

**FABRICATION OF GALLIUM NITRIDE
NANOWIRES VIA CHEMICAL VAPOUR
DEPOSITION**

LOW LI LI

UNIVERSITI SAINS MALAYSIA

2012

**FABRICATION OF GALLIUM NITRIDE NANOWIRES VIA CHEMICAL
VAPOUR DEPOSITION**

by

LOW LI LI

**Thesis submitted in fulfilment of the
requirements for the degree
of Master of Science**

February 2012

ACKNOWLEDGEMENTS

I greatly appreciate and wish to thank my main supervisor, Dr Yam Fong Kwong for his great guidance, patience, support, kindness and dedication throughout my works in this project. Without his guidance, this dissertation could not be completed smoothly. It is a great experience for me to work under his supervision.

I would like to take the opportunity to thank my research colleagues who spent their time and shared their knowledge for helping me to complete my research with the best possible result: Beh Khi Poay, Ng Siow Woon and Tneh Sau Siong.

Not forgetting also our helpful lab assistants for their constant help and technical support during my laboratorial work.

I would also like to express my gratitude to my parents and siblings for always encouraging me to further my education and pursue graduate study.

Last but not least, I am grateful to my dearest husband, Teoh Boon Chin for his encouragement, patience, support and understanding throughout my study.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF SYMBOLS	x
LIST OF MAJOR ABBREVIATIONS	xi
ABSTRAK	xii
ABSTRACT	xiv
CHAPTER 1 : INTRODUCTION	1
1.1 Introduction to Nanoscience and Nanotechnology	1
1.2 Introduction to Nanostructures	3
1.3 Introduction to III-nitrides	7
1.4 Research Background	8
1.4.1 Development of One-Dimensional GaN Nanostructured Materials	8
1.5 Research Objectives	10
1.5.1 Originality of the research works	10
1.6 Outline of the Thesis	11
CHAPTER 2 : LITERATURE REVIEW	12
2.1 Introduction	12
2.2 Growth Mechanism of Nanowires	12
2.2.1 Vapour-Liquid-Solid Growth Mechanism	12
2.2.2 Vapour-Solid Growth Mechanism	13
2.3 Growth Techniques of GaN Nanowires	14
2.3.1 Chemical Vapour Deposition	14
2.3.2 Molecular Beam Epitaxy	17
2.3.3 Thermal Evaporation	18
2.3.4 Template Assisted Growth	19
2.3.5 Laser Assisted Catalytic Growth	20

2.4	Factors Influencing the Morphological, Structural and Optical Characteristics of GaN Nanowires	21
2.4.1	Substrates	21
2.4.1.1	Sapphire	22
2.4.2	Catalysts	23
2.4.3	Source Materials	23
2.4.4	Process Parameters	24
CHAPTER 3: MATERIALS, INSTRUMENTATIONS AND METHODS		28
3.1	Introduction	28
3.2	Materials	28
3.3	Principle of Metal Catalyst Coating	29
3.3.1	Radio Frequency Sputtering	29
3.4	Growth System	30
3.4.1	Chemical Vapour Deposition	30
3.5	Principle of the Characterization Tools	32
3.5.1	Field Emission Scanning Electron Microscopy	32
3.5.2	Transmission Electron Microscopy	34
3.5.3	Energy Dispersive X-Ray	35
3.5.4	X-Ray Diffraction	36
3.5.5	Photoluminescence Spectroscopy	37
3.5.6	Raman Spectroscopy	38
3.6	Substrates Preparation	40
3.7	Experimental Procedures and Growth Conditions	40
3.8	Characterization	43
CHAPTER 4: RESULTS AND DISCUSSIONS		44
4.1	Introduction	44
4.2	The Influence of Gallium Source and Substrate Position on the Characteristic of Low Dimensional of GaN wires	44
4.2.1	Field Emission Scanning Electron Microscopy	44
4.2.2	X-Ray Diffraction	47
4.2.3	Photoluminescence	48
4.2.4	Raman Scattering	49

4.2.5	Summary	51
4.3	The Effect of Growth Temperature on the characteristics of GaN Nanowires	51
4.3.1	Field Emission Scanning Electron Microscopy	51
4.3.2	Energy Dispersive X-Ray	53
4.3.3	X-Ray Diffraction	54
4.3.4	Photoluminescence	57
4.3.5	Raman Scattering	60
4.3.6	Summary	62
4.4	The Impact of Ammonia Gas Flow Rate on the Characteristics of GaN Nanowires	63
4.4.1	Field Emission Scanning Electron Microscopy	63
4.4.2	X-Ray Diffraction	66
4.4.3	Photoluminescence	67
4.4.4	Raman Scattering	69
4.4.5	Summary	72
4.5	The Influence of Reaction Period on the Characteristics of GaN nanowires	72
4.5.1	Field Emission Scanning Electron Microscopy	72
4.5.2	X-Ray Diffraction	74
4.5.3	Photoluminescence	76
4.5.4	Raman Scattering	78
4.5.5	Summary	80
CHAPTER 5: CONCLUSION AND FURTHER STUDIES		81
5.1	Conclusion	81
5.2	Future Studies	83
REFERENCES		84
LIST OF PUBLICATION		92

LIST OF TABLES

		Page
Table 2.1	Lattice parameters and thermal expansion coefficient of prospective substrates for nitrides epitaxial growth. (Data extracted from Popovici and Morkoc 2000).	22
Table 2.2	Summary of the literature reviews on the growth of GaN nanowires (GaN precursors, catalysts, growth methods, process parameters/growth conditions).	25
Table 3.1	Growth Conditions for each experimental parameter study.	42
Table 3.2	Type of characterizations of GaN samples for each experimental parameter study.	43
Table 4.1	Phonon frequencies appeared in GaN samples grown at different temperatures of 750°C, 850°C, 900°C, 950°C and 1000°C.	62

LIST OF FIGURES

		Page
Fig. 1.1	Explanation of the superparamagnetic effect. (Adapted from Kulisch, W. et al., 2009).	6
Fig. 2.1	Schematic of overall evolution of the growth of GaN nanowire by Fe metal catalyzed VLS mechanism (Adapted from Duan and Lieber, 2000).	13
Fig. 2.2	Schematics of a CVD process: (a) typical CVD system and (b) a CVD model. (Adapted from Xu and Yan, 2010).	15
Fig. 2.3	Schematic diagram of the MBE growth chamber. (Adapted from Franchi, et al 2003).	18
Fig. 2.4	A typical schematic diagram of the thermal evaporation system. (Adapted from Wang, N. et al., 2008).	19
Fig. 2.5	Schematic illustration of the template assisted synthesis of nanowires. (Adapted from Barth et al., 2010)	20
Fig. 3.1	A typical RF sputtering system.	29
Fig. 3.2	Horizontal two-furnace CVD system setup.	30
Fig. 3.3	Schematic drawing of horizontal two-furnace CVD system setup.	31
Fig. 3.4	Mass flow controller.	31
Fig. 3.5	Schematic diagram of FESEM principle. (Adapted from infohost.nmt.edu).	33
Fig. 3.6	Schematic diagram of TEM principle. (Adapted from Nobel Media).	34
Fig. 3.7	An example of EDX spectrum from the EDX measurement of GaN sample grown on sapphire substrate.	35
Fig. 3.8	Diffraction of x-rays by a crystal. (Adapted from William, 1994).	36
Fig. 3.9	Energy diagram showing the states involved in Raman scattering.	39
Fig. 3.10	Flow chart of substrates preparation and experimental procedures.	41

