractive index $n_{\text{Bi}_2\text{Te}_3}$ obtained from Zhao et al. [158]) while the medium of the background is SiO_2 ($n_{\text{SiO}_2} = 1.5$). The dipole is located 5 nm above the surface and its orientation is normal to the tangent of the sphere.

Figure 6.10.a shows the calculated emission rate enhancement via dipole radiation power of finite-element method. We observe a similar diameter-dependence peak shift as in the calcu-

Figure 6.10: Calculated emission rate enhancements for different-diameter Bi_2Te_3 nanospheres inside SiO_2 medium using (a) dipole radiation power of finite-element method, (b) solution of full Maxwell's equations via NPBEM, and (c) Mie scattering. The dipole is located 5 nm above the surface while its orientation is perpendicular.

lated emission rate enhancement of single nano-plates in figure 6.8. The peak shifts to longer wavelength from 400 to 800 nm for single nano-plates with diameters varying from 200 to 500 nm, respectively. In addition at 500-nm diameter, another peak starts to appear at 400-nm wavelength. The maximum emission rate enhancement of emitter in the single sphere is 4.5 folds which is 1.6 times larger than the 2.8 folds for single nano-plates in figure 6.8. For figure 6.10.b, the calculations using NPBEM yield show almost the same trend as those using dipole radiation power. However, the maximum emission rate enhancement of 4.2 folds is slightly smaller than that calculated by dipole radiation power. With Mie scattering [172], we can also calculate the emission rate enhancement as shown in figure 6.10.c. In this case, we have only 2.5 fold maximum emission rate enhancement but the relation between the diameter and the emission wavelength is still the same as the two other methods.

For showing the mode that is responsible for the enhancement, we present Figs. 6.8.c and 6.8.d as the simulated field and the energy distribution for point dipole located 5 nm above 800 nm diameter Bi_2Te_3 nano-plate. The emission is set to be at the enhancement peak of 455 nm. The confined field in figure 6.8.c is about two folds relative to incident $|E|^2$ and is delocalised over the entire Bi_2Te_3 nano-plate except the edge. The latter is already classified as the characteristics for the breathing mode of the surface plasmon [158, 163].

6.A.5 Conclusion

In conclusion, we observed the emission rate enhancements from N-GQDs coupled with single Bi₂Te₃ nano-plates. With 497 ± 151 nm-diameter Bi₂Te₃ nano-plates, we obtained 2.9 ± 0.3 folds of the emission rate enhancement. Our experimental results well matched with the calculations based on dipole radiation power for emitter with $QY \sim 1$ and show similar order as the boundary element methods and Mie scattering of Bi₂Te₃ nanospheres. From this result, we first conclude that the QY of the N-GQDs is almost unity, showing a promising active medium for optoelectronic applications. Also, we found that single Bi₂Te₃ nano-plate is the alternative plasmonic antenna for enhancing spontaneous emission rate beside semiconductor [174] and conventional metal antennas [175, 176]. Finally, the recent observation of the thermoelectric enhancement from the GQD embedded in Bi₂Te₃ nano-plate [156] supports that this system is promising for the development of broadly functional material systems.

CHAPTER 7

Conclusions and Perspectives

This thesis developed three major axis from the the synthesis of semiconductors, visible range emission of defects to enhancement of the emission rate.

The synthesis of Gallium Nitride nanowires conducted by Low-Pressure Chemical Vapour Deposition (LPCVD) system showed randomly oriented nanowires. The crystallinity of GaN has been shown to vary depending on the catalyst. Ni catalyst resulted in randomly grown twisted nanowires while Ge catalyst showed single crystal and straight nanowires growing along the c-axis. Combining both catalysts resulted in uncommon pine tree-like structure with a central spine made of a straight nanowire and lateral growth, which width is proportional to the growth time and gives a pine tree-like shape to the whole ensemble. Raman spectroscopy characterises the structure as Wurtzite GaN crystal while photoluminescence shows wide defect-related visible emission.

Although the LPCVD system shows promising synthesis of GaN nanowires, the limitations of the system are not to be neglected for further studies. The configuration of our system itself limits greatly further studies, the source of Gallium is solid and does not allow a high repeatability rate due to the size of the reaction chamber - $L: 1050\text{ mm}$ & $\varnothing_{in}: 210\text{ mm}$ - with random distribution and non-uniform vapour-pressure of Ga atoms. Simulations and empirical experiments allowed us to use the solid source quite efficiently but the use of trimethylgallium gas is pressing for further long term studies of GaN nanowires. Allowing more gases also allows to study growth of hetero-structures and a wider range of III-V semiconductor nanostructures, this opens path for other research areas. Although, dense nanowire ensembles have been proven, with good crystallinity of GaN, approaching growth quality of MOCVD or MBE state-of-the-art systems. But exploiting these nanowires remains a challenge, regardless of the growth method. Therefore we explored other structures and materials, with high energy emission, such as hBN and GQD.

