

**THE GROWTH OF GaN-BASED LOW
DIMENSIONAL STRUCTURES BY CVD USING
PLATINUM AND PALLADIUM CATALYSTS**

by

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LIST OF SYMBOLS

T	Absolute temperature
E_g	Bandgap energy
ϵ	Dielectric constant
A	Effective diode area
m_e	Electron effective mass
A^*	Effective Richardson constant
m_e	Electron effective mass
q	Electronic charge
V	Forward bias voltage
I	Forward current
η	Ideality factor
d	Interplanar distance
n	Refractive index
I_0	Reverse saturation current
θ	Scattering angle
ϕ_b	Schottky barrier height
k	Thermal conductivity/Boltzmann constant
α	Thermal expansion coefficient
λ	Wavelength of incident radiation

LIST OF ABBREVIATIONS

AO	Acoustic Overtones
CVD	Chemical Vapor Deposition
EDS	Energy Dispersive X-Ray Spectroscopy
FESEM	Field-emission Scanning Electron Microscope
FWHM	Full Width at Half Maximum
GaN	Gallium Nitride
HRTEM	High Resolution Transmission Electron Microscopy
HVPE	Hydride Vapor Phase Epitaxy
ITO	Indium Tin Oxide
IV	Current-voltage
IT	Current-time
LED	Light Emitting Diode
MBE	Molecular Beam Epitaxy
MOCVD	Metal-organic Chemical Vapor Deposition
MOVPE	Metal Organic Vapor Phase Epitaxy
OMCVD	Organo-metallic Chemical Vapor Deposition
OMVPE	Organo-metallic Vapor Phase Epitaxy
PCB	Printed Circuit Board
PL	Photoluminescence
RF	Radio Frequency
SBH	Schottky Barrier Height
SCCM	Standard Cubic Centimeters Per Minute
SEM	Scanning Electron Microscopy

SO	Surface Optical
TEM	Transmission Electron Microscopy
UV	Ultraviolet
VLS	Vapor-liquid-solid
VS	Vapor-solid
VSS	Vapor-solid-solid
XRD	X-ray Diffraction

**PERTUMBUHAN STRUKTUR DIMENSI RENDAH BERASASKAN GaN
DENGAN PEMENDAPAN WAP KIMIA MENGGUNAKAN PEMANGKIN
PLATINUM DAN PALADIUM**

ABSTRAK

Projek penyelidikan ini membentangkan pertumbuhan struktur GaN dimensi rendah menggunakan pemangkin logam satu unsur (Pt dan Pd) dan pemangkin logam dua unsur (Pd/Pt) dengan kaedah pemendapan wap kimia berdasarkan mekanisme wap-cecair-pepejal. Suhu pertumbuhan minima didapati bergantung kepada jenis pemangkin, 900 °C untuk nanostruktur GaN yang dimangkin oleh logam Pt dan 1100 °C untuk pemangkin logam Pd dan Pd/Pt. Walau bagaimanapun, suhu pertumbuhan optimum untuk menumbuh nanostruktur GaN adalah 1100 °C, tanpa mengira jenis pemangkin. Saiz nanodawai GaN meningkat dan bentuk berubah kepada nanokristal dengan peningkatan kadar aliran gas NH₃. Kajian XRD dan Raman menunjukkan bahawa nanodawai GaN yang dihasilkan mempunyai struktur kristal wurzite heksagon. Berbanding dengan pemangkin logam satu unsur, nanodawai GaN yang dihasilkan oleh pemangkin Pd/Pt mempunyai kualiti kristal dan kandungan N yang tertinggi. Analisis mengenai komposisi unsur telah menunjukkan bahawa orientasi pertumbuhan lebih cenderung kepada orientasi (002) dengan kandungan N yang lebih tinggi. Dalam kajian Raman, anjakan E₂(high) and A₁(LO) kepada frekuensi rendah telah dikaitkan dengan kesan terkurung fonon. Kehadiran mod-mod Raman dilarang mewakili terdapatnya kemusnahan kesempurnaan struktur kristal dalam sampel. Di sebaliknya, untuk nanostruktur GaN yang bersaiz besar, mod AO dan SO(A₁) tidak dapat diperhatikan. Penyelidikan Raman juga telah mendedahkan bahawa nanostruktur GaN bersaiz besar akan mempamerkan sifat Raman sama

seperti bahan pukal. Dengan menggunakan nanodawai GaN yang dimangkin oleh logam Pd/Pt, pengesan foto UV berdasarkan nanodawai telah berjaya dihasilkan. Arus foto telah didapati meningkat dengan sinaran cahaya UV. Secara keseluruhannya, peranti pengesan foto UV yang difabrikasi mempunyai kitaran intensity arus foto yang stabil dan boleh diulang.

THE GROWTH OF GaN-BASED LOW DIMENSIONAL STRUCTURES BY CVD USING PLATINUM AND PALLADIUM CATALYSTS

ABSTRACT

This research project presents the growth of low dimensional GaN structures employing monometallic catalyst (Pt and Pd) and bimetallic catalysts (Pd/Pt) by means of chemical vapor deposition based on vapor-liquid-solid mechanism. Minimum growth temperature was found catalyst-dependent, 900 °C for Pt-grown nanostructures and 1100 °C for Pd and Pd/Pt bimetallic catalysts. However, the optimum growth temperature for growing GaN nanostructures was 1100 °C, regardless of catalyst type. By increasing NH₃ flow rate, GaN nanowires increased in size and converted into nanocrystals. XRD and Raman studies indicated that grown GaN nanowires have hexagonal wurtzite crystal structure. The growth of Pd/Pt-catalyzed GaN nanowires had the highest crystalline quality and highest N content compared to monometallic catalyst. EDS analysis showed that growth orientation tended to be (002)-dominant with higher N content in GaN. In Raman studies, low-frequency shifts of E₂(high) and A₁(LO) were attributed to the phonon confinement effect. Presence of forbidden modes represented the destruction of crystalline perfection in the samples. AO and SO(A₁) modes were absent in GaN nanostructures with large diameter. Raman studies also revealed that large-sized GaN nanostructures exhibited the similar Raman properties as the bulks. Utilizing Pd/Pt-catalyzed GaN nanowires, a nanowires-based UV photodetector was successfully fabricated. The photocurrent was found to increase with the illumination of UV light. In overall, the fabricated GaN nanowires UV photodetector had the stable and reproducible cycle of photocurrent intensity.