Fig. 3.11	The side view of the location of Ga precursor and substrates position during the growth process. (a) A thin layer of Ga melt was spread on the Ni coated sapphire substrate, denoted as S1 and no Ga melt was spread on another Ni coated sapphire, denoted as S2 which was placed 5mm away from S1. (b) Ga melt was loaded into quartz boat and the substrate was placed downstream, 5mm away from the Ga melt.	42
Fig. 4.1	FE-SEM images of GaN samples: (a) GaN micro-wires grown on S1; (b) GaN nanowires grown on S2. Insets show the higher magnification image of both samples S1 and S2. (Adapted from Low et al., 2011a).	45
Fig. 4.2	XRD patterns of GaN sample S1 and S2. (Adapted from Low et al., 2011a).	47
Fig. 4.3	Room temperature PL spectra of GaN samples S1 and S2. (Adapted from Low et al., 2011a).	49
Fig. 4.4	Raman spectra of GaN samples: (a) S1 and (b) S2. (Adapted from Low et al., 2011a).	50
Fig. 4.5	FESEM images of GaN samples grown at different temperatures: (a) 750°C, (b) 850°C, (c) 900°C, the inset of TEM image depicts the Ni nanoparticle at the tip of the nanowires, (d) 950°C and (e) 1000°C. (Adapted from Low et al., 2011b).	53
Fig. 4.6	Atomic ratio of N/Ga and O/Ga elements in the synthesized GaN nanostructures as the function of growth temperature.	54
Fig. 4.7	XRD patterns of GaN samples grown at different temperatures: (a) 750°C, 850°C, 900°C, 950°C and 1000°C. (b) An expansion of the XRD patterns of 900°C, 950°C and 1000°C. (Adapted from Low et al., 2011b).	56
Fig. 4.8	Room temperature PL spectra of GaN samples grown at different temperatures: (a) 750°C, (b) 850°C, (c) 900°C, (d) 950°C, (e) 1000°C and (f) Phonon replicas in the blue emission region for all the samples. (Adapted from Low et al., 2011b).	59
Fig. 4.9	Raman spectra of GaN samples grown at different temperatures of 750°C, 850°C, 900°C, 950°C and 1000°C. (Adapted from Low et al., 2011b).	61
Fig. 4.10	FESEM images of GaN nanowires sample P1, P2 and P3 grown at NH ₃ gas flow rate of (a) 75 sccm, (b) 100 sccm and (c) 125 sccm.	64

Fig. 4.11	XRD patterns of GaN nanowires sample P1, P2 and P3 grown at NH ₃ gas flow rate of (a) 75 sccm, (b) 100 sccm and (c) 125 sccm.	66
Fig. 4.12	Room temperature PL spectra of GaN nanowires sample P1, P2 and P3 grown at NH ₃ gas flow rate of 75 sccm, 100 sccm and 125 sccm, respectively.	67
Fig. 4.13	Raman spectra of GaN nanowires sample P1, P2 and P3 grown at NH ₃ gas flow rate of (a) 75 sccm, (b) 100 sccm and (c) 125 sccm.	71
Fig. 4.14	FESEM images of GaN nanowires sample R1, R2 and R3 grown under reaction period of (a) 20 minutes, (b) 30 minutes and (c) 40 minutes.	73
Fig. 4.15	XRD patterns of GaN nanowires sample R1, R2 and R3 grown at reaction period of (a) 20 minutes, (b) 30 minutes and (c) 40 minutes. The insets show the expansion of XRD patterns in the range of 32° - 38°.	75
Fig. 4.16	Room temperature PL spectra of GaN nanowires sample R1, R2 and R3 grown at reaction period of (a) 20 minutes, (b) 30 minutes and (c) 40 minutes.	77
Fig. 4.17	Raman spectra of GaN nanowires sample R1, R2 and R3 grown at reaction period of (a) 20 minutes, (b) 30 minutes and (c) 40 minutes.	79

LIST OF SYMBOLS

a	lattice constant
c	lattice constant
d	Distance
d_{hkl}	Interplanar spacing of the crystal planes
n	Order of diffraction
(hkl)	Miller-Bravais indices
ε	Dielectric constant
ε_c	Out of plane strain parameter
θ	Incident / Diffraction angle
λ	wavelength

LIST OF MAJOR ABBREVIATIONS

CVD	Chemical vapour deposition
EDX	Energy-dispersive x-ray spectroscopy
ECR	Electron cyclotron resonance
EDX	Energy-dispersive x-ray spectroscopy
FESEM	Field emission scanning electron microscopy
HVPE	Hydride vapour phase epitaxy
LD	Laser diode
LED	Light emitting diode
MBE	Molecular beam epitaxy
MOCVD	Metal-organic chemical vapour deposition
PL	Photoluminescence
PAA	Porous anodic alumina
RF	Radio frequency
RGA	Residual gas analysis
RHEED	Reflection high energy electron diffraction
TEM	Transmission electron microscopy
UV	Ultraviolet
VLS	Vapour-liquid-solid
VS	Vapour-solid
XRD	X-ray diffraction

FABRIKASI NANO-DAWAI GALLIUM NITRIDA MELALUI PEMENDAPAN WAP KIMIA

ABSTRAK

Dalam projek ini, kerja adalah ditumpukan kepada kajian pertumbuhan dan pencirian nano-dawai gallium nitrida (GaN) yang disintesis melalui teknik pemendapan wap kimia dengan bantuan pemangkin nikel di bawah pelbagai keadaan parameter eksperimen termasuk lokasi sumber gallium dan substrat, suhu pertumbuhan, kadar aliran gas ammonia dan tempoh masa tindak balas. Kajian perbandingan terhadap pengaruh parameter eksperimen tersebut ke atas ciri-ciri morfologi, struktur dan optik nano-dawai GaN telah dijalankan dalam projek ini. Sifat morfologi dawai GaN berdimensi rendah yang disintesis amat bergantung kepada lokasi sumber gallium dan substrat. Didapati bahawa lokasi sumber gallium dan substrat mampu mengaruhi takat tepu gas-gas yang bertindak balas, di mana ia sangat penting dalam mekanisma gas-cecair-pepejal. Justeru itu, dua jenis dawai GaN, iaitu mikro dan nano-dawai telah dihasilkan dalam kajian ini. Kajian mengenai suhu pertumbuhan menunjukkan 950°C merupakan suhu yang optimum untuk menghasilkan nano-dawai GaN yang seragam, lurus dan licin serta mempunyai komposisi unsur yang bagus. Selain daripada itu, sifat morfologi dan mekanisma pertumbuhan nano-dawai GaN yang disintesis adalah bergantung kepada kadar aliran gas ammonia. Didapati bahawa, nano-dawai GaN yang lurus telah dihasilkan di bawah keadaan kadar aliran gas ammonia yang rendah, iaitu melalui mekanisma gas-cecair-pepejal sedangkan nano-dawai yang berbentuk seperti cacing telah disintesis melalui mekanisma gas-pepejal di bawah keadaan kadar aliran gas ammonia yang tinggi. Tambahan pula, kajian mengenai tempoh masa tindak balas menunjukkan bahawa nano-dawai yang seragam dan lurus telah disintesis pada proses permulaan dan terjelma menjadi bentuk seperti cacing apabila tempoh masa tindak balas dilanjutkan. Di samping itu, keputusan pembelauan sinar-X (XRD) menunjukkan

nano-dawai GaN yang disintesis dalam projek ini merupakan fasa heksagon wurtzit. Pemancaran sinaran ultra-ungu dan biru dapat diperhatikan dalam spektra fotoluminesen (PL) dan ianya disebabkan oleh kehadiran kecacatan dalam sampel. Tambahan pula, kewujudan replikasi phonons telah diperhatikan di bahagian kawasan pemancaran biru dalam spektra PL semasa kajian terhadap parameter suhu pertumbuhan dijalankan. Jalur-jalur yang bersifat asimetris dan luas dalam spektra Raman mungkin disebabkan oleh ketegangan dalaman, kesan saiz dan permukaan tidak teratur yang wujud dalam nano-dawai GaN yang disintesis.

