GROWTH AND CHARACTERIZATIONS OF SPIN COATED GALLIUM NITRIDE THIN FILMS ON SILICON SUBSTRATES

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GROWTH AND CHARACTERIZATIONS OF SPIN COATED GALLIUM NITRIDE THIN FILMS ON SILICON SUBSTRATES

by

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LIST OF SYMBOLS

A^*	Effective Richardson coefficient
a	Lattice constant a
θ_B	Bragg angle
c	Lattice constant c
D	Crystallite size
E	Electric field vector
h	Planck’s constant
h, k, i, and l	Miller indices
I	Current
I_o	Saturation current
I_p	Photocurrent
k	Boltzmann’s constant
K	Shape factor
m^*	Effective hole mass
m_0	Electron mass
n	Ideality factor
$\boldsymbol{n}$	Refractive index
P	Incident light power
q	Electron charge
R_λ	Responsivity
T	Temperature
v	Frequency
α	Thermal expansion coefficient
ε_{zz}	Average uniform strain
ϕ_B	Barrier height
ω-2θ	Omega-2theta

LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
AMP	Amplifier
BE	Binding energy
CCD	Charge-coupled device
C_N	Carbon substituting for nitrogen
CRT	Cathode ray tube
DC	Direct current
DEA	Diethanolamine
EDX	Energy dispersive X-ray
FESEM	Field-emission scanning electron microscopy
FETs	Filed-effect transistors
FTIR	Fourier transform infrared
FWHM	Full width at half maximum
HVPE	Hydride vapor phase epitaxy
IMFP	Inelastic mean-free path
IR	Infrared
I-V	Current-voltage
KE	Kinetic energy
LO	Longitudinal optic
MBE	Molecular beam epitaxy
MOCVD	Metal-organic chemical vapor deposition
MSM	Metal-semiconductor-metal
NBE	Near band edge
PA-MOCVD	Plasma assisted metal organic chemical vapor deposition
PL	Photoluminescence
PMT	Photomultiplier tube
PVDNC	Plasma vapor deposition of nano-columns
RF	Radio frequency
SBH	Schottky-barrier height
SMU	Source measure unit
TEM	Transmission electron microscopy

TO	Transverse optic
UV-A	Ultraviolet A
UV-B	Ultraviolet B
UV-C	Ultraviolet C
UHV	Ultra-high vacuum
UV	Ultraviolet
V_{Ga}	Gallium vacancies
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRD-PA	X-ray diffraction phase analysis
XRD-RC	X-ray diffraction rocking curve
YL	Yellow luminescence

PERTUMBUHAN DAN PENCIRIAN FILEM NIPIS GALIUM NITRIDA TERSALUT PUTARAN DI ATAS SUBSTRAT SILIKON

ABSTRAK

Galium nitrida (GaN) dengan jurang jalur langsung 3.4 eV telah menjadi tumpuan penyelidikan bahan. Ini adalah disebabkan oleh ciri-ciri dan kepentingan teknologinya untuk digunakan dalam pelbagai aplikasi seperti peranti optoelektronik dan peranti elektronik berkuasa tinggi. Pelbagai kaedah tradisional telah dibangunkan untuk mensintesis filem nipis GaN pada masa dahulu. Walau bagaimanapun, hanya terdapat beberapa kajian yang dilaporkan berkaitan dengan pertumbuhan filem nipis GaN dengan menggunakan kaedah salutan putaran sol-gel yang agak mudah dan lebih murah berbanding dengan kaedah yang dinyatakan sebelum ini. Oleh itu, objektif utama kajian ini adalah untuk menumbuhkan filem nipis GaN dengan kaedah salutan putaran sol-gel. Fasa awal projek ini melibatkan sintesis dan pencirian filem nipis GaN ditumbuh dengan menggunakan kaedah salutan putaran sol-gel tanpa diethanolamina (DEA). Keputusan menunjukkan bahawa pertumbuhan filem nipis GaN adalah tidak berjaya dengan menggunakan kaedah ini. Dengan bantuan DEA, keputusan mendedahkan bahawa filem nipis wurtzit GaN berorientasi-*c* telah berjaya ditumbuhkan. Hal ini disebabkan DEA dengan kelikatan yang lebih tinggi dapat meningkat kelikatan pelopor. Melalui kajian ini, didapati bahawa suhu dan tempoh penitridaan optimum adalah 950 ℃ dan 75 min, masing-masing. Manakala kejayaan pertumbuhan filem nipis GaN berorientasi-*c* memerlukan suatu pembentukan metastabil galium (I) oxida (Ga_2O) amorfus. Disebabkan pelbagai isu tentang sistem pemercikan RF, kualiti lapisan penampan aluminium nitrida (AlN) yang ditumbuhkan sendiri adalah tidak konsisten. Lantaran itu, ini telah menghalang pertumbuhan filem nipis GaN. Untuk mengatasi masalah ini, komersial templat AlN digunakan. Kesan ketebalan lapisan penampan AlN terhadap pertumbuhan filem nipis GaN telah disiasat. Semua keputusan mendedahkan bahawa lapisan penampan AlN dengan ketebalan 25 nm adalah ketebalan yang sesuai digunakan untuk pertumbuhan filem nipis GaN yang berkualiti. Kesan bilangan kitaran proses salutan terhadap kualiti kristal filem nipis GaN yang ditumbuh juga telah disiasat. Akhirnya, pengesan foto ultraungu (UV) berasaskan GaN telah difabrikasi. Sentuhan Schottky platinum dimendapkan dengan menggunakan suatu corak topeng logam-semikonduktor-logam. Pengukuran arus-voltan telah dijalankan dalam keadaan gelap dan pencahayaan cahaya UV. Arus foto didapati meningkat dengan pencahayaan UV. Ketinggian halangan Schottky (SBH) yang ditentukan pada suhu bilik (298 K) didapati bernilai 0.35 eV dan 0.34 eV untuk arus gelap dan arus foto, masing-masing. Nilai ketinggian halangan Schottky yang diperoleh adalah agak bersetuju dengan nilai-nilai yang dilaporkan. Secara keseluruhan, keputusan menunjukkan bahawa filem nipis GaN berstruktur wurtzit dengan orientasi keutamaan GaN(002) telah berjaya ditumbuhkan di atas substrat AlN/Si(100) dengan menggunakan kaedah salutan putaran sol-gel dengan bantuan DEA dan sintesis ini adalah boleh dihasilkan semula.