CHAPTER 1

INTRODUCTION

1.1 Introduction

This introductory chapter generalizes the theme of this research project which firstly briefs the research background, the introduction of the subject material along with the motivation of the research. Later, the purpose of this research and the research originalities are defined at the subsection followed by a description outlining the thesis organization at the end of this chapter.

1.2 Research Background

Tracing back to the history, semiconductor whisker growth in the scale of nanometer (nm) was pioneered by a research group led by Haraguchi [1] who designed p-n junction from GaAs whiskers with diameter of about 100nm in the year of 1991. The growth of nanowires was then be popularized in late 90s after the research work published by Morales and Lieber [2] in 1998. This group has developed the smaller size of Si and Ge whiskers, in the range of 3 to 20 nm.

Primarily owing to their dimensionality and quantum confinement effect, semiconductor nanowires have been shown to exhibit novel properties in electronic and optical which are unobservable in bulk materials. Many exciting achievements have been reported in the past years, showing the remarkable enhanced performance based on the semiconductor nanowires [3-5]. More importantly, they generated the devices and systems that are closely bound up with the life we live, e.g., light emitting diodes (LED), optical lasers, sensors, transistors as well as solar panels [6-8]. These situations are certainly bound to intrigue the urge of scientists to further open

up the possibilities in nanoscale research.

Speaking of which, gallium nitride (GaN) is one of the semiconductor materials that being actively investigated in electronic and optoelectronic applications, specifically. In power electronics, five key features are expected in GaN devices: (i) high breakdown strength, (ii) high current density, (iii) high operating temperature, (iv) high speed switching and (v) low-on resistance. In optoelectronics, GaN emits visible and ultraviolet light due to its wide bandgap property; it offers high electrical efficiency, high brightness and cost effectiveness for solid state lighting.

Nanostructures of GaN with those aforementioned nano- effects, nanowires in particular, are undoubtedly going to further improve the GaN devices characteristics. As a matter of fact, it resolved the long-standing flaws that have been encountered in bulk and thin film systems. For example, GaN nanowires eliminate the issue of lattice misfit which often observed in GaN thin films on Si substrate by providing the strain-relaxed growth without defect formation [9]. Further, with the possibility of defect-free fabrication (almost perfect crystal structure), GaN nanowires offer remarkable improvement in LED technology [8, 10].

To be effectually integrated into functional assemblies, the growth of nanowires should be, ideally, be controllable in terms of nanowires physical properties such as the length and diameter of nanowires, uniformity and growth orientation. Besides, it should be reproducible. In the research of Morales and Lieber [2], the synthesis of nanowires employed the vapor-liquid-solid (VLS) approach whereby a metal catalyst is essential in the growth process. This method has been widely accepted in majority of nanowires growth [11-14] for its capability of 'controllable' and 'reproducible' which also assures the quality of production.

[15]Conceptually, manipulation on VLS driven nanowires growth can be achieved provided that the growth behavior of a particular (selected) catalyst is well-understood. According to documentary evidences, scientists can have precise control on the nanowires diameter and density by modifying the catalyst thickness [16-18]. In most cases, the thicker the catalyst film, the larger the nanowires size [18-20]. Furthermore, one of the key parameters in nanowires synthesis, the growth temperature, is indirectly determined by the chosen catalyst as the nanowires growth generally occurs above the eutectic temperature of metal catalyst and semiconductor material. Considering the critical role of catalyst in VLS deposition, studies on nanowires growth by various catalysts are necessary.

In literature, the common catalysts reported in GaN nanowires growth are Ni and Au [21-24]. There are many potential catalysts remain unexplored. Indeed, it is of great interest to discover new candidates as a substitution of the regular catalysts, without depriving the characteristics achieved in previous researches. Alloying of metal catalyst is another interesting technique to developing the properties of nanowires. It has been demonstrated that bimetallic catalysts act more effectively in the catalytic reduction process compared to the monometallic catalyst. Bimetallic catalysts have also been employed in other semiconductor nanowires such as ZnO NWs (Pd and Zn as catalyst) [25], Si NWs (Au and Pd as catalyst) [26] , and indium tin oxide (ITO) nanowires (Au and Cu as catalyst) [27] .

1.3 Problem Statements

Catalyst is indispensable in VLS mechanism. Ideally, metal catalyst must be “physically active” and yet “chemically stable”. The classic catalyst used for VLS growth of GaN nanowires is Au [15, 23, 28-30]. However, Au is not “physically

active” due to the low solubility of N in Au metal [31] which hinders the catalyzing process. Besides, Au is also not “chemically stable” for GaN nanowires growth especially by CVD method which requires high growth temperature ranging from 800 °C to 1000 °C [32]. Consequently, the products become contaminated with Au as catalyst in the growth.

Another commonly used metal catalyst in VLS growth of GaN nanowires is Ni. Ni dissolves both Ga and N, which renders it as a good catalyst candidate. However, Ni has a tendency to introduce impurities and defects in the grown GaN nanowires [33]. During the growth process, Ni would have been oxidized to NiO. Therefore, additional deposition of Au thin layer is necessary to protect Ni from oxidation [32].

In this research, two noble metals Pt and Pd were selected to catalyze the growth of GaN nanowires. Pt and Pd are known as noble metals, which are resistant to oxidation even at high temperatures. This feature has made them the suitable catalyst for GaN nanowires VLS growth via CVD approach. Few years earlier, Park et al. [34] conducted a study on the growth of GaN nanowires using Ni and Pt as catalyst. The growth was a two-step growth process. The first stage was at temperature of 700 °C while second stage at 900 °C for Ni catalyst and 950 °C for Pt catalyst. Furthermore, GaN nanowires were only successfully grown on microcrystal structures by keeping the temperature for 6 hours. Catalyst-assisted growth had always been reported to degrade the optical properties of grown nanowires by introducing stacking fault defect [35, 36] due to the unintentional impurities incorporation in GaN nanowires.