Usually exploited for their direct band-to-band UV recombination, we have shown promising emission from GaN nanowires and hBN monolayers in the visible range. Defects in LPCVD-grown GaN nanowires have shown to emit yellow and green luminescences, the earlier emission is shown to be related to surface defects. Then, femto-second pulsed laser is used, on defect-free MBE-grown nanowires, to induce localised defects. Above a laser thresh-

old power the irradiated GaN nanowires melt, higher power sublimates the crystal. Irradiated GaN is characterised as Wurtzite crystal and shown emitting in the visible range, additionally to the band-to-band UV emission. Similar experiment on hBN monolayer show defect-related visible emission near the irradiated area. Contrary to GaN nanowires where a wide emission is observed, hBN defects show strong and sharp emission. Point defects created in hBN - monolayers and flakes - are shown to be single photon emitters.

Typical GaN-based optoelectronics consist in InGaN - or AlGaIn, AlGaInN,... - quantum wells sandwiched between layers of GaN. Varying In/Ga ratio in the quantum wells allows modulation of the emission wavelength from blue to green. Instead of these hetero-structures, the method demonstrated here explores the use of point defects as active region. Femto-second laser shows a promising method to locally induce radiative defects, as shown with GaN nanowires and hBN monolayers and flakes. The sharp and single photon nature of emission from hBN suggests the feasibility of quantum well-like structures where a localised defect acts as active region. Further studies may focus on achieving smaller size defects with femto-second laser beam while downing the wavelength of irradiation - second and third harmonics may be interesting - or targeting diffraction limit size of beam. Other irradiation methods are also to be studied such as electron-beam and focused ion beam, the use of much smaller beam size may help achieve point defects in a single GaN nanowire or hBN nano-flake that could emit single photons.

Finally, we explore the use of surface plasmons to enhance the emission rate from a nano-emitter such as Graphene quantum dot. For optoelectronic applications, dense photonic networks require ultra-small light emitting devices modulated at high bit rates and operated at low energy. Yet, the maximum bit rates of devices are limited to the intrinsic τ of the nano-emitters. For achieving faster recombinaison and brighter emission, we demonstrate emission rate enhancement in Nitrogen-doped Graphene quantum dots by coupling them with single Bi₂Te₃ nano-plates. This allows a nanoscale electromagnetic environment to enhance the spontaneous emission rate. We find that single Bi₂Te₃ nano-plate is the alternative plasmonic antenna for enhancing spontaneous emission rate beside semiconductors and conventional metal antennas.

The improvement of intrinsic emission has its limitations if considering only the emitter

system, using external means to enhance the emission rate is encouraging for the development of even faster and brighter nano-emitters. Demonstration with Graphene quantum dots and Bi_2Te_3 nano-plates is encouraging. The flexibility of GaN nanowires sonicated in alcoholic solution then dispersed allows to couple them with Silver nanoparticles, similar surface plasmon-assisted enhancements can be expected, equivalently with hBN nano-flakes.

In closing, the synthesis of wide band-gap semiconductors is well mastered and extensive work is ongoing to understand and better predict the growth mechanisms. We were able to add our piece of contribution by showing Ge-catalysed growth of GaN nanowires allowing a CMOS-compatible method. We introduced a novel type of GaN nanostructure in the shape of pine trees, that helps better understand catalyst-assisted growth processes and may show applications for directional nano-antennas. For nano-emitters in the visible range, we reported yellow and green luminescence from LPCVD-grown GaN nanowires and intentionally induced point defects in 2D hBN and 1D GaN using femto-second pulsed laser. The enhancement of the emission rate was promulgated by coupling Graphene quantum dots to Bismuth Telluride nano-plates. To continue this work, the natural path is to push forward these three axis developed during this thesis while aiming towards the development of nano-emitter-based integrated optoelectronic devices.