GROWTH AND CHARACTERIZATIONS OF SPIN COATED GALLIUM NITRIDE THIN FILMS ON SILICON SUBSTRATES

ABSTRACT

Gallium nitride (GaN) which has a direct band gap of 3.4 eV has become the focus of materials research. This is due to its unique combination of properties and technological importance for use in various applications such as optoelectronic devices and high power electronic devices. Various conventional methods have been developed to synthesize GaN thin films in the past few decades. However, there are only a few reported studies dealing with the growth of GaN thin films by using sol-gel spin coating method which is simpler and cheaper as compared to the conventional methods. Thus, the main objective of this work is to grow GaN thin films using sol-gel spin coating method. The initial phase of this work involved the synthesis and characterization of GaN thin films grown by using sol-gel spin coating method without diethanolamine (DEA). The results show that the growth of GaN thin films was not successful by using this method. With the aid of DEA, the results reveal that highly *c*-oriented wurtzite GaN thin films were successfully grown. This is mainly due to the DEA with higher viscosity was able to increase the viscosity of the precursor. Through these studies, it was found that optimum nitridation temperatures and durations are 950 ℃ and 75 min, respectively. While the successful growth of *c*-oriented GaN thin films requires a formation of metastable amorphous gallium (I) oxide (Ga_2O). Due to various issues of the RF sputtering system, the quality of the home grown aluminium nitride (AlN) buffer layers was inconsistent. Consequently, this has hindered the growth of GaN thin films. To overcome this issue, commercial AlN templates were used. The effects of AlN buffer layer thickness on the growth of the GaN thin films were investigated. All the results revealed that AlN buffer layer with thickness of 25 nm was the suitable thickness for the growth of good quality GaN thin films. The effects of the number of coated process cycle on the crystalline quality of deposited GaN thin films were also investigated. Finally, GaN-based UV photodetector was fabricated. Platinum Schottky contacts were deposited by using a metal-semiconductor-metal pattern mask. Current-voltage measurements were performed in the dark and ultraviolet illuminated conditions. The photocurrent was found to be increased with the illumination of UV light. The Schottky barrier height (SBH) evaluated at room temperature (298 K) was found to be 0.35 eV and 0.34 eV for dark current and photocurrent, respectively. The obtained SBH values are in reasonable agreement with the reported values. Overall, the results revealed that wurtzite structure GaN thin film with GaN(002) preferential orientation was successfully deposited on AlN/Si(100) substrates by sol-gel spin coating method with the aid of DEA and the synthesis is reproducible.

CHAPTER 1

INTRODUCTION

1.1 Introduction

III-nitride semiconductors are the materials of choice for a variety of device applications. The wide tunable band gap of III-nitrides from value of 0.7～6.2 eV which make them fit to be used as versatile solid state lighting applications. Among all of the III-nitrides, gallium nitride (GaN) thin films have attracted considerable academic and commercial interest in the past few decades. GaN with band gap value of 3.4 eV is one of the III-V materials that turned into the new semiconductor research and industry buzzword. In the early 1990s, the scientific community has exerted an enormous effort to prepare a wide band gap GaN semiconductor. This is owing to its outstanding physical properties and high optical transition probability have make it the ideal building blocks for great potential applications in photo-electronic devices, laser diode and other material of choice. Apart from that, with its high electron drift saturation velocity, strong atomic bonding, and stronger thermal stability properties make it suited for high power and temperature electronic applications (Ma et al., 2010, Wood et al., 2012).

Although GaN has been explored more detailed than indium nitride (InN) and aluminium nitride (AlN), however the required details understanding about the technological developments for this material has not yet accomplished. Therefore, it should be explored and investigated more in order to produce new products and applications for future advance technologies.

The four most common epitaxial approaches used in growing the high quality GaN semiconductors are namely: molecular beam epitaxy (MBE), metal-organic chemical vapor deposition (MOCVD), radio frequency (RF) magnetron sputtering and hydride vapor phase epitaxy (HVPE). Even though all of these methods could successfully grow the GaN thin films, the production cost for these method are relatively high and the setup are complicated. Nowadays, emphasis is put in improving the world by creating products that are affordable and accessible to the poor and needy. Hence, discover a method that having the ability to produce good quality GaN thin films at a significant lower cost is necessary.

Sol-gel spin coating deposition method has the potential to grow GaN thin films (Ogi et al., 2005). This is because sol-gel spin-coating method is rather simpler, cheaper and safer as compared with the conventional methods as discussed previously. This method has been widely used to produce metal oxides. However, it must be pointed out that the studies about the growth of GaN thin films via sol-gel spin coating method are still rarely reported and many issues still remain unclear. Hence, there is an absolute need for thorough studies on this deposition method.

1.2 Problem statements

GaN-based semiconductors have been grown by various methods. Nevertheless, these techniques involve sophisticated technologies and are relatively expensive and complicated. Moreover, some growth techniques require use of metal-organic and hydride precursors which are extremely toxic. Therefore, a low-cost, simple, safe, non-toxic, and scalable method is highly desirable. The most promising candidate is sol-gel spin coating method. This method uses chemical solution (precursor) to produce thin and uniform film on substrate.