Bimetallic catalysts, which are the combination of Pt and Pd is also the subject of interest in this research. Bimetallic catalysts had shown the unusual

catalytic properties compared to their individual metal components. Not only having the combined properties of the two single-component metals, bimetallic catalysts also generated the new and distinctive properties. Besides, it has been demonstrated that the catalytic activity of bimetallic catalysts is higher than the respective individual catalyst [37]. Because of this, the solubility of N in catalyst is hypothesized to increase by introducing the bimetallic Pd/Pt catalysts in GaN nanowires growth.

1.4 Research Objectives

The objectives of this research project are:

- (i) To study the growth of GaN nanowires assisted by Pt catalyst.
- (ii) To study the growth of GaN nanowires assisted by Pd catalyst.
- (iii) To investigate the growth of GaN nanowires assisted by bimetallic Pd/Pt catalyst.

1.5 Originality of Research Work

The focus of this research work is on the type of metal catalyst which drives the growth of GaN nanowires. In literature, there are studies of GaN nanowires using Pt and Pd as catalysts [38, 39]. However, the number of the research is limited. Additionally, the attention of the published works was on reporting the successful of GaN nanowires growth employing the two above-mentioned catalysts. The knowledge of applying these catalysts in the synthesis of GaN nanowires is still inadequate. Detailed and systematic investigations are required for improvement. On top of that, Pt and Pd are recognized as the noble metals. There could be the possibility to eliminate the issue of impurities in the production of nanostructured

GaN. It is therefore worth to explore and develop the new potentials of these two rarely seen catalysts in the synthesis of GaN nanowires.

The idea of integrating two metals as catalyst is considered novel in the community of GaN nanowires. Throughout the years, publications on the growth of GaN nanowires were assisted by monometallic catalyst. It is a challenge to produce GaN nanowires based on bimetallic catalysts scheme, especially by employing Pt and Pd as catalyst in this research. The catalyst activity has been shown to be more aggressive with the combination of two or more chemical elements for alloys [40]. The dynamic behavior of catalyst, particularly during the phase of catalyst alloying is affected by the growth temperature [41]. The employment of this new kind of metal catalyst in the growth of GaN nanowires is compelling and worth exploring.

1.6 Thesis Organization

This thesis comprises of seven chapters. Chapter 1 is an overview of the research project by briefly reviewing the research background which gives the inspiration to the presented research. It also identifies the objectives as well as the novelties of the research.

Chapter 2 provides an in-depth analysis of the relevant published research works in all the years, covering the topics of basic properties of GaN, introduction to GaN nanostructures, the deposition methods of GaN nanowires, the growth mechanisms, the growth parameters as well as the requirements of being the catalyst candidate in GaN nanowires growth.

Chapter 3 details the complete process of GaN nanowires synthesis, from substrate preparation, catalyst deposition to CVD reactions. The experimental setup is presented and the growth parameters for each experiment are elaborated in detail.

Before ending the chapter, it is included as well the explanation on all the characterization instruments involved in the research.

Results and discussions are divided into three chapters, chapter 4 to 6. The focus of chapter 4 and 5 is on catalytic growth of GaN nanowires assisted by monometallic catalyst, viz. Pt and Pd which are uncommon in the VLS growth of GaN nanostructures.

After the study of monometallic catalytic growth, chapter 6 extends the study to examine bimetallic catalytic growth by alloying the two aforementioned catalysts, Pt and Pd. Comparisons are made between the monometallic and bimetallic catalytic growth. Based on the bimetallic catalytic growth, GaN-nanowires based UV photodetector was fabricated. The results for current-voltage (IV) and current-time (IT) characteristics of the device are discussed in this chapter as well.

The last chapter, chapter 7, is an executive summary of the entire project which contains a few paragraphs summarizing and finalizing all the research findings. Throughout the study, it somehow remains some unanswered questions arisen from the research limitations. Based on the obtained results, future recommendations are hence proposed, for the need of further investigation.

CHAPTER 2

LITERATURE REVIEW AND THEORETICAL BACKGROUND

2.1 Introduction

GaN is generally introduced at the beginning of this chapter. This chapter also introduces the classifications of nanostructures based on their dimensionality. Subsequent sections review the synthetic approach of growing GaN nanowires, the common growth mechanisms involved as well as the factors affecting the growth of GaN nanowires.

2.2 Gallium Nitride

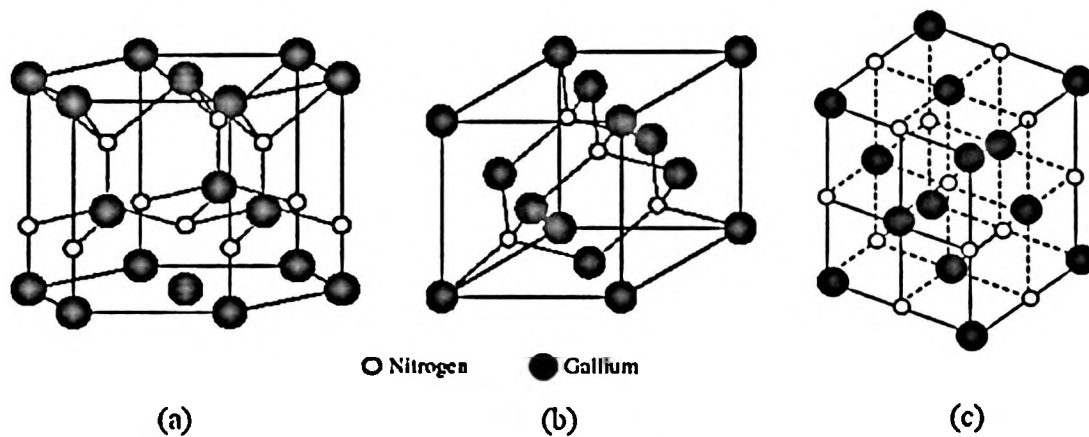


Figure 2.1 The crystal structures of GaN. (a) Wurtzite. (b) Zinc blende. (c) Rocksalt [42].

As is known, GaN crystallizes in two structural phases, either in the hexagonal equilibrium wurtzite structure or the metastable cubic zinc blende structure (Figure 2.1). It is also possible for GaN to exist in the third crystal structure named rocksalt, which may be formed at relatively high pressure [43]. Except for their stacking sequence along the (111) axis, both wurtzite and zinc blende GaN are essentially identical; one Ga atom is tetragonally coordinated with four N atoms, and vice versa. Wurtzite crystal stacks in ABABAB...configuration while the zinc blende

has the stacking sequence of ABCABC...[44]. Mainly, GaN is of the thermodynamically stable hexagonal wurtzite structure with lattice parameters $a = 3.189 \text{ \AA}$ and $c = 5.185 \text{ \AA}$ [45, 46].