FABRICATION OF GALLIUM NITRIDE NANOWIRES VIA CHEMICAL VAPOUR DEPOSITION

ABSTRACT

In this project, works are focusing on the investigation of the growth and characterization of GaN nanowires synthesized by Ni-catalyzed chemical vapour deposition under various experimental parameters including gallium source and substrate position, growth temperature, ammonia flow rate and reaction period. The comparative studies of the influence of these parameters on the morphological, structural and optical characteristics of the synthesized GaN were carried out in this project. The morphology of the synthesized GaN low dimensional wires was dependent on the position of Ga precursor and substrates. The position of Ga precursor and substrates was found to be able to affect the degree of supersaturation of gaseous reactants, which is essential in the growth of GaN wires by vapour-liquid-solid mechanism. Thus two different dimensional aspects of GaN micro- and nanowires were synthesized in this parameter study. The study of growth temperature revealed that 950°C was the optimal growth temperature for synthesizing uniform, straight and smooth morphology of GaN nanowires with good elemental composition. On the other hand, the morphology and growth mechanism of GaN nanowires were dependent on NH₃ flow rate. It was found that straight GaN nanowires were synthesized under low NH₃ gas flow rate via vapour-liquid-solid mechanism whereas vermicular-like nanowires were synthesized under high NH₃ gas flow rate via the vapour-solid mechanism. Additionally, the study of reaction period revealed that the synthesized GaN nanowires showing a uniform and straight morphology in the early growth process and subsequently transforming to vermicular-shape of nanowires with the increase of reaction period. Apart from that, x-ray diffraction results indicated that the synthesized GaN nanowires were hexagonal wurtzite phase. Ultraviolet and blue

emissions were observed from photoluminescence measurements and attributed to the presence of defect in the samples. In addition, several phonon replicas have been observed in the blue emission region of photoluminescence spectra during the study of growth temperature parameter. Raman spectra displayed asymmetrical and broadened bands which could be ascribed to the internal strain, size effect and surface disorder of the synthesized GaN nanowires.

CHAPTER 1

INTRODUCTION

1.1 Introduction to Nanoscience and Nanotechnology

What is nanoscience? Nanoscience is a science of study the properties of ultra-small structures, usually in physical size of 1 to 100 nm. Nanoscience is based on the fact that properties of materials change as a function of the physical dimension of that material, therefore the motivation in nanoscience is to try to understand how materials behave when sample sizes are close to nanoscale or atomic dimensions. The properties of materials can be different at the nanoscale for two main reasons. First, nanomaterials have a relatively larger surface area compared with the same materials at larger size. The increase in surface area to volume ratio makes materials usually have strong surface effects. Second, quantum effects begin to dominate the behaviour of matter at the nanoscale and significantly change material's optical, magnetic or electrical properties. On the other hand, nanotechnology is a brand of engineering that allows scientists to manipulate matter on the nanometer level by applying selected property modifications, and learn to exploit the new generation of materials (with enhanced mechanical, optical, transport and magnetic properties) to produce novel applications and devices in atomic scale.

The modern conceptual idea of nanoscience and nanotechnology was firstly sketched by the renowned physicist Richard Feynman, 1959 (Feynman, R.) in his lecture 'There is plenty of room at the bottom'. Feynman first explored the possibility of manipulating material at the scale of individual atoms and molecules (definition of nanotechnology). In 1974, Norio Taniguchi (Taniguchi, 1974) was the first researcher who used the term of nanotechnology to describe the ability of

manipulating materials at the nanometre level. Furthermore, the scanning tunnelling microscope (STM), invented by Gerhard Binnig and Heinrich Rohrer, who were awarded the Nobel Prize for their invention in 1986, enabled scientists to characterize, investigate and manipulate matter at the nanoscale. This novel measuring instrument accelerated the further research in nanoscience and nanotechnology areas. Apart from that, the increasing efforts and interests of the electronics industry, which aimed at miniaturization of electronic devices, was also one of the primary driving forces during the 1980s for the emergence of nanoscience and nanotechnology. During the mid-1990s, Roco (Roco, M. C.) and his group promoted nanoscience and nanotechnology research as a national priority in the USA. The National Science Foundation (NSF), USA, established the National Nanotechnology Initiative in 2000 to support research in the area of nanotechnology. Nanoscience and nanotechnology were subject to the growing public awareness and controversy in the early of 2000s about its potential implications and feasibility of applications in materials, health care and environment.

The commercial applications of nanoscience and nanotechnology (Patra et al., 2009, Otto, M.) have been available in the early of 2000s. For examples, the applications of the nanomaterials such as the nanoparticle-based transparent sunscreens, carbon nanotubes for stain-resistant textiles, and Silver Nano antibacterial technology (introduced by Samsung in 2003) which uses silver nanoparticles as antibacterial agent in washing machines, refrigerators, air conditioners, air purifiers and vacuum cleaners. In the area of technology, nanoscale electronic devices and chips have been fabricated. In the area of food, nanoscience and nanotechnology have been applied to improve flavour delivery and maintain the food freshness. In the area of health care, it would be possible to grow artificial

organs and implant them in human-being. For the environmental applications, nanoscale photocatalysts, nanoscaled zero-valent iron and polymeric nanoparticles to address organic contaminants, iron nanoparticles have been used in ground water remediation, and nanomaterials arranged in superlattices that could allow the generation of electricity from waste heat in consumer appliances, automobiles and industrial processes. It is expected that development of nanoscience and nanotechnology applications will be significantly increased in the near future.

1.2 Introduction to Nanostructures

Nanostructures refer to material systems with length scale in the range of 1 to 100 nm in at least one dimension. Nanostructures have a dimension size that is intermediate between molecular and microscopic (micrometer-sized) structures. Therefore, they are also called as mesoscopic structures.

In a nanostructure, electrons are confined in the nanoscale dimension(s) but they are free to move in other dimension(s). Based on the dimensions in which electrons freely move, nanostructures are classified as below:

- Quantum well or two-dimensional system: Electrons are confined in one dimension but free moving in other two dimensions. Examples: interface between two semiconductors and ultra-thin film on a substrate.
- Quantum wires or one-dimensional system: Electrons are confined in two dimensions but free moving in other one dimension. Examples: polymer chains, nanowires, nanotubes, nanorods and nanobelts.
- Quantum dots or zero-dimensional system: Electrons are confined in all dimensions. Examples: nanoclusters or nanocrystallites on a surface.

Nanostructures are unique as compared to both individual atoms/molecules at a smaller scale and bulk materials due to the fact that as sizes approaching to the atomic scale, the relevant physical laws change from the classical to the quantum-mechanical laws of physics. The following phenomena are experienced by matter on the nanometer level:

- Quantum confinement: the confinement of electrons in the nanoscale dimensions result in quantization of energy and momentum, and reduced dimensionality of electronic states.
- Quantum coherence: certain phase relation of wave function is conserved for electrons moving in a nanostructure, so wave interference effect must be counted. However, in nanostructures, the coherence is often disrupted by defects in the nanostructures. These quantum coherent and de-coherent effects have complicated the description of electronic motion in a nanostructure. This is in contrast to atoms/molecules and bulk materials: in an atom, all processes are coherent whereas in bulk materials, all are de-coherent.
- Surface/interface effects: a majority of atoms in nanostructure is located at and near the surfaces or interfaces. The mechanic, thermodynamic, electronic, magnetic, optical and chemical properties of these atoms can be diverse from those bulk/interior atoms.