There are still a lot of significant challenges for the growth of GaN thin films via sol-gel spin coating method. Difficulty in preparation of the suitable precursor solution with good wetting properties on hydrophobic substrates (such as sapphire, Si, and glass) is the main problem for sol-gel spin coating method. To obtain the critical thickness and the crystallinity of the films, the preparation of the precursor solution with a suitable viscosity is also a challenge. In addition, coating thickness and concentration of the precursor are also major concerns for spin coating on a flat substrate. Therefore, a suitable precursor solution that can alleviate these difficulties is necessary.

1.3 Research objectives

The main objectives of this work are:

1. To grow and characterize GaN thin films via sol-gel spin coating method on Si substrates with and without the aid of diethanolamine.
2. To investigate the effects of nitridation temperature and duration on the surface morphologies, structural and optical properties of deposited GaN thin films.
3. To investigate the growth mechanism of the formation of GaN thin films using a variety of characterization tools.
4. To investigate the effects of aluminium nitride (AlN) buffer layer thickness and various number of coated process cycles on the surface morphologies, structural and optical properties of GaN thin films prepared via sol-gel spin coating method.
5. To fabricate a metal-semiconductor-metal (MSM) ultraviolet (UV) photodetector based on the GaN thin films on Si substrates and to study the photoelectrical properties of the fabricated device.

1.4 Originality of the research works

The main originality of this research work lies in the growth and characterizations of wurtzite GaN thin films via sol-gel spin coating method, which is rather simpler, cheaper and safer as compared with the other conventional methods. It is already well known that sol-gel spin coating method has successfully been applied to grow zinc oxide (ZnO) thin films and nanostructures. However, it must be pointed out that the growth of GaN thin films via sol-gel spin coating method is rarely reported. In this work, sol-gel spin coating method is efficiently applied for the growth of hexagonal wurtzite structure GaN thin film with GaN(002) preferential orientation on Si(100) substrates and the fabrication is repeatable and reproducible.

Apart from that, a new ethanol-based precursor solution with the aid of DEA, which has faster evaporation rate and better wetting property, is introduced in this study. Knowing that the solution with DEA as stabilizer is commonly being used in synthesis of ZnO thin films, however, the use of DEA solution for the synthesis of GaN thin films has not yet been further studied. The GaN thin films might successfully growth with the used of ethanol-based precursor solution and the addition of DEA.

Besides that, it must be pointed out that the fundamental understanding of the sol-gel spin coating growth mechanism of GaN thin films is still not fully explored. Therefore, the growth mechanism of GaN thin films prepared via sol-gel spin coating method was studied for the first time. In-depth investigation on the whole growth processes is conducted and the growth mechanism is obtained. In addition, fabrication of MSM UV photodetector based on GaN thin film using simple, facile, and low cost sol-gel spin coating method was reported for the first time.

1.5 Organization of dissertation

The content of this dissertation is divided into 9 chapters.

Chapter 2 includes a detailed literature review on the deposition of GaN thin films by sol-gel method. In addition, factors that influence the deposition of GaN thin films are explained. The discussions also cover the overview of GaN-based MSM photodetectors.

Chapter 3 describes the fundamental properties of GaN material and the basic principle of sol-gel method. In addition, a brief introduction to the working principle of the characterization tools will be discussed. Furthermore, the principle of GaN-based photodetector is also presented.

Chapter 4 describes the methodology and the parameters used for characterizations of the GaN thin films. In chapter 5, preliminary works on the growths and characterizations of GaN thin films on Si(100) via sol-gel spin coating method are presented. It is divided into two main sections, i.e., the characterizations of GaN thin films grown at various nitridation temperatures and various number of spin coated layers. The unsuccessful growth of GaN thin films is explained.

With the use of sol-gel spin coating method coupled with the aid of DEA, the growth and characterizations of GaN thin films is then presented in chapter 6. The effects of nitridation temperatures and durations on the synthesis of GaN thin films are investigated. Furthermore, the individual steps needed for the growth of GaN thin films starting from the spin coating process, annealing to nitridation as well as the growth mechanism for each steps are discussed in detail.

Chapter 7 presents and discusses the effects of different thickness of AlN buffer layer and various number of spin coated cycles on the growth of GaN thin films. Formation of GaN-based MSM UV photodetector with platinum as schottky metal contacts is discussed in chapter 8.

Finally, chapter 9 concludes the results obtained of the research work. In addition, recommendations for possible future research will be proposed.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter provides a literature review in preparing the GaN thin films via sol-gel spin coating method. The review is mainly focusing on factors influencing the growth of GaN thin films. These factors include the choice of substrate, buffer layer, precursors and nitridation conditions. Furthermore, GaN-based photodetectors such as MSM will be reviewed.

2.2 An overview of sol-gel spin coating growth of GaN thin films

In general, the three most common epitaxial approaches used to grow the high quality GaN semiconductors are namely: HVPE, MOCVD, and MBE. When III-nitrides was first investigated at the early stage, the most successful epitaxial approach of growing GaN thin films was HVPE, which was developed by Maruska and Tietjen in year 1969. This epitaxial method was the very first approach being developed to deposit GaN and AlN more than 40 years ago. By applying this high growth rates method, several microns thick layers is possible to be achieved (Wang and Yoshikawa, 2004). High deposition rate method that able to form thick single crystal GaN thin films on non-native substrates have paved the way to the demonstration of free-standing GaN substrates. Thus, there are many studies reported the growth of GaN prepared by HVPE method. However, HVPE has several disadvantages. The nature of chemistry is an important concern when GaN is grown. For instance, nitrogen trichloride, which has high toxicity and explosiveness, can be formed. This could happen when ammonia (NH_3), a source of nitrogen, dissociates and start reacting with hydrochloric acid.