Hexagonal wurtzite GaN crystal contains different surface planes such as polar, semi-polar and non-polar surfaces. Some of the possible growth planes of hexagonal wurtzite GaN are shown in Figure 2.2. In GaN crystal growth, the polar (0001) plane (c -axis) which features the piezoelectric polarization effect is the most commonly observed growth orientation. Owing to the absence of polarization field, growth on other planes is interesting; in the meantime, it is also challenging.

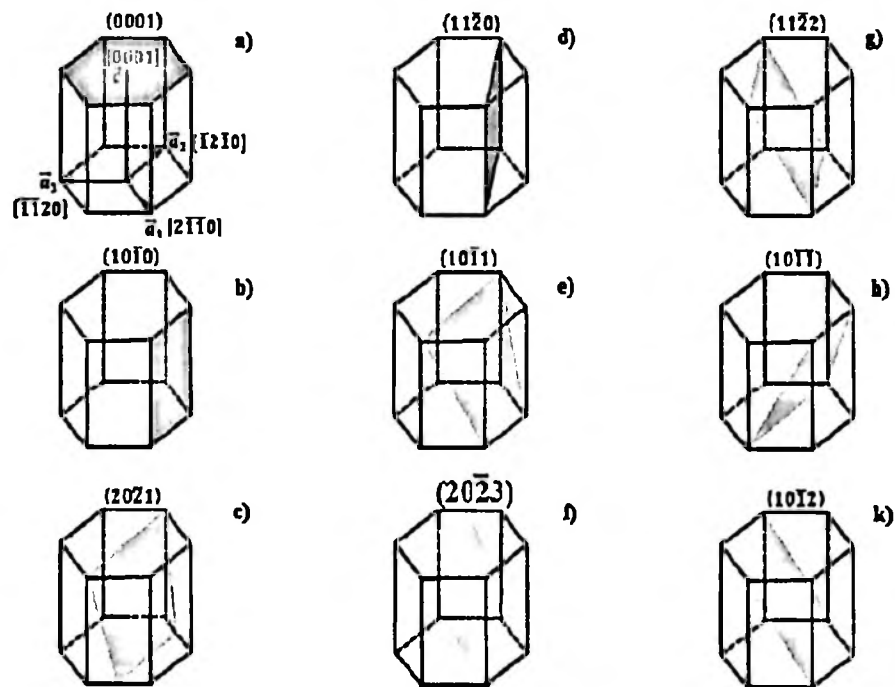


Figure 2.2 Schematic representations of (a) polar, (b) non-polar and (c) to (k) semi-polar growth planes of hexagonal wurtzite GaN [47].

GaN is considered as the next important semiconductor after Si. It features the attractive characteristics such as wide direct bandgap (3.4 eV), high chemical stability at elevated temperatures and high electron mobility, which render it the suitable candidate for high-power applications and utilization in caustic environments [44, 48]. Over the decades, GaN material has been extensively

investigated and the information on its properties can be easily found in many review papers [44, 48, 49]. Listed in Table 2.1 below are the typical properties of hexagonal wurtzite GaN.

Table 2.1 Basic properties of hexagonal wurtzite GaN [44].

Properties	Hexagonal wurtzite GaN
Lattice parameters ($T = 300$ K)	$a = 3.189 \text{ \AA}$ $c = 5.185 \text{ \AA}$
Density	6.15 g/cm^3
Melting point	$> 2573 \text{ K}$
Thermal expansion coefficient, α ($T = 300$ K)	$\alpha_a = 5.59 \times 10^{-6} / \text{K}$ $\alpha_b = 3.17 \times 10^{-6} / \text{K}$
Bandgap energy, E_g	$E_g(300 \text{ K}) = 3.39 \text{ eV}$ $E_g(1.6 \text{ K}) = 3.50 \text{ eV}$
Refractive index, n	$n(1 \text{ eV}) = 2.33$ $n(3.38 \text{ eV}) = 2.67$
Thermal conductivity, k	$k = 1.3 \text{ W/cm K}$
Dielectric constants, ϵ	$\epsilon_0 \approx 8.9$ $\epsilon_\infty \approx 5.35$
Electron effective mass, m_e	$m_e = 0.20 \pm 0.02 m_0$

2.3 Gallium Nitride Nanostructures

In comparison, GaN nanostructures offer a wide range of potential advantages over the conventional GaN thin film technology. Before going further, let's have a brief introduction regarding to nanostructures. According to Pokropivny and Skorokhod [50], nanostructures can be classified into four categories: (i) zero-dimensional, (ii) one-dimensional, (iii) two-dimensional and (iv) three-dimensional nanostructures. Table 2.2 clarifies the dimensionality classification of nanostructures with some examples. Nanowires, which are frequently referred to as one-dimensional material, behave differently from other low dimensional material systems—

quantization of particle occurs in two directions, leaving one unconfined direction available for electrical conduction [51, 52] . In addition, they are unique in overall geometry; they have great length-to-width ratio. They also exhibit quantum confinement property. All these special characteristics have rendered the one-dimensional nanowires becoming the subject of interest for current research activities.

Table 2.2 Classification of nanostructures by dimensionality

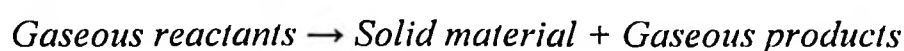
Dimensional classification	Examples
Zero-dimensional	Nanoparticles, nanodots
One-dimensional	Nanowires, nanorods, nanoribbons, nanobelts
Two-dimensional	Nanosheets, nanoplates, nanodisks
Three-dimensional	Nanoflowers, nanocoils, dendritic structures

2.4 Synthetic Approaches to One-dimensional Gallium Nitride Nanowires

The synthesis of one-dimensional GaN nanowires has been demonstrated successfully by variety of growth methods such as CVD, metal-organic chemical vapor deposition (MOCVD), hydride vapor phase epitaxy (HVPE), laser ablation and molecular beam epitaxy (MBE). Through years, these growth techniques have undergone advanced developments to yield high quality nanowires for electronic applications.