These quantum and surface/interface effects lead to completely new kinds of optical, electrical, thermal, magnetic and mechanical properties of the nanoscaled materials. For examples:

- Optical properties: When the size of nanostructures becoming smaller than the de Broglie wavelength and the mean free path of electrons, amazing quantum confinement effects play an important role. The band gap increases

and instead of a continuous density of state as in bulk materials, there are discrete energy levels in nanostructures. This has impacted the optical properties of nanostructures. For instance, the shift of absorption edge in nanostructures (Rastogi et al., 2000).

- **Electrical properties:** The changes of electrical properties in the nanoscaled materials are mainly due to the increasing influence of the wavelike properties of the electrons and the scarcity of scattering centres. As the dimension(s) of the nanostructures become comparable with the de Broglie wavelengths of electrons, the discrete nature of energy becomes apparent. The changes of the energy spectrum have serious implications on the electrical properties of nanostructured semiconductor. For example, the property of quantized current due to single electron charging effect in charge-couple device (Fujiwara et al., 2004).
- **Thermal properties:** The large ratio of surface area to volume (the number of surface/interface atoms to all atoms in a nanostructure) has significant effect on the stability of nanostructures. The cohesive energy is dramatically lowered because of atoms on the surface are incompletely bonded. As a result, the melting point of nanostructures is obviously lower than corresponding bulk material. For example, the melting point of bulk gold is 1064°C. However, as the size of gold particles decreases to the range of a few nanometers, the melting point drops significantly to ~300 – 400°C (Bieri et al., 2003, Buffat and Borel, 1975).
- **Magnetic properties:** Ferromagnetic materials consist of domains with parallel magnetization (Fig. 1.1(a)). If a magnetic field H is applied, the magnetization of all domains will align according to the direction of the field

and remains in this direction even though the magnetic field is removed. However, if the size of ferromagnetic nanomaterials becomes sufficiently small (10-20 nm), only one domain of magnetization remains in the particle (Fig. 1.1(b)). Again, if a magnetic field is applied, the magnetization domain of particles will align to this field (Fig. 1.1(c)). However, when the magnetic field is removed, the magnetization can be randomly flipped (Fig. 1.1(d)) under the influence of temperature. This behaviour is called as superparamagnetism effect.

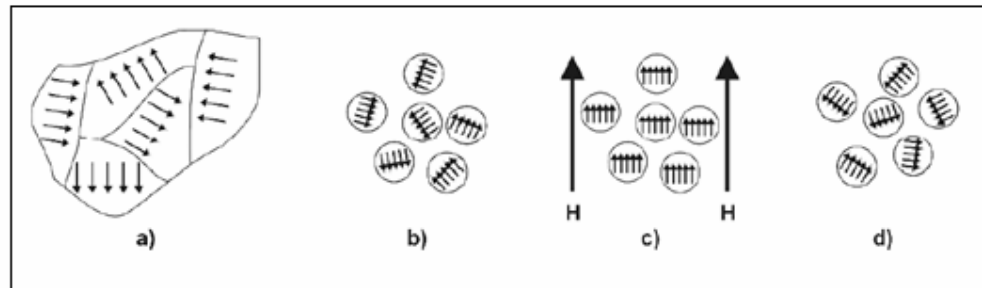


Fig. 1.1. Explanation of the superparamagnetic effect. (Adapted from Kulisch et al., 2009).

- Mechanical properties: elastic properties (stiffness, resistance to deformation) are due to atomic arrangement and nature of chemical bonds. All materials possess a certain degree of elasticity. The Young modulus, Y_m is a measure of intrinsic elasticity of a material. Y_m is the ratio of the stress to the strain as a material is stretched. In classical mechanics, it should be a material constant and independent of scale. However, as the materials sizes reduced to nanoscale, the large ratio of surface area to volume and also the surface/interface strong effects have made the Y_m as a function of material

scale length. Therefore, it is no longer a material constant in nanoscaled materials.

By exploiting the quantum mechanic effects, various novel applications have been developed such as: (i) large ratio of surface area to volume is favourable for gas storage (where molecules are absorbed on the surfaces) as well as for catalyst (where reactions occur on the surface) applications. (ii) nanostructures are promising for optoelectronic applications due to their high quantum confinement effect. (iii) the superparamagnetism effect plays an important role in magnetic data storage application as well as in biomedical applications such as magnetic resonance imaging, magnetic hyperthermia and magnetofection.

1.3 Introduction to III-nitrides

Group III-nitrides semiconductor materials (AlN, GaN, InN) and including their ternary alloys are excellent wide bandgap semiconductors. They can crystallize in wurtzite, zinc-blende and rock salt polytypes. Under ambient condition, the thermodynamically stable structure is wurtzite. The wurtzite structure of GaN, AlN and InN form a continuous alloy system with direct bandgap range from ~0.7 eV for InN, to 3.4 eV for GaN and to 6.1 eV for AlN which covering a very broad optical spectrum range from the infrared to deep ultraviolet (UV). This has made the III-nitride system as promising semiconductors for optoelectronic device applications, such as light emitting diodes (LEDs), laser diodes (LDs) and UV detectors.

GaN has attracted considerable interest from the researchers over the past decades, mainly owing to its attractive wide bandgap of 3.4 eV. The bandgap of 3.4 eV makes it the best candidate for optoelectronic devices operating in blue or UV region of the optical spectrum. Apart from that, the superior properties such as quick

saturation speed of the electronics drift, high breakdown voltage as well as high thermal, chemical and mechanical stability of GaN also make it as an ideal material for fabricating high frequency, high power and high density integrated electronic devices.

AlN has high thermal conductivity, low thermal expansion coefficient, outstanding chemical and mechanical stability as well as good dielectric properties. Due to the above properties, AlN is widely used as substrates for electronic packages, heat sinks, power transistor bases, electronic device packages and molten metal handling components.

InN is the least studied III-nitride semiconductor and still in process of evolution due to its difficulty in growth. InN is more difficult to grow than GaN because of its low dissociation temperature (~630 °C) (Bottcher et al., 1998) and high equilibrium vapour pressure of nitrogen (MacChesney et al., 1970). As a result, lower temperature is particular important in synthesizing the high quality InN. Nevertheless, InN has been extensively used in alloy system (InGaN (Yoshimoto et al., 1991, Wu, J. et al., 2002) and InAlN (Kim, K. S, et al., 1997, Kubota et al., 1989)).

1.4 Research Background

1.4.1 Development of One-Dimensional GaN Nanostructured Materials

One-dimensional GaN nanostructured materials have attracted considerable attention due to their unique optical, electrical, thermal, magnetic and mechanical properties, distinctive from those of the bulk materials. Several attempts to grow the GaN nanostructures have been reported such as laser ablation (Duan and Lieber, 2000), arc discharge (Han et al., 2000), template-assisted growth (Cheng et al., 1999),

thermal evaporation (Stach et al., 2003), metal-organic chemical vapour deposition (MOCVD) (Wang, G. T. et al., 2006), molecular beam epitaxy (MBE) (Robins et al., 2007, Cerutti et al., 2006) and chemical vapour deposition (CVD) (Chen, C. C. et al., 2001, Kim, H. M. et al., 2002).