Over the past two decades, development on MOCVD has been expanded and it has become the leading technique for epitaxial growth of group III-nitrides. HVPE, which is a near equilibrium technique, is not a suitable method when it deals with the nucleation onto a surface that is chemically different. In fact, it has been proven by many researchers that if an alkyl organometallic for the group III element and a hydride gas for group V element were to be combined, deposition of layers of GaAs on a variety of different surfaces would be seen. This issue leads to the born of another technique, MOCVD in the late 1980. It becomes the main production technique after improving the purity of organometallic precursors and hydrides. There will be a gas phase transport of organometallic precursors, hydrides and carrier gases to a heated substrate when MOVCD is applied. This approach results in higher deposition temperature allow the volatile precursors to pyrolyse at the substrate surface. Consequently, a stable solid film can be grown. GaN source is typically trimethylgallium (TMGa) whereas high-purity anhydrous NH_3 is used as the hydride source. MOCVD has been widely applied in synthesizing semiconductor thin films as well as growing GaN thin films. Nonetheless, this method has its shortcomings. Apparently, metal-organic compounds are costly than inorganic compounds. In addition, large quantities of NH_3 gas are needed during the process, which has a high risk of explosion.

Apart from HVPE and MOCVD, MBE is another method that is used for the growth of high quality GaN layers, super-lattices, and hetero-structures with good uniformity, excellent thickness control, and sharp dopant profiles. Constituent elements of a semiconductor in the form of “molecular beams” are supplied as a beam of gas onto the heated substrate surface under the ultra-high vacuum environment (Wang and Yoshikawa, 2004). Growth temperatures for MBE method is typically much more lower as compared to MOCVD method. However, ultra-high vacuum is needed for this method with very low in growth rate. Furthermore, this method is relatively high in production cost and the operation conditions must accurately be monitored and controlled.

Besides of the methods mentioned above, RF sputtering method is another way in which the GaN thin films can be grown. In the RF sputtering process the target material is bombarded by ions having high kinetic energy and as a result of this bombardment atoms are ejected from the target material. These ejected atoms are then transported in a gas phase to the substrate and where they condense on the surface to form a film. GaN thin films were grown through the use of middle-frequency magnetron sputtering method. The substrate temperature, total pressure, and target-substrate distance were found to be the key parameters that influenced the crystal quality of the deposited GaN thin films (Zou et al., 2007). The growth of GaN thin films using sputtering method also been reported; however direct current (DC) magnetron sputtering under different substrates temperature was used. For this study, best quality GaN film was achieved under the substrate temperature of 615 K (Xie et al., 2007). Even though the sputtering method could successfully grow the GaN thin films, the setup and the materials (GaN target) used for this process were relatively expensive.

Nowadays, creating products that are affordable and accessible to the poor and needy is one of the primary goals. Hence, an alternative method which capable to produce good quality GaN thin films at a significantly lower cost is highly desirable. For instance, a bottom up deposition method, namely the electrochemical deposition is usually opted to deposit both GaN thin films as well as GaN nanostructure. Electrochemistry is the principle applied behind this method and this allows the targeted ions to be attracted towards the substrates. This method was then successfully demonstrated by Hashim and Al-Heuseen (2011) in depositing GaN thin films on Si(111) substrate. It was done below room temperature under different durations. Both the cubic and hexagonal phases of GaN could be observed from the deposited thin films (Hashim and Al-Heuseen, 2011). As compared to other techniques, electrochemical deposition from aqueous solution possesses few more advantages. These include large-area, low-cost, and generally low processing temperature (often room temperature) and soft processing of materials (Gong et al., 2010). However, possible disadvantages of this method are requirement of the substrates which have reasonable electric conductivity and contaminations might occur during the process (Gary, 2001). Furthermore, there have been many studies reported on the success in depositing GaN thin films by using electrochemical deposition method (Ghazali et al., 2014). Thus, other similar aqueous solution method has to be explored to grow GaN thin films and it seems that sol-gel spin coating deposition method has a high potential to be a practical method for growing GaN thin films.

Generally speaking, it is well known that both sol and gel exist naturally and increased scientific interests for a long time. Sol-gel method can be divided into six basic groups which are spin coating, dip coating, spray coating, flow coating, capillary coating, and roll coating. Sol-gel spin coating method is well-known in depositing of oxide thin films such as zinc oxide (ZnO) (Attia et al., 2002). Nevertheless, it must be pointed out that this approach is still not fully explored in III-nitrides materials. In addition, there are a lot of challenges need to overcome to grow good quality GaN thin films through this method. This makes the researchers shift their attention to concentrate on other methods due to the difficulty in the growth of GaN thin films using this method. Table 2.1 summarizes the studies related to the growth via sol-gel method.

Table 2.1: Summary of the sol-gel growth of GaN.