2.4.1 Chemical Vapor Deposition

CVD, by definition, is a synthesis process of depositing a solid material from the vaporized reactants by a chemical reaction taking place near to or on a surface of heated substrate [53] :



It is the preferred growth method for nanowires deposition owing to the advantages that it offers: (i) high deposition rate is possible, (ii) good reproducibility, (iii) facile and simple, and (iv) cheap; requires no ultra-high vacuum condition.

The very first synthesis of GaN nanowires employing CVD method was demonstrated by Han and his colleagues [54] in 1997. They prepared GaN nanowires through carbon nanotube-confined reaction by reacting Ga₂O vapor with flowing ammonia (NH₃) gas and obtained nanowires with diameter in the range of 4 to 50 nm, and length up to 25 micrometer (μm). Later, another experimental group [55] synthesized straight and smooth GaN nanowires directly onto lanthanum aluminate substrate, without templates, but used NiO particles as catalyst from reaction of Ga metal and NH₃. The resultant GaN nanowires exhibited a range of 10 to 40nm in diameter and maximum length of 500 μm.

For many years, growth of GaN nanowires via CVD route is highly popular among researchers. The disadvantage of CVD is that majority of the cases were reported at very high growth temperatures which are normally at or above 900 °C [38, 39, 46, 55, 56]. A breakthrough came in 2008 when Yu et al. [57] successfully presented a low-temperature CVD synthesis route at 650 °C to grow GaN nanowires with an introduction of inert salt, Calcium Fluoride as dispersant which is much safer than the Ga acetylacetonate used by Chang et al. [58] in their work proposing low-temperature catalytic CVD in the year of 2002.

2.4.2 Metal-organic Chemical Vapor Deposition

MOCVD is actually one of the derivatives of CVD terminology. It is a process of producing epitaxial films on substrate from metal-organic precursors by involving gas phase reactions. Quite often, MOCVD is also recognized by different

names like organo-metallic chemical vapor deposition (OMCVD), organo-metallic vapor phase epitaxy (OMVPE) and metal organic vapor phase epitaxy (MOVPE).

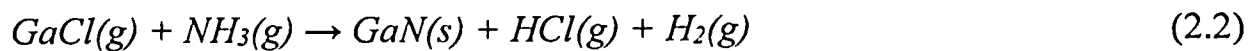
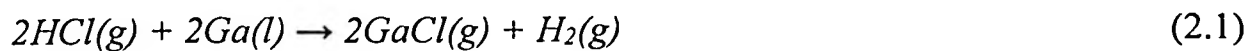
In 2003, a research group from University of California Berkeley [59] took the lead in synthesizing GaN nanowires using MOCVD technique. Governed by VLS mechanism, they successfully synthesized high quality GaN nanowires with triangular cross-section. Since then, synthesis of GaN nanowires by MOCVD had also been reported by a number of research groups such as Su et al. [60], Hersee et al. [61], Navamathavan et al. [62], Ra et al. [63] and many more. Of these reports, Hersee et al. [61] fabricated highly uniform of GaN nanowires array by pulsed MOCVD without the assistance of metal catalyst in the growth process.

Compared to MBE growth technique (will be discussed in section 2.4.4), MOCVD is claimed to have the advantages of faster growth rate, larger scale production, higher flexibility and shorter maintenance periods. It is, however, a deposition process with higher safety risk as it requires highly harmful and toxic gaseous materials, for example, metal-organic compounds or hydrides as precursors. Because of this, expensive precaution tools are necessary to be in place while handling MOCVD process. Additionally, the use of carrier gas is also required to transport the reactants towards substrates.

2.4.3 Hydride Vapor Phase Epitaxy

Similar to the other growth modes, HVPE uses a furnace system for material deposition. One of the differences between them is the chemical sources that applied to the growth. In HVPE process, one gas stream supplies hydrogen chloride gas which is transported by carrier gas, H₂ or N₂ to a metal reservoir to produce a volatile metal chloride. The resultant product is then reacted with Group V element,

depositing the desired material on the substrate surface. Taking GaN as an example, the chemical reaction can be described as:



The publications on HVPE-based GaN nanowires growth are limited, not many can be found in the literature. The growth of GaN nanowires happens to be well-controlled via this approach, as demonstrated in the study of Kim and co-workers [64] and Lekhal et al. [65]. Published in 2015, a group from Korea has even produced the extremely well-aligned GaN nanowires without the assistance of a catalyst or any intentional pretreatment, but just by means of HVPE [66]. Catalytic HVPE growth has also been reported [67] in which the GaN nanowires were shown to have synthesized in a controllable manner, as well.

HVPE has a low equipment cost and its deposition rate is the highest among all the epitaxy processes developed. Technically, HVPE provides the better control process than the often-used CVD technique. The disadvantage of HVPE is the need of hydrides, which are extremely hazardous. As described in equation (2.2), gaseous HCl is the sub-product of the chemical reaction in HVPE. The release of HCl is believed to result in the damage of metal catalyst which is required for VLS nanowires growth [67]. Due to these reasons, HVPE is not popular, especially in VLS GaN nanowires growth.

2.4.4 Molecular Beam Epitaxy

If sample uniformity is a major issue, perhaps MBE would be the good option for growth. MBE is a precise growth system to deposit a crystal in which the

deposition happens under ultra-high vacuum environment on a heated substrate utilizing elemental sources, typically [68]. It was an invention in the late 1960s by Arthur and Cho [69] and has been exploited for growing excellent crystal quality of GaN nanowires on varieties of substrate.

The earliest research work on GaN nanowires growth by means of MBE was published in the year of 1997 [70]. The morphological, structural and optical properties of MBE-grown GaN nanowires were then studied by numerous researchers [71-73]. As is known, material properties do rely on the growth methods. Using MBE, the growth of GaN nanowires is manipulated by factors of surface energies, diffusion coefficients and sticking coefficients on the various crystal planes [73]. Besides, MBE growth works at high temperatures with a slow growth rate, enabling the formation of defect-free material through a complete relaxation of the crystal structure [73].