As a consequence, various morphologies of one-dimensional GaN nanostructures have been synthesized and reported by researchers, such as

- nanowires (Xiang et al., 2006, Li, Z. J. et al., 2001, Seryogin et al., 2005, Nam et al., 2004, Kuykendall et al., 2003, Jian et al., 2003, 2004, Dong et al., 2005, Peng et al., 2002, Chang and Wu, 2003, Xu, B. S. et al., 2006)
- porous nanowires (Bae et al., 2003)
- nanotubes (Yin et al., 2004)
- nanobelts (Bae et al., 2002, Li, Z. J. et al., 2001)
- nanorings (Li, Z. J. et al., 2001) and
- nanorods (Li, Z. J. et al., 2001).

Apart from that, one-dimensional GaN nanostructures have been regarded as interconnect and functional units for the fabrication of electronic and optoelectronic devices in nanoscale. For examples:

- Logic and computational circuits have been produced using GaN nanowires (Huang, Y. et al., 2001), which is an important breakthrough in nanotechnology.
- GaN nanowires have been widely used for fabricating ultraviolet nanolasers (Gradečak et al., 2005, Pauzauskic et al., 2006, Huang, M. H. et al., 2001).
- GaN nanowires have been used to fabricate low power field-effect transistors (Huang, Y. et al., 2002).

- GaN nanowires have been used to fabricate hydrogen sensors (Johnson et al., 2008).
- GaN nanorods have been used for fabrication of ultraviolet-light emitting diodes (Kim, H. M. et al., 2003).

1.5 Research Objectives

In this project, the research mainly focuses on the growth and characterization of GaN nanowires by nickel catalyzed CVD technique. Horizontal two-furnace CVD system is used to grow the GaN nanowires in this project. This system offers greater flexibility in term of growth and substrate temperatures compare to single temperature zone furnace. The first furnace is used for the decomposition of ammonia gas at high temperature whereas the second furnace is employed for the growth of GaN nanowires.

The GaN nanowires have been grown under various growth parameters, i.e. growth temperature, NH_3 gas flow rate and total reaction time. In addition, the impact of the physical location of Ga source and substrate position on the characteristics of GaN nanowires has been investigated as well.

The comparative studies about the influence of the experimental parameters on the morphological, structural and optical characteristics of synthesized GaN nanowires have been carried out in this project.

1.5.1 Originality of the Research Works

The original work in this project is the investigation of the effect of Ga source and substrate position on the growth of two different types of low dimensional GaN wires. This work has not been investigated and reported in the literature review.

Apart from that, detailed studies of the influence of growth temperature on the characteristics of GaN nanowires have been carried out in wide range of temperatures from 750 to 1000 °C. This study is believed has not been reported in the literature review.

Furthermore, the study of phonon replicas in the blue emission of photoluminescence spectra of synthesized GaN nanowires has been performed in this project. This work has not been reported as well in the literature of GaN nanostructures. To our knowledge, the literature study of phonon replicas has only been investigated in the ultraviolet emission of photoluminescence spectra of GaN nanostructures.

1.6 Outline of the Thesis

In brief, the content of this thesis is arranged as follows:-

Chapter 2 provides an overview of GaN nanowires technology, such as the growth techniques and factors influencing the morphological, structural and optical characteristics of GaN nanowires.

Chapter 3 presents the materials that used in the fabrication of GaN samples and principle operation of instrumentations that involved in this project. Methods in studying the influence of experimental parameters on the characteristics of GaN nanowires are reported as well in this chapter.

Chapter 4 presents the results and discussions on the characteristics of the synthesized GaN samples.

Chapter 5 presents the conclusion of the thesis with a summary of the research work. A few recommendations for the future research are also included.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, a brief overview of GaN nanowires technology is presented. The review mainly focuses on the growth mechanism and techniques in synthesizing GaN nanowires, and factors that influencing the morphological, structural and optical characteristics of GaN nanowires.

2.2 Growth Mechanism of Nanowires

During the last decade, several approaches for synthesizing nanowires have been developed. Generally, the growth of nanowires involves one of two typical mechanisms: vapour-liquid-solid (VLS) or vapour-solid (VS). The VLS mechanism utilizes the transition metal vapour-liquid-solid catalyst for the growth of nanowires whereas VS mechanism relies on direct crystallization from the vapour.

2.2.1 Vapour-Liquid-Solid Growth Mechanism

VLS process (also known as metal catalytic growth) is a well-known self-organized growth mechanism for synthesizing nanowires. This technique can produce free-standing crystalline nanowires of semiconductor with fully controlled of nanowires diameters through the pre-determined sizes of metal catalysts.

During the growth of nanowires by VLS mechanism, for example the growth of GaN nanowires using Fe metal catalyst, the Fe film breaks up into liquid Fe nano-droplets on the surface of substrate upon heating at a certain high temperature. These nano-droplets act as favourable nucleation sites for the adsorption of Ga vapour as well as nitrogen radical (N^*) to form Fe-Ga-N alloy. When the

concentration of the Ga-N flux exceeds the saturation point within the Fe-Ga-N droplets, the GaN begins to diffuse and precipitate from the alloys droplets to form nanowires. The whole process of absorption, diffusion and precipitation of the growth of GaN nanowires involves vapour, liquid and solid phases. In this regards, this metal catalytic growth process has been known as VLS mechanism (Low et al., 2011a, 2011b, Chen, C. C. et al., 2001, Biswas et. al., 2007). The growth of GaN nanowire by Fe metal catalyzed VLS mechanism is illustrated in Fig. 2.1.

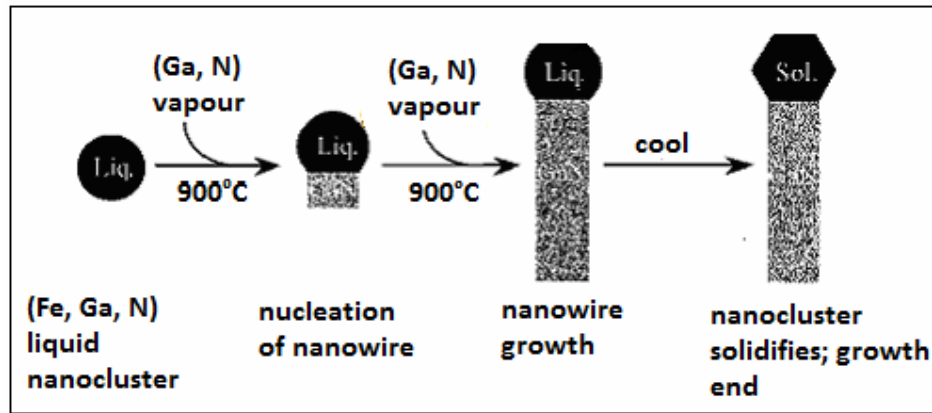


Fig. 2.1. Schematic of overall evolution of the growth of GaN nanowire by Fe metal catalyzed VLS mechanism. (Adapted from Duan and Lieber, 2000).

2.2.2 Vapour-Solid Growth Mechanism

VS process is also called as self-catalytic growth since the nanowires grow directly from the vapour without the transition metal catalyst. In the beginning of the VS process, for example the growth of GaN nanowires, the Ga vapour reacts with the N* to form a GaN buffer layer on the substrate surface. The GaN nanowires nucleate on the GaN buffer layer and the continuous feeding of Ga-N flux as well as the subsequent precipitation results into the growth of GaN nanowires (Biswas et. al., 2007, Choi et al., 2006).