Methods	**Materials**	**Substrates**	**References**
Sol-gel	GaN nanocrystal	-	(Li et al., 2009)
Sol-gel	GaN nanocrystal	-	(Cao et al., 2007)
Sol-gel	GaN nanorod	-	(Wu et al., 2006)
Sol-gel	GaN powder	-	(Liu et al., 2006)
Sol-gel	GaN nanostructure	-	(Woo, 2006)
Sol-gel	GaN nanowire	-	(Woo et al., 2005)
Sol-gel (dip coating)	GaN thin film	Quartz	(Sinha et al., 2008)
Sol-gel (dip coating)	GaN thin film	Si & Al_2O_3	(Niesen et al., 2002)
Sol-gel (Spin coating)	GaN thin film	Al_2O_3	(Andi et al., 2011)
Sol-gel (Spin coating)	GaN thin film	Si	(Heri et al., 2008)
Sol-gel (Spin coating)	GaN thin film	SiO_2	(Lee and Kim, 2007)
Sol-gel (Spin coating)	GaN thin film	Al_2O_3	(Sardar et al., 2003)

GaN nanocrystals were synthesized by using sol-gel method with gallium oxide (Ga_2O_3) as the Ga source (Li et al., 2009). In year 2007, single-phase wurtzite GaN nanocrystals were synthesized from readily available gallium nitrate [$Ga(NO_3)_3$] (Cao et al., 2007). Apart from that, some researchers reported the growth of GaN thin films by applying sol-gel dip coating method. For instance, *c*-axis oriented GaN nanocrystalline thin films were synthesized after nitriding the sol-gel dip coating thin films (Sinha et al., 2008). Besides, the sol-gel dip coating method was also used in depositing Ga- and N- containing thin films on silicon and sapphire substrates (Niesen et al., 2002). Even though the attempts to deposit GaN thin films on silicon and sapphire substrates were successful, Niesen et al. suggested further work is necessary to optimize the conditions for films formation.

There are plenty of works related to the sol-gel growth of GaN material that have been reported, however there are only a few studies related to sol-gel spin coating method (see Table 2.1). Furthermore, there are significant challenges when applying this approach to synthesize GaN thin films. Based on the literature review, the preparation of the precursor solution is very complex and difficult. In addition, the poor wetting of water-based precursor solution on hydrophobic substrates is also an issue. Due to these reasons, there are few studies regarding the sol-gel spin coating growth of GaN thin films. In the year 2011, sol-gel spin coating technique was successfully used in depositing GaN thin films on sapphire (Al_2O_3) substrates by Andi et al. using gallium-citrate-amine gel and nitrogen (N_2) gas; while the effects of the deposition temperatures (i.e., varied at 1123, 1173, and 1223 K) on the physical characteristic of deposited GaN films were investigated. In year 2008, Heri et al. reported that there was a relationship between the growth temperature and the properties of GaN thin film on Si substrates when sol-gel spin coating method was applied. From the study, 1000 ℃ was found to be the optimum temperature for the growth of GaN thin films. However, low quality GaN thin films were synthesized where only two weak diffraction peaks of GaN(100) and GaN(103) were observed in XRD pattern.

Lee and Kim (2007) fabricated polycrystalline GaN thin films with crystalline size of 10-100 nm by spin coating gallium oxide hydroxide [GaO(OH)] precursor on silicon dioxide (SiO_2) substrates. The thermal treatment of the deposited GaO(OH) precursor in NH_3 ambient under different temperatures was studied. The authors found that 900 ℃ was the optimal temperatures to obtain hexagonal plate and column type GaN thin film. In year 2003, as reported by Sardar et al., a modified citrate route was used for the growth of GaN thin films deposited on Al_2O_3(0001) substrates by the sol–gel technique. However, only polycrystalline GaN thin films were successfully grown on the substrates.

2.3 Factors influencing the sol-gel spin coating growth of GaN

There are many factors that could affect the growth of GaN thin films via sol-gel spin coating method. These include well-suited substrates, lower lattice mismatch buffer layers, precursor route used for spin coating and also the nitridation conditions. All of these factors must be taken into consideration to obtain good quality of GaN thin films.

2.3.1 Choice of substrate

Unlike other semiconductors, growth of native III-nitride substrates is extremely challenging because the quality and properties of the GaN thin films are primarily determined by the substrate on which it is deposited (Edgar and Liu, 2002). Most of the researchers have to rely on the heteroepitaxy growth, which is crystal growth on substrate of another material due to the bulk GaN crystals are very expensive. A summary of the crystal structure, thermal expansion coefficient, and lattice constants of the common substrates use for the growth of GaN thin films is given in Table 2.2.

Table 2.2: Crystal structure, thermal expansion coefficient, and lattice constants of some substrate candidates for GaN thin films (Edgar and Liu, 2002).

Material	**Structure**	**Thermal expansion coefficient ($\times 10^{-6}$ K^{-1})**		**Lattice constant (nm)**	
		a	***c***	***a***	***c***
GaN	Wurtzite	5.59	3.17	0.3189	0.5185
GaN	Zincblende	-	-	0.4511	-
AlN	Wurtzite	4.20	5.30	0.3112	0.4982
ZnO	Wurtzite	8.25	4.75	0.3250	0.5207
Si	Diamond	3.59	-	0.5431	-
6H-SiC	Wurtzite	4.20	4.68	0.3081	1.5117
3C-SiC	Zincblende	-	-	0.4360	-
Al_2O_3	Hexagonal	7.50	8.50	0.4765	1.2982
GaAs	Zincblende	6.00	-	0.4538	-
GaP	Zincblende	-	-	0.5431	-
MgO	Zincblende	10.50	-	0.4210	-
BP	Zincblende	-	-	0.4538	-

In practice, the way to determine the suitability substrates used for the growth of GaN thin films depends on both crystal structure and lattice constants. As can be seen from Table 2.2, 6H-silicon carbide (6H-SiC), AlN, and ZnO materials have the lattice constant values closer to the wurtzite GaN as compared to other materials. These materials are suitable and preferable to use as the substrate for the growth of

GaN thin films. Larger difference of the lattice constant mismatch between substrate and GaN thin films may contribute to the high density defect.

Apart from lattice constants and crystal structure, the lattice constant mismatch has been the primary criteria to determine the suitability of a material as a substrate for GaN thin films. Consequently a wide variety of foreign substrate materials have been studied for nitride thin films, including Al_2O_3, SiC, Si, GaP, ZnO and etc. The most promising results so far have been obtained on Al_2O_3, Si, and SiC. However, there is significant mismatch of lattice constants between III–nitrides and these substrates as shown in Table 2.3.