Reviewed by Bertness et al. [73], characteristics of GaN nanowires grown by MBE are distinctively unique. These properties include the absence of residual strain, long photoluminescence lifetime, low surface recombination velocity, high mechanical quality factor and high purity [73]. In spite of the high quality, the equipment of MBE is incredibly complex and high cost. Besides, the growth process of MBE is known to be slow. Approximately 0.25 $\mu\text{m}/\text{hour}$ of growth rate was reported by Goodman et al. [74]. The growth rate is relatively slow compared to 2 $\mu\text{m}/\text{hour}$ by using MOCVD process [61]. With its low throughput, it is difficult to scale up for production.

2.5 Growth Mechanism of Gallium Nitride Nanowires

Through literature study, it is realized that the growth of GaN nanowires can

be governed by various growth models. Basically, nanowires growth can be categorized into two groups, i.e., catalytic and non-catalytic growth. Catalytic growth is further divided into VLS, vapor-solid-solid (VSS), solution-liquid-solid and solid-liquid-solid while non-catalytic growth is normally based on vapor-solid (VS) growth process. Here, attention is solely paid to the growth mechanisms that are commonly seen in producing GaN nanowires.

2.5.1 Classical Growth Theory

Growth in general is considered as the ideal case of epitaxial process, whereby nucleation happens when new species are satisfactorily registered to the existing atoms on a surface. Traditionally, growth is often assumed to occur under supersaturated condition, in which the system is not close to equilibrium. In literature, three growth models have been identified for nucleation in 1958. They are Frank-van der Merwe, Stranski-Krastanov and Volmer-Weber as shown in Figure 2.3.

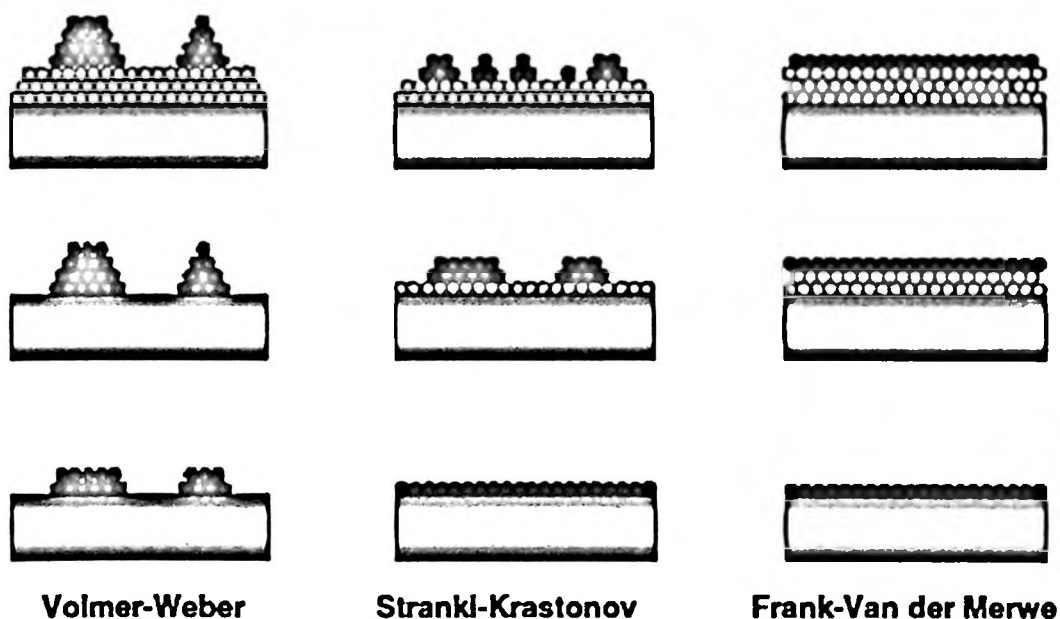


Figure 2.3 Schematic illustration of Volmer-Weber, Stranski-Krastanov and Frank-van der Merwe growth models [75].

In Frank-van der Merwe growth model, adatoms are preferentially attached to

the substrate surface than to each other, leading to the formation of complete monolayer on the surface prior to the growth of subsequent layer. This growth model is also described as “layer-by-layer” growth. Volmer-Weber growth, or island growth mode shows the opposite characteristics. Because of the stronger interaction between adatoms and adatoms compared to the surface, adatom clusters are nucleated directly on substrate surface and form islands of the condensed phase. This growth of clusters will cause the rough feature to the substrate surface. Stranski-Krastanov model is a mixed alternative with both layer and island growth. The growth is initiated layer-by-layer and shifts to island growth mode after a critical layer thickness [75, 76].

2.5.2 Vapor-liquid-solid

Originally, VLS growth was founded in 1964 by Wagner and Ellis to explain their work on Si whisker growth catalyzed by Au catalyst [77]. The utilization of a metal catalyst in VLS is to form liquid alloy droplets as preferred sinking sites for nanowires nucleation. Nanowires growth happens by precipitation through absorption of reactants from vapor phase by these droplets until supersaturated.

According to Barth et al [78], a catalyst performs not only the regular catalytic activity but also assists in lowering the activation energy of the sources as well as precipitation of the growth materials at the particle-substrate interface. There are several groups reported different activation energies for metal-catalyzed nanowires growth [79, 80]. The catalyst for most VLS growths, however, does not lower the chemical potential at all times.

Current opinion to VLS mechanism is said to be different from the past and has been re-examined. Modern researchers tailor VLS growth by relating it to the

corresponding alloy phase diagram [67, 81]. Phase diagram carries important aspects for VLS nanowires growth, the equilibrium composition of the alloy, for instance, and can be used as a prediction on the growth behavior of a specific catalyst.

Because of the feasibility to manipulate the nanowires growth, VLS appears to be remained interested in today's investigations. To ensure the success of this vapor-based synthesis method, the key component lies in the degree of vapor supersaturation. The control of vapor supersaturation can be adjusted by temperature, pressure, precursors used and the catalyst type [82] which in general is selected based on the study of the specific alloy phase diagram.