Publications

Part of the work presented in this manuscript has resulted in the publication of the following peer-reviewed research papers:

- **Saleem Umar**, Muhammad Danang Birowosuto, Noelle Gogneau, Philippe Coquet, Maria Tchernycheva, and Hong Wang. 2017. “Yellow and Green Luminescence in Single-Crystal Ge-Catalyzed GaN Nanowires Grown by Low Pressure Chemical Vapor Deposition.” *Optical Materials Express* 7 (6):1995.
- **Saleem Umar**, Fitri A. Permatasari, Ferry Iskandar, Takashi Ogi, Kikuo Okuyama, Yudi Darma, Meng Zhao, et al. 2017. “Surface Plasmon Enhanced Nitrogen-Doped Graphene Quantum Dot Emission by Single Bismuth Telluride Nanoplates.” *Advanced Optical Materials* 5 (17):1700176.
- Hou SONGYAN, Muhammad Danang Birowosuto, **Saleem Umar**, Anicet Maurice Ange, Tay Roland, Philippe Coquet, Beng Kang Tay, Hong Wang, et al. 2017. “Localized Emission from Laser-Irradiated Defects in 2D Hexagonal Boron Nitride.” *2D Materials* 5 (1):15010.
- **Saleem Umar**, Hong Wang, David Peyrot, Aurélien Olivier, Jun Zhang, Philippe Coquet, and Serene Lay Geok Ng. 2016. “Germanium-Catalyzed Growth of Single-Crystal GaN Nanowires.” *Journal of Crystal Growth* 439 (April):2832.
- **Saleem Umar**, Muhammad Danang Birowosuto, Hou Songyan, Anicet Maurice Ange, Edwin Teo, Beng Kang Tay, Maria Tchernycheva, Noelle Gogneau, Hong Wang. 2018. “Light emission from localised point defects induced in GaN crystal by femto-second-pulsed laser.” *Optical Materials Express* 8, 9, pp. 2703-2712 (2018)
- **Saleem Umar**, Muhammad Danang Birowosuto, Hong Wang. 2018. “GaN Pine Tree-like nanostructure catalyst-assisted synthesis.” *Writing in progress*.
- **Saleem Umar**, Hong Wang. 2018. “GaN/Pd interfacial properties for high-temperature Hydrogen sensing” *Writing in progress*.

Part of the work presented in this manuscript was presented in the following conferences and workshops:

- **Umar, Saleem,** and Wang Hong. 2015. “Single-Crystal GaN Nanowire Synthesis Assisted by Germanium Catalyst.” In MRS Boston, USA.
- **Umar, Saleem,** and Wang Hong. 2015. “Ge-Catalysed GaN Nanowires.” NTT Basic Research laboratories, Tokyo, Japan.
- **Umar, Saleem,** Muhammad Danang Birowosuto, Noelle Gogneau, Maria Tchernycheva, and Wang Hong. 2016. “Yellow and Green Luminescence Study from Ge-Catalysed GaN Nanowires Grown by Low Pressure Chemical Vapour Deposition.” Meudon, France.

This thesis was carried out at Nanyang Technological University (NTU) in the School of Electronic and Electrical Engineering (EEE) under the CNRS-NTU-THALES Research Alliance framework in Singapore. A short period was carried out at the Center of Nanosciences and Nanotechnologies (C2N) in France.

Appendix A: Radio Corporation of America (RCA) cleaning process

1. Prepare the Si substrates: cut Si wafer into small samples: $1 \times 2 \text{ cm}^2$
 2. Eliminate the organic contaminants
 - (a) Acetone - $\text{C}_3\text{H}_6\text{O}$: 60°C on hotplate for 3 mins
 - (b) Isopropanol - $\text{C}_3\text{H}_8\text{O}$: 60°C on hotplate for 3 mins
 - (c) Deionised water rinse
 - (d) N_2 blow to avoid any 'water marks'
 3. Elimination of the native oxide by chemical attack
 - (a) Sulfuric acid: Hydrogen peroxide - H_2SO_4 : H_2O_2 - 3:1 ratio for 10 mins
 - (b) Deionised Water rinse: few mins
 - (c) Hydrofluoric acid: Water - HF : H_2O - 1:10 ratio for few minutes
 - (d) Deionised water rinse: few mins
 4. Elimination of deep contaminants by the acid attack
 - (a) Nitric Acid - HNO_3 for 10 mins at 80°C
 - (b) Deionised water rinse for few mins
 5. Hydrogenation of Si to passivate the surface
 - (a) Ammonium Fluoride - NH_4F for few minutes
 - (b) Deionised water rinse for few mins
 - (c) N_2 blow
-

Table T7.1: Substrate preparation and cleaning protocol

Appendix B: Protocol to prepare nanowire-based devices

The following protocols aim to show a method to fabricate nanowire-based devices. We also present some examples of devices fabricated with ensemble and single nanowires. We keep a focus on the practical side of the fabrication process, what needs to be avoided to achieve best quality devices. The applications to this method can be numerous.