In spite of the large lattice mismatch, Al_2O_3 (~ 15%) has been the substrate of choice for GaN growth due to its good physical properties. So far, the most common orientations of Al_2O_3 used for GaN is the *c*-plane or basal plane of Al_2O_3. However, there are no cleavage planes suitable for diode laser mirror faces by using *c*-plane Al_2O_3 substrate. Post-nitridation growth of wurtzite structure GaN layer on Al_2O_3 substrate has been reported (Yang et al., 2002a). Besides, the nucleation behaviors of GaN thin films on patterned Al_2O_3 substrate have also been studied (Zhou et al., 2014).

In year 1905, MBE grown of GaN thin films on SiC substrate was demonstrated by Hughes et al. In fact, SiC substrate has several advantages over Al_2O_3 substrate for GaN epitaxy (Edgar and Liu, 2002). For instance, its lattice constant mismatch with GaN thin films is only 3.1% while it has higher thermal conductivity as compared to Al_2O_3. However, SiC substrate does have its disadvantages. For instance, the poor wetting issue may cause the difficulty in the growth of GaN thin films on SiC substrate. Besides, SiC substrates are very expensive as compared to other substrates.

Table 2.3: Lattice mismatch between GaN and most favored foreign substrates.

Substrate	**Lattice mismatch (%)**	**References**
Si	16.9	(Watson, 2013)
Al_2O_3	15.0	(Edgar and Liu, 2002)
6H-SiC	3.1	(Edgar and Liu, 2002)
GaP	5.2	(Elwell and Elwell, 1988)

Silicon (Si) substrate shows its potential as an ideal substrate for the growth of GaN thin films due to its favorable physical properties such as high crystal quality, large area size, and low manufacturing cost. For these reasons, most of the researchers were used Si instead of other substrates. In addition, Si is favored for the growth of GaN thin films because it is the material for possible integration of GaN devices with Si electronics. Currently, most of the commercial photo-electronics devices are based on Si. Although the thermal expansion coefficient and the lattice mismatch between Si wafer and GaN layers are large, however there are still many studies related to the growth of GaN film directly on bare Si substrates.

Generally, GaN thin films with wurtzite and zincblende structures were deposited on Si substrates by using MBE (Yang et al., 2009), MOCVD (Hassan et al., 2004), and RF sputtering (Xiao et al., 2009) methods. However, directly grown of GaN thin films on Si(100) might produce mixed phase or wurtzite phase only (Edgar and Liu, 2002). On the other hand, pure zincblende phase GaN is difficult to grow directly on the Si(100) substrates (Edgar and Liu, 2002).

2.3.2 Buffer layer for GaN

GaN thin films with good quality have been achieved when the growth started by growing a thin film called “buffer layer” at low temperature. To produce high efficiency, high reliability III-nitride devices, dislocation density must be reduced by using a buffer layer especially fabrication of GaN thin films on bare Si substrates.

A variety of approaches have been used to mitigate tensile stress, elimination of cracks, and reduce threading dislocation densities in GaN on Si substrate. The most common approach has been to incorporate AlN, GaN, ZnO, or AlGaN as a transition layer, interlayer or super-lattice for the growth of GaN on bare Si substrates. The first high quality wurtzite structure GaN films were successfully synthesized by Nakamura (1991) where GaN layer was used as the buffer layer on Al_2O_3 substrate. The optimum thickness of the GaN buffer layer was found to be 200 Å. Up to date, most of the researchers use AlN buffer layer as their choice instead of GaN due to its low cost and easy fabrication.

In year 2007, GaN films were grown on Si(111) substrates through the use of MOCVD method (Zhang et al., 2007). The photoluminescence (PL) and structural properties of the GaN films were investigated. They found that direct growth of GaN layers on the surface of a bare Si substrate without any buffer layer was very difficult. Defects such as edge, screw, and mixed types of dislocation and even dense micro-cracks can be generated. Consequently, they proposed that the use of AlN buffer layer to reduce the dislocation density. Besides, the effects of AlN buffer layer on the growth of GaN layer on Si substrate was reported (Yoo et al., 2002). In their study, three types of AlN buffer layer which grown by various methods were investigated.

They found that buffer layer with good crystalline quality is critical to achieve nucleation site for the growth of GaN thin films.

Thickness of the buffer layer is another factor must also be taken into consideration after a suitable buffer layer material was chosen. The properties of the deposited GaN thin films will be affected by the thickness of the buffer layer. There are many studies about the effects of AlN buffer layer thickness to the growth of GaN thin films. The influence of AlN buffer layer thickness on GaN grown on Si(111) by gas source MBE with ammonia was reported (Lin et al., 2008). AlN buffer layer thickness varied from 9 to 72 nm was studied and they found that the optimal crystalline quality and surface morphology can be achieved when the GaN layer was grown on a 36 nm thick AlN buffer layer. In year 2009, another work related to the influences on the thickness of AlN buffer layer was investigated (Yoon et al., 2009b). They found that good quality GaN thin films can be achieved when the GaN layer was grown on a 50 nm AlN buffer layer deposited by RF sputtering method and 65 nm AlN buffer layer deposited by MOCVD method.

2.3.3 Precursor for GaN

In sol-gel method, the precursor plays an important role. To grow a good quality GaN thin film is depend solely on the precursor. Generally, the precursor will be prepared by using a suitable starting material, solvent and other surfactant, etc. Next, the viscosity and the pH of the precursor need to be adjusted so that the coated layer with desire thickness can be produced. Table 2.4 summarizes the precursor materials for the growth of GaN using sol-gel method.