2.3 Growth Techniques of GaN Nanowires

In an effort to grow high quality of GaN nanowires, many growth techniques including CVD (Kim, T. Y. et al., 2003, Kim, H. M. et al., 2002, Wang, G. T. et al., 2006, Kang et al., 2011), MBE (Robins et al., 2007, Cerutti et al., 2006), thermal evaporation (Stach et al., 2003, Zhou et al., 2003), template assisted (Cheng et al., 1999, 2000a, 2000b) and laser assisted catalytic growth (Duan and Lieber, 2000) have been developed.

2.3.1 Chemical Vapour Deposition

CVD is a technique used to deposit a high purity solid material on the surface of a substrate from gaseous phase. Reactive gases are fed into reaction chamber and these gases react on a substrate and form a solid material such as thin film, powder or low dimensional structures (micro- or nano-structures).

Fig. 2.2 (a) shows a typical example of a CVD system where the reactant gases or usually called as precursor gases are flowed into the reaction chamber at desired growth temperature. Usually, an inert gas such as argon or nitrogen is used as carrier gas. As they pass through the reactor, these precursors react and form a solid material on the heated surface of substrate. After the reactions, by-product species (exhaust gases) are being filtered, and then released into the atmosphere.

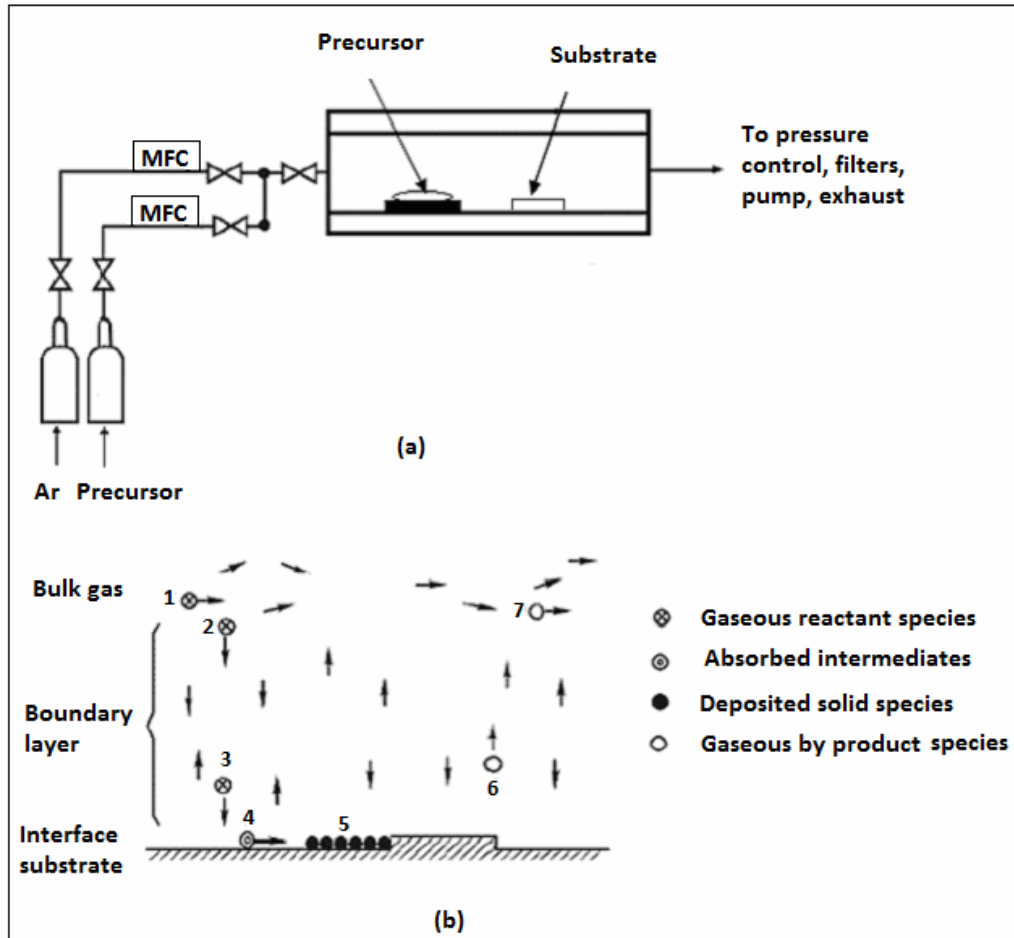


Fig. 2.2. Schematics of a CVD process: (a) typical CVD system and (b) a CVD model. (Adapted from Xu and Yan, 2010).

Fig. 2.2 (b) illustrates the series of the physical and chemical steps that occurred during the CVD process, developed by Spear in 1982 (Spear, 1982).

Following are the descriptions for each step (Xu and Yan, 2010):

- 1) Reactant gaseous species transport to vicinity of substrate.
- 2) Reactant species diffuse through the boundary layer to the surface to form intermediates.
- 3) Reactant species or intermediates adsorb on the surface of substrate.
- 4) Series of reactions including surface migration, heterogeneous reaction and formation of by-product species occur in this step.

- 5) By-product species desorb from the surface reaction.
- 6) By-product species diffuse into the bulk gas.
- 7) By-product species are being released into the atmosphere as exhaust gases.

The CVD method has been employed in the fabrication of GaN nanowires in this project due to many advantages, as described below (Xu and Yan, 2010, Hart, J.):

- Flexibility - CVD offers a greater flexibility of using a wide range of precursors such as metallic and organo-metallic compounds.
- Purity - High purity of GaN nanowires are able to be synthesized by CVD.
- Deposition temperature - CVD requires relatively low deposition temperatures. This permits the desired materials to be synthesized in-situ at low energies through vapour phase reactions.
- Growth rate - CVD possesses relatively high growth rates.
- Growth pressure - CVD does not require as high vacuum as physical vapour deposition methods.
- Growth distribution - CVD enables uniform distribution of GaN nanowires deposition over large areas.
- Cost – CVD requires relatively low cost of the equipment.

However, the CVD method does consist of disadvantages (Xu and Yan, 2010) as below:

- Safety and health - CVD technique mostly involves safety and healthy issues as the precursors used can be highly reactive and pyrophoric (e.g trimethylgallium, trimethylaluminum, trimethylindium), corrosive (ammonia gas) or toxic (e.g gallium acetylacetonate and ammonia gas). The exhaust gases consist of chemical reaction by-products, intermediates and others can also be hazardous, toxin, corrosive and flammable.

- Complexity - CVD technique is perhaps the most complex if compare to other vapour-phase deposition methods. Multiple test cases are required in CVD in order to determine the optimum experimental parameters.

2.3.2 Molecular Beam Epitaxy

MBE technique has been exploited to synthesize GaN nanowires based on the VLS growth mechanism (Robins et al., 2007, Cerutti et al., 2006). Fig. 2.3 shows the schematic diagram of the MBE growth chamber. During the growth process, elemental sources are heated in Knudsen cells and evaporated from the effusion cells at controlled rate onto a heated substrate. MBE works under ultra-high vacuum condition $\sim 10^{-10} - 10^{-11}$ torr. Under ultra-high vacuum condition, the long mean-free path of particles reduces and minimizes collisions or reactions between molecules in the beam, which results in a line-sight growth reaction at the surface.

MBE has several advantages over other synthesis techniques:

- Ultra-high vacuum condition provides an ultra clean growth environment which can reduce contamination on the surface of substrate.
- Radio frequency (RF) or electron cyclotron resonance (ECR) plasma sources are commonly employed to activate the nitrogen species in the nitrides growth. The low growth temperature due to this atomic nitrogen source results in lower thermal stress upon cooling, less diffusion, and reduced alloy segregation in the nanostructures.
- Precise control of the beam fluxes and growth condition.
- Easy implementation of in situ diagnostic instruments such as Mass spectrometer for residual gas analysis (RGA) and reflection high energy

electron diffraction (RHEED) to monitor the growth rate and epitaxial nanostructures quality during growth process.