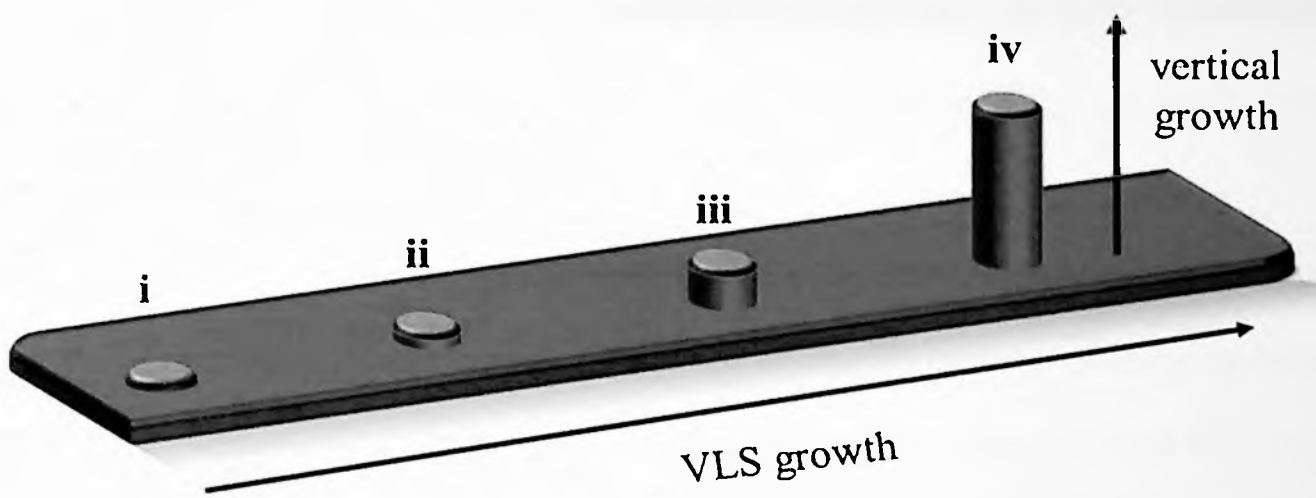


Figure 2.4 VLS growth model. (i) A distribution of island sizes (catalyst particles) are formed on the substrate. (ii) Metal catalyst forms liquid alloy droplets by adsorbing vapor components. (iii) The alloy is further supersaturated. It then drives the precipitation of the components at the liquid-solid interface. (iv) The one-dimensional crystal growth begins.

There are three major growth stages involved in the VLS mechanism: (i) metal alloying, (ii) nucleation, and (iii) axial growth [83]. Below description is based on the VLS growth of GaN nanowires. At appropriate temperature, mostly high temperature depending on the eutectic alloy temperature, liquefied catalyst droplets are formed on the substrate. These droplets serve as the energetic nucleation sites

which continuously adsorb the Ga and N reactants from vapor phase, promoting the catalyst-Ga-N alloying process. The initiation of nucleation process occurs as the concentration of Ga-N in liquid alloy droplets increases. Further adsorption of vapor reactants generates the precipitation upon the supersaturation of Ga-N, eventually results in the GaN nanowires growth at the solid/liquid interface, leaving the catalyst droplets at the tip of nanowires as demonstrated in Figure 2.4.

2.5.3 Vapor-solid-solid

When the catalyst is in solid phase during the growth, VSS growth mode is applied. In this mechanism, the solid alloy catalyst behaves distinctly from that of VLS mechanism in terms of sticking probability of precursor, adatoms' diffusivity and the behavior of phase transformation [84], resulting in the different precipitation rate of nanowires.

Synthesis of nanowires by this means is carried out at comparatively low temperature, normally lower than the eutectic temperature (based on phase diagram), which is advantageous to the fabrication of low-temperature devices. Apart from that, low-temperature fabrication also reduces or minimizes the likeliness of unwanted impurities from being incorporated into the synthesized nanowires.

In fact, VSS mechanism has also been suggested for other nanostructured materials system like Si, Ge and metal-oxide nanowires [85-87]. For GaN, research on VSS growth is poorly studied in the research community. To date, there are just two groups, Weng et al. [24] and Ho et al. [88], reported about the VSS growths of GaN nanowires which are assisted by Au and Ni catalyst, respectively. With the limited publications, deep understanding in connection with the VSS mechanism is not possible at the moment and further investigation is necessary for better

comprehension.

2.5.4 Vapor-solid

VS growth is the mechanism deployed by researchers to describe nanowires growth in the absence of a foreign catalyst. The growth takes place when nanowires are formed from the direct condensation of vapor phase and it occurs in many of the self-catalytic growth processes.

Only three interfaces to be considered, VS growth is thus not as complicated as the catalytic growth. Vapor-substrate interface should be first valued owing to the fact that it is where the nanowires nucleation happens. Essentially, the nucleation relies on a few experiment parameters such as pressure, synthesis temperature and surface treatment of substrate [82]. Another two interfaces are vapor-solid interface and solid-substrate interface. The former is possibly established only if the vapor-substrate interface is effectively accomplished; the latter is the situation of crystal nucleus formation of which the lattice match or mismatch should be aware [82].

Without the application of a metal catalyst, VS growth eliminates the presence of impurities by unintentional doping and avoids the synthesized nanowires from contamination. For the same reason, VS growth lacks of the energetically preferred nucleation sites provided by the catalysts; as a consequence, it requires a relatively higher deposition temperature than the VLS and VSS processes in order to promote the growth of nanowires [82].

2.6 Factors Affecting the Growth of Gallium Nitride Nanowires

Growth of GaN nanowires is largely influenced by the growth environment. It is always desirable and favorable to control the nanowires growth. This is because

when nanowires growth is controllable, there is possibility for new application.

2.6.1 Growth Temperature

Growth temperature is critical in VLS growth of GaN nanowires. It varies in different growth systems, depending on the precursor used, the catalyst chosen as well as the growth method applied. For a VLS nanowires growth to occur, it is necessary to reach above the minimum growth temperature, which is known as the eutectic temperature, of the catalyst-nanowires system. In particular for GaN nanowires using Au as catalyst, the eutectic temperature would be based on the Au-Ga system. For most CVD cases, GaN nanowires are reported to be grown at high temperatures ranging from 900 °C to 1200 °C, which is due to the low vapor pressure of Ga at temperature below 900 °C [89].

Growth temperature is responsible for controlling many properties in nanowires growth, e.g. the nanowires diffusion length which has affection on nanowires length [90, 91]. Studies have shown that the diffusion length of nanowires is longer at higher temperatures [90]. In addition, contamination can be also eliminated by manipulating growth temperature. In the report of Low et al. [92], the undesired oxygen content in GaN nanowires reduces as the growth temperature increases. A sharp increase of conductivity has also been observed for GaN nanowires by temperature increment of 100°C [93].