Table 2.4: Precursor materials for the growth of GaN using sol-gel method.

Starting material	Solvent	Addition solvent	References
Ga_2O_3	HCl, HNO_3	NH_4OH	(Li et al., 2009)
GaO(OH)	Ethanol	$C_2H_4O_2$	(Sinha et al., 2008)
$Ga(NO_3)_3$	HNO_3	Citrate acid	(Cao et al., 2007)
$NH_4(Ga(OC_2H_5)_3)$	Ethanol	-	(Wu et al., 2006)
$[Ga(C_6H_5O_7)_2] \cdot 4H_2O$	HCl, HNO_3	NH_4OH	(Sardar et al., 2003)

There are many types of starting materials used as the Ga source. Li et al. (2009) prepared the precursor by adding and dissolving 2.5 g Ga_2O_3 powder into the mixture of nitric acid (HNO_3) and HCl. The pH value for the precursor was then adjusted to 7.5-8.0 by adding ammonium hydroxide (NH_4OH). Then, few drops of citric acid were added. Besides, $Ga(NO_3)_3$ powder was used as the starting material by Cao et al. (2007a), where 6 g $Ga(NO_3)_3$ powder was dissolved in 10 ml concentrated HNO_3 and the solution was adjusted to pH 7.5-8.2 by adding NH_4OH.

2.3.4 Nitridation conditions

Nitridation is a process where the formation of a compound through an action of NH_3 gas and this process has existed for nearly a century. During the nitridation process, NH_3 gas disassociates into nitrogen and hydrogen when heat is supplied. The nitrogen then diffuses onto the surface of the samples creating a nitride layer. The chemical reactions for the nitridation process to the growth of GaN could be described by:

$$2NH_3 \rightarrow N_2 + 3H_2 \tag{2.1}$$

$$NH_3 \rightarrow H + NH_2 \tag{2.2}$$

$$Ga_2O_3 + 2H_2 \rightarrow Ga_2O + 2H_2O \tag{2.3}$$

$$Ga_2O + 2NH_3 \rightarrow 2GaN + 4H_2 + H_2O \tag{2.4}$$

There are many studies regarding the growth of III-nitride layers by using nitridation process. No matter what methods they used for the growth of GaN layers, nitridation process is one of the important steps for the conversion of the thin film to GaN. In year 2009, RF sputtering growth of GaN nanostructure followed by ammoniated in NH_3 ambient was reported by Xue et al. The ammoniating temperatures vary from 800 to 1000 ℃ were investigated.

Table 2.5 summarizes some of the nitridation parameters used for the growth of GaN layer. The use of NH_3 gas for nitridation process is the main focus on this review. From Table 2.5, the nitridation temperatures of 600 ℃ and above were used for most of the studies. As we know, the dissociation of the NH_3 gas is highly dependent to the temperature. Fig 2.1 shows the relationship between temperature and the percentage of NH_3 decomposition. The percentage of NH_3 decomposition increases with increasing of temperatures has been reported (Morkoç, 2009, White and Melville, 1905). For dry NH_3, around 30% of NH_3 gas will be decomposed at the temperature of 730 ℃.

Normally, NH_3 gas was used instead of N_2 gas in most of the studies. These may be due to the difficulties in breaking the strong and stable triple bond in N_2 gas at temperature below 1000 ℃. Apart from the NH_3 gas, other parameters such as temperature, duration, and NH_3 gas flow rate are also important to obtain good quality GaN thin film.

Table 2.5: Nitridation parameters used for the growth of GaN.

Growth Method	Gas	Temperature (℃)	Duration (min)	Gas flow rate (sccm)	References
CVD	NH_3	600-1200	30	50	(Ning et al., 2012)
MOCVD	NH_3	900	60	500	(Vilchis et al., 2012)
MOCVD	NH_3	950	300	400-800	(Lee et al., 2008)
Sol-gel	NH_3	1000	-	30	(Sinha et al., 2008)
Sol-gel	NH_3	900	60	-	(Cao et al., 2007)
Sputtering	NH_3	950	5-30	300	(Gao, 2006)
Sol-gel	NH_3	600-1100	180	50	(Jung, 2006)
Sol-gel	NH_3	950	20	-	(Liu et al., 2006)
Sol-gel	NH_3	1000	20	400	(Wu et al., 2006)
Sol-gel	NH_3	850	180	-	(Sardar et al., 2003)

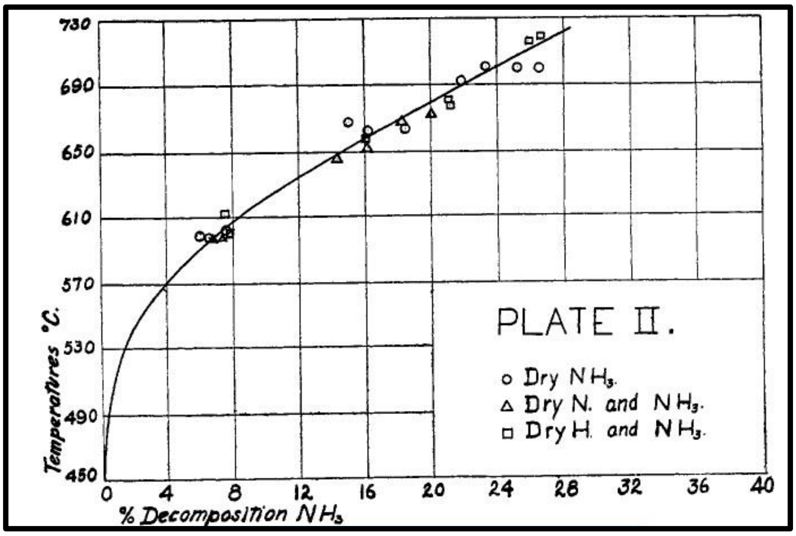

Fig. 2.1: Relationship between temperatures and percentage of NH_3 decomposition (White and Melville, 1905).