Protocol for nanowire-based device fabrication by photolithography

1. Device substrate preparation The substrates used are heavily-doped ($\rho \simeq 0.001\text{--}0.005\ \Omega\text{-cm}$) 1, 2 or 3 inch Si wafers with 200 nm layer of SiO_2
 - (a) Clean wafer by submersing it using a tweezer into a 600 ml beaker with ~ 100 ml of acetone for 5 min
 - (b) Remove wafer from acetone and immediately rinse off both sides of the wafer using a squirt bottle of IPA over an empty 600 ml beaker, which will be used for solvent waste
 - (c) Repeat step b. using IPA
 - (d) Repeat step c. rinsing the wafer with deionised H_2O over the solvent waste beaker
 - (e) Repeat step b. using deionised H_2O
 - (f) Blow wafer dry using compressed dry N_2
 - (g) Oxygen plasma: 100 W and 50 sccm of O_2 for 200 s.
2. Nanowire Dispersal
 - (a) Cleave the clean wafer into 4 equal quarters if 2 or 3 inch wafer is used
 - (b) Set the micropipette to the desired drop size (20–200 μl)
 - (c) Take the wafer that will be used for dispersal and ensure that it is level so that the nanowire suspension does not migrate away to the edges
 - (d) Dispense the nanowire suspension onto the (oxidised) front surface of the Si substrate in the general area where the contact pattern will be deposited. If desired, deposit additional drops of the nanowire suspension in the same area, after the solvent from the previous drop has completely evaporated
 - (e) Repeat step d for the other areas where a contact pattern will be.
Do not dispense the nanowire suspension from more than 1 growth run on a single substrate piece in order to avoid cross contamination.
 - (f) After the final drop of nanowire suspension has evaporated, gently dip in successive baths of acetone and isopropanol to remove unwanted impurities. Rinse in deionised H_2O , and blow dry in N_2 .
Do not use squirt bottles or sonicate the solvent during this cleaning process to avoid excess removal of nanowires from the surface

3. Photolithography of Contact Pattern

Use standard photolithographic techniques to create the contact pattern in a clean room with ambient conditions of $\sim 20^\circ\text{C}$ and $\sim 40\%$ relative humidity. Mask aligner intensity, exposure time and develop time will be equipment-dependent and should be adjusted to produce maximum pattern definition with a lift-off-resist undercut of about $0.5\ \mu\text{m}$.

- (a) Spin coat AZ 5214 photoresist: 40 s, 4 000 rpm ($1.40\ \mu\text{m}$)
- (b) Soft bake: 105°C , 1 min on foil hotplate
- (c) Karl Suss MJB4 Mask Aligner
 - i. For light field mask: Expose $58\text{--}60\ \text{mW}/\text{cm}^2$ for 5 s
 - ii. For dark field mask: Expose $58\text{--}60\ \text{mW}/\text{cm}^2$ for 7 s
- (d) Reversal bake: 120°C , 10 to 90 s - Crucial step
- (e) Flood Expose: $58\text{--}60\ \text{mW}/\text{cm}^2$ for 20 s
- (f) Develop:
 - i. Light field mask: 23-25 s, AZMIF 312 - 1:1 - H_2O
 - ii. Dark field mask: 40 s, AFMIF 312 - 1:1.2 - H_2O
Always check the development time on a test sample first - sometimes it needs to be shorter. Constantly agitate the sample in the developer.
 - iii. Deionised Water rinse: $\sim 1\text{min}$
 - iv. Dry with N_2 blow
 - v. Inspect under optical microscope
 - vi. Clean the chip using an oxygen plasma: 30 W and 50 sccm O_2 for 60 s

4. Electron-beam Evaporation of Contact Metals

Immediately after pretreatment, mount the samples to the platen using screws and clips and secure platen in the e-beam evaporator. Make sure that sufficient Ni and Au are available for deposition.

- (a) Deposit Ni - 50 nm at $\sim 0.1\text{nm/s}$
- (b) Deposit Au - 100 nm at $\sim 0.1\text{nm/s}$

5. Contact Metal Lift-off

6. Contact Annealing

Perform the contact anneal of the Ni/Au films using a rapid thermal annealing (RTA) with ultra-high-purity N_2/O_2 (3:1) as the process gas at 550°C for 10 mins

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