- Compatibility with other high vacuum processing methods (metal evaporation, ion beam milling, ion implantation).

However, MBE technique is slow, sophisticated and expensive than other synthesis technique such as CVD.

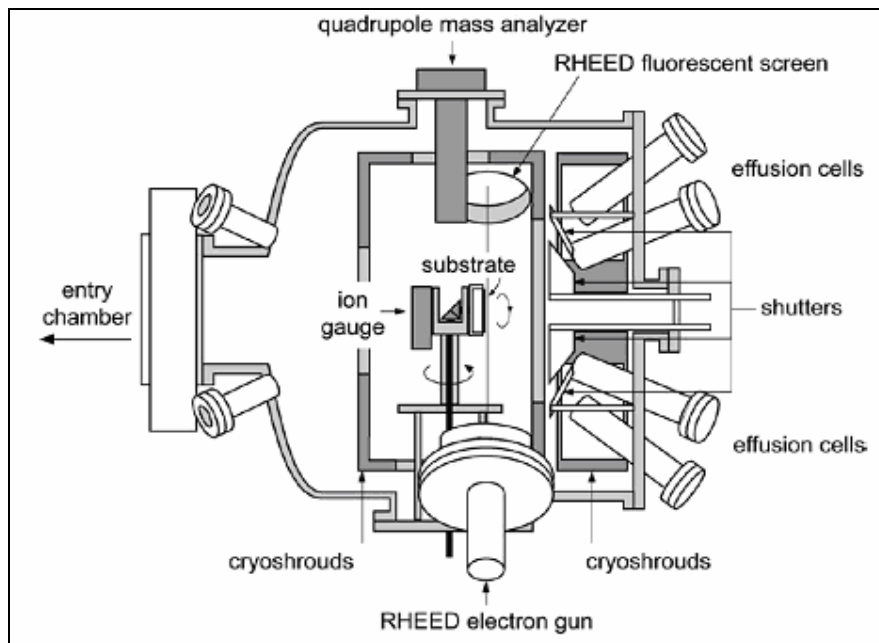


Fig. 2.3. Schematic diagram of the MBE growth chamber. (Adapted from Franchi, *et al* 2003).

2.3.3 Thermal Evaporation

GaN nanowires can be fabricated by a simple method of thermal evaporation of commercial GaN powder. Fig. 2.4 shows the typical schematic diagram of the thermal evaporation system. The temperature gradient is the critical parameter for the formation of nanowires by this technique. The formation of GaN nanowires is through evaporating the GaN powder at elevated temperature under a vacuum or inert gas atmosphere (carrier gas). The GaN vapour transports to the surface of

substrate and the nanowires form directly from the vapour phase of GaN at the low temperature zone of furnace.

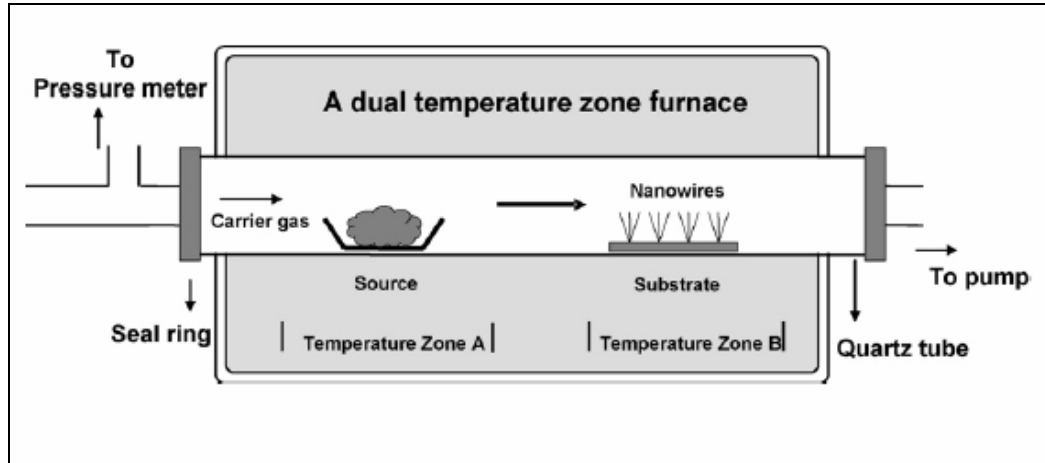


Fig. 2.4. A typical schematic diagram of the thermal evaporation system. (Adapted from Wang, N. et al., 2008).

2.3.4 Template Assisted Growth

The template assisted synthesis of nanowires is another simple way to fabricate GaN nanowires. These templates contain pre-defined pores. The chemical and mechanical stability as well as the diameter, uniformity and density of the pores are important factors to consider in determining the template type. The template that frequently used for GaN nanowires synthesis is porous anodic alumina (PAA) (Cheng et al., 1999, 2000a, 2000b).

During the growth process, the pores on the template are filled with the desired material to make nanowires by using proper filling technique like CVD (Cheng et al., 1999, 2000a, 2000b). Fig. 2.5 shows the schematic diagram of the template assisted synthesis of nanowires. Removal of the template releases the nanowires.

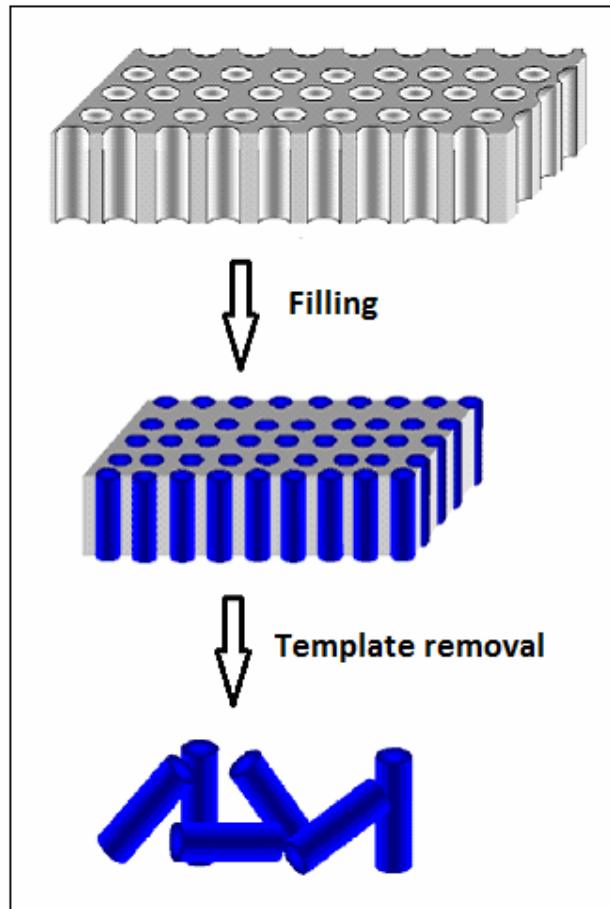


Fig. 2.5. Schematic illustration of the template assisted synthesis of nanowires. (Adapted from Barth et al., 2010)

2.3.5 Laser Assisted Catalytic Growth

Laser assisted catalytic growth is a technique used to synthesis nanowires, for example GaN nanowires (Duan and Lieber, 2000) by using high power pulse laser to ablate a target in an evacuated quartz tube with inert gas (He, H₂, Ar or N₂) as the ambient gas. The reactant vapour generated by laser ablation dissolves in a molten metal catalyst and generates liquid nanoclusters that serve as reactive sites confining and directing the growth of nanowires through VLS mechanism.