In crystal growth, crystallographic defect level is known to be temperature-dependent. In the report of Zettler et al. [94], they commented that point defect concentration is high at both low and high growth temperatures while minimum defect concentration was found at intermediate temperatures. Another research on MOCVD-grown GaN nanowires by Wang et al. [93] also found the relation of

growth temperature and defect states of nanowires and concluded that optimal optical and electrical properties can be obtained at higher growth temperatures.

Nanowires morphologies are also affected by growth temperature. As will be discussed in Chapter 4, the partially aligned of GaN nanowires were obtained at high growth temperature. Since the electrical, morphological, optical and structural are strongly connected to the growth temperature, investigation on growth temperature is therefore absolutely necessary.

2.6.2 Ammonia Flow Rate

NH₃ flow rate is reckoned as the next important process parameter for GaN nanowires after growth temperature. It is the source of N-radicals to GaN nanowires growth. By adjusting the NH₃ flow rate, it is actually modulating the III/V ratio. Regarding to this, morphology development is often observed under the influence of various NH₃ flow rates. Evolution to large-diameter of GaN nanostructures, e.g. nanocrystals, nanorods and nanosheets is the result of increasing NH₃ flow rate. From low NH₃ flow rate to high NH₃ flow rate, Nam et al. [95] observed the morphological change from nanowires to polyhedral crystals to nanobelts. In addition, phenomenon of nanowires tapering was also found at high NH₃ flow rate of 250 standard cubic centimeters per minute (sccm).

In comparison of NH₃ and N₂, NH₃ is preferred to be used as the source of nitrogen in the CVD synthesis of GaN nanowires due to its lower dissociation temperature at approximately 500 °C [96]. In their report, Rizal et al. [97] summarizes the role of NH₃ in nanowires fabrication as follows: (1) as a reducing agent which causes nanowires deposition rate to decrease, (2) as a ligand at metal-cap nanowires and (3) as surface passivation to alter the ad-atoms absorption. With

different III/V ratio, different characteristics of morphological, optical and electronics have been observed in semiconductor nanowires [98-100]. Therefore, it is worth investigating the influence of NH_3 flow rates on the characteristics of GaN nanowires in this research.

2.6.3 Catalyst

2.6.3(a) Requirements for Catalyst Candidate

As mentioned, catalyst is indispensable in VLS mechanism. However, not all the metals work well. Preliminary studies have demonstrated the unsuccessful VLS growth of GaN nanowires with the assistance of metals silver, indium, tantalum and titanium. Normally, catalyst is chosen from the transition metals in periodic table. To be selected, the catalyst should meet some of the requirements as follows [11]: (i) it has to form a liquid solution with the crystalline growth material at growth temperature, (ii) its solubility limit in liquid phase is much higher than that in the solid phase, (iii) low vapor pressure, otherwise catalyst particles will vaporize easily during the growth and (iv) it must be inert to the growth reactions. These criteria are the prerequisites to be considered for the catalyst candidate in a VLS nanowires growth. To ensure the effectiveness of the chosen catalyst, growth factor like growth temperature, which will be discussed in results and discussions, is also significant.

Since VLS growth mechanism involves thermodynamic processes such as adsorption, dissolving, mixing, diffusion and precipitation in liquid phase, a phase diagram is useful to anticipate the catalyst behavior in a growth system. Figure 2.5 depicts the typical phase diagram of Au-Si system. To grow Si nanostructures, the minimum growth temperature is indicated to be higher than the eutetic point of the system, 363 °C. At this temperature or above, Au is in liquid phase.

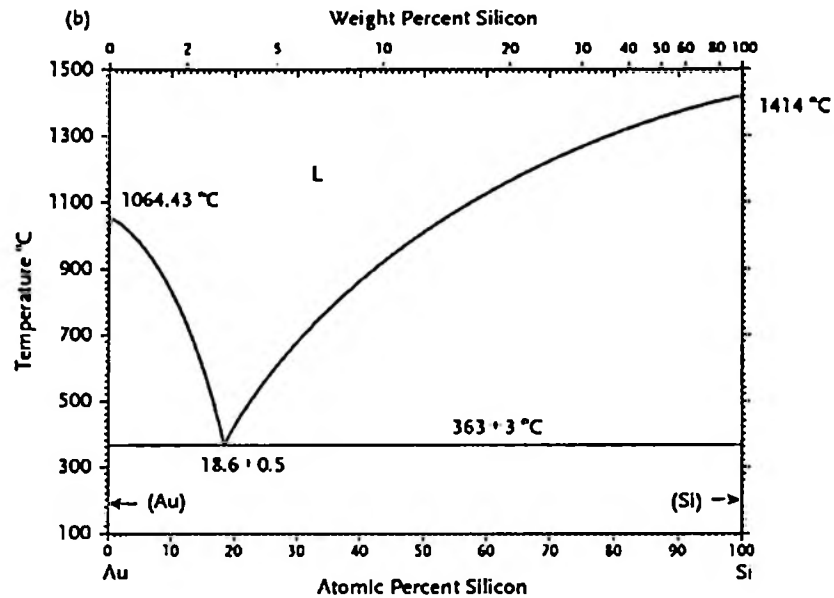


Figure 2.5 Phase diagram of Au-Si system [101].

The reaction starts with the pure, solid Au particle on the left side of phase diagram. When growth material Si from vapor phase begins to dissolve in Au catalyst, a mixture of liquid Au-Si and solid Au is formed. Once the concentration of Si is sufficiently high, the mixture crosses the liquidus line and Au-Si particles liquefy until its concentration is high enough to cross the second liquidus line. At this point, Si nanowires start nucleating and the growth continues with the replenishment of the liquid Au-Si particles from vapor phase [101].

Statistically, Ni and Au catalysts are vastly popular in VLS growth of GaN nanowires. Figure 2.6 is a pie chart analyzing the usage of different catalyst types in growing GaN nanowires. As shown in the pie chart, Ni and Au accounts for 40 and 38 percent, respectively in a total of 50 studies [15, 22-24, 28-30, 58, 67, 92, 102-141]. In comparison, Au which has the higher defect formation energy (~ 4 eV) was claimed to be the better choice than Ni (~ 1.2 eV) for metal-catalyzed growth of GaN nanowires [109]. Nevertheless, the statement was argued due to the very low solubility of N in Au [31].