2.4 Factors Influencing the Morphological, Structural and Optical Characteristics of GaN Nanowires

One of the major issues which restrained the GaN research is the lack of a suitable substrate material that is lattice matched and thermally compatible with GaN, which leads to the generation of structural defects. In addition to the substrates issue, there are several factors including catalysts, source materials and process parameters exploited during the growth also playing a critical role to determine the characteristics and quality of the GaN nanowires.

2.4.1 Substrates

It is well known, the mismatch of lattice constant and thermal expansion coefficient between the substrate and GaN have been leading to high threading dislocation density, mosaic crystal structure, biaxial induced stress and wafer bowing. These defects reduce the charge carrier mobility, reduce the minority carrier lifetime, and decrease the thermal conductivity, subsequently degrade the device performance. Therefore, many efforts have been laboured by the researchers in searching the new and suitable substrate material to improve the quality of GaN epitaxial. Table 2.1 shows the lattice constant and thermal expansion coefficient for some prospective substrates as compared to GaN.

Table 2.1. Lattice parameters and thermal expansion coefficient of prospective substrates for nitrides epitaxial growth. (Data extracted from Popovici and Morkoc 2000).

Crystal	Symmetry	Lattice Constant (nm)	Thermal Expansion Coef.
		(<i>a</i> ; <i>c</i>)	(<i>a</i> ; <i>c</i>) ($\times 10^{-6} \text{K}^{-1}$)
GaN	Wurtzite	(0.3189; 0.5185)	(5.59; 3.17)
GaN	Cubic	0.452	-
Sapphire	Hexagonal	(0.4758; 1.299)	(7.5; 8.5)
6H-SiC	Wurtzite	(0.308; 1.512)	(4.2; 4.68)
Si	Cubic	0.54301	-3.59
GaAs	Cubic	0.56533	6
AlN	Wurtzite	(0.3112; 0.4982)	(4.2; 5.3)
ZnO	Wurtzite	(0.3250; 0.5213)	(8.25; 4.75)
3C-SiC	Cubic	0.436	-
InP	Cubic	0.5869	4.5
MgO	Cubic	0.4216	10.5
MgAlO ₂	Cubic	0.8083	7.45
LiAlO ₂	Tetragonal	(0.5406; 0.626)	-
ScMgAlO ₄	Tetrahedral	(0.3240; 2.511)	(6.2; 12.2)

2.4.1.1 Sapphire

Sapphire (Al₂O₃) was first used as a substrate in Maruskas and Tietjen's pioneering study of GaN epitaxy by HVPE in 1969 (Maruska and Tietjen, 1969). Sapphire possesses a different lattice constant and thermal expansion coefficient from GaN. Beside that, sapphire is also electrically insulating, hence all electrical contacts have to be formed on the front side of the device, reducing the area available for devices and complicating the device fabrication. However, it is still commonly and widely used substrate for GaN growth. This is due to its wide availability, hexagonal symmetry, and ease of handling and pre-growth cleaning. Apart from that, sapphire is also stable at high temperature (~1000 °C). High thermal stability makes it as a suitable substrate for the synthesis of GaN which is normally conducted at

high temperature. As a result, sapphire has been used as substrate for the growth of GaN nanowires in this project.

2.4.2 Catalysts

There are two types of metal catalysts that have been used to fabricate GaN nanowires, i.e. foreign metal catalysts and Ga-based catalysts. Foreign metal catalysts that frequently reported in literature are Au, Pt, Fe, Ni, Ag and In, as listed in Table 2.2. However, such foreign metal catalysts may contaminate the GaN nanowire, causing strain (Kipshidze et al., 2005) and non-radiative recombination (Qian et al., 1990) which can be detrimental to device performance.

As a consequence, Ga-based catalysts assisted growth of GaN nanowires has been pursued by researchers. The use of Ga-based catalysts could eliminate the risk of nanowires contamination due to foreign metals and at the same time providing the spatial control of nanowires associated with catalyst-based techniques. Ga-based catalyst that reported in literature is $\text{Ga}(\text{NO}_3)_3$ (Simpkins et al., 2006). Nevertheless, the drawback of $\text{Ga}(\text{NO}_3)_3$ is the oxygen incorporation from $\text{Ga}(\text{NO}_3)_3$ which would result in an increase in n-type conductivity.

In this work, foreign metal catalyst of Ni has been adopted as catalyst due to its ease of handling and wide availability as well as its popularity as a catalyst for the growth of GaN nanowires.

2.4.3 Source Materials

The precursor source materials that commonly used to fabricate GaN nanowires are metallic Ga and ammonia gas. Other Ga precursors that usually reported are trimethylgallium, mixture of Ga and GaN, gallium acetylacetonate, Ga_2O_3 , mixture of Ga and Ga_2O_3 . In addition, beside the ammonia gas, nitrogen

plasma has been also used as N precursor in the growth of GaN nanowires. The GaN precursors are summarized as Table 2.2.

Metallic Ga has been chosen as Ga precursor in this research due to the safety concern whereas ammonia gas has been used as N precursor owing to the CVD growth technique.

2.4.4 Process Parameters

The morphological, structural and optical characteristics of GaN nanowires are greatly dependent on the process parameters/growth conditions such as growth temperature, heating rate, gases (precursors and carrier) flow rate, N/Ga flux ratio, total reaction time, pressure during growth, annealing temperature and time as well as the location between Ga source and substrate. Several works have been done by researchers to study the relationship of process parameters to the growth of GaN nanowires as shown in Table 2.2.

In this project, studies of process parameters including growth temperature, ammonia flow rate, reaction period and position of Ga precursor and substrate have been carried out and investigated.

Table 2.2. Summary of the literature reviews on the growth of GaN nanowires (GaN precursors, catalysts, growth methods, process parameters/growth conditions).

Precursors		Growth method	Substrate	Catalyst	Growth conditions									Ref.
Ga	N				Growth temperature (°C)	Heating rate	N precursor flow rate	Carrier flow rate (sccm)	Reaction period (min)	N/Ga flux ratio	Pressure	Annealing		
												Temperature (°C)	Period (min)	
Metallic Ga	NH ₃	CVD	sapphire	Pt or Ni	900 to 970	–	20 sccm	–	360	–	–	–	–	1
		CVD	LiAlO ₂	Au	1000	40 °C/min	–	–	15	–	–	–	–	2
		CVD	MgO	Ag	870-890	–	10 cm ³ /min	–	5-10	–	–	450-550	20-30	3
		CVD	Si	Ni	700	–	100 sccm	–	5	–	100 mTorr	–	–	4
		CVD	–	Fe/Al	950	–	80 sccm	–	60	–	–	–	–	5
		CVD	Si	In	920	30 °C/min	20 sccm	80	20	–	20 mTorr	–	–	6
		CVD	Si	Ga	950	50 °C/min	Total flow rate of 40 to 80 sccm (2:3 ratio of N ₂ to NH ₃)		–	–	atm	–	–	–
TMGa/ TMG	NH ₃	MOCVD	Al ₂ O ₃	Ni	750-850	–	300 sccm	–	–	–	–	800	10	8
MOCVD		sapphire	Ni	900	–	100 sccm	250	5-20	–	–	–	–	9	
gallium acetylic-etonate	NH ₃	CVD	Si	Ni	620 and 750	–	100 sccm	–	–	–	200 Torr	–	–	10