As mentioned earlier that the crystalline quality of the GaN thin film will be affected by the nitridation temperature. Generally, nitridation temperature ranging from 550 to 1200 ℃ was used for the growth of GaN thin films, as listed in Table 2.5. However, studies from Lee et al. (2008), Gao et al. (2006), and Liu et al. (2006) reported that nitridation temperature of ~ 950 ℃ was the optimum temperature. In year 2006, Jung investigated the conversion of GaN from Ga_2O_3 using nitridation process under different temperatures, i.e., from 600 to 1100 ℃. Based on the XRD results, polycrystalline wurtzite GaN without Ga_2O_3 can be obtained under nitridation temperature of 800 ℃ and above. In summary, the nitridation temperature is crucial in order to produce a good crystalline quality GaN thin film.

Besides the nitridation temperature, nitridation duration is also one of the factors that most of the researchers concerned about. Researchers tend to find a way to obtain good quality GaN thin films within the shortest nitridation duration. Thus, there are many works reported on the effects of nitridation duration to the growth of GaN thin films. For instance, it was reported that the optimal duration for nitridation process was 300 min (Lee et al., 2008). However, some studies reported that good crystalline GaN thin films can be obtained with nitridation duration less than 60 min (Liu et al., 2006, Wu et al., 2006).

2.4 Overview on GaN-based metal-semiconductor-metal photodetectors

Photodetectors fall under a broader type of optical based systems called photonic devices, which have been of significant importance due to the recent optical communications revolution. Photodetector is an important device that converts the energy of photons into some other form of energy such as electrical or thermal energy. The photodetectors can detect the optical signals over a range of the electromagnetic spectrum that is predominantly defined by the material properties. A detector is selected depending on the requirements of the particular application. The general requirements include wavelength of light to be detected, sensitivity needed, and the response speed. In general, photodetectors respond uniformly within a specific range of the electromagnetic spectrum, so the wavelength of light detected determines the selection of the photodetector material.

Photodetectors fall into two basic categories which are vacuum tube and solid-state devices (DeCorby, 1998). The classification system of the photodetectors is shown in Fig. 2.2. MSM photodetector will be the main device focused in this dissertation and this section is intended to give some perspective on their particular strengths and applications. Generally, MSM photodetectors are under the group of solid-state devices without gain. The important characteristics of these MSM photodetectors are high electrical bandwidth, high responsivity and speed, simple in processing, and compatibility with large-scale planar integrated circuit technology, and ability to generate ultra-short electrical pulses (Wang et al., 2003).

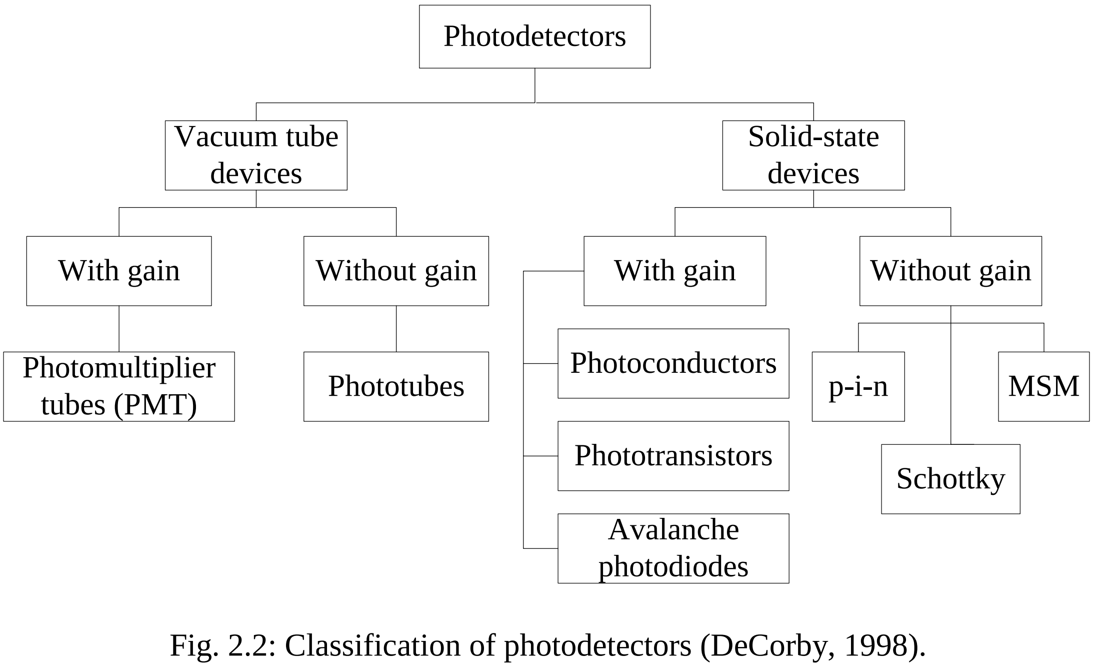

Fig. 2.2: Classification of photodetectors (DeCorby, 1998).

Metal contacts are crucial in fabricate a good quality semiconductor devices. They provide electrical connections and forming active device junctions. A metal contact on the surface of a semiconductor can be formed either as an Ohmic or a Schottky contact. Theoretically, this is depends solely on the work-function of the metal contact and the electron affinity of the semiconductor. However, the contact properties are determined by a more complex structure that includes an interfacial layer, which always exist between the metal and the semiconductor. A MSM photodetector is made by forming two Schottky contacts on a semiconductor layer. The contacts can be single contacts or interdigitated contacts connected back to back as shown in Fig 2.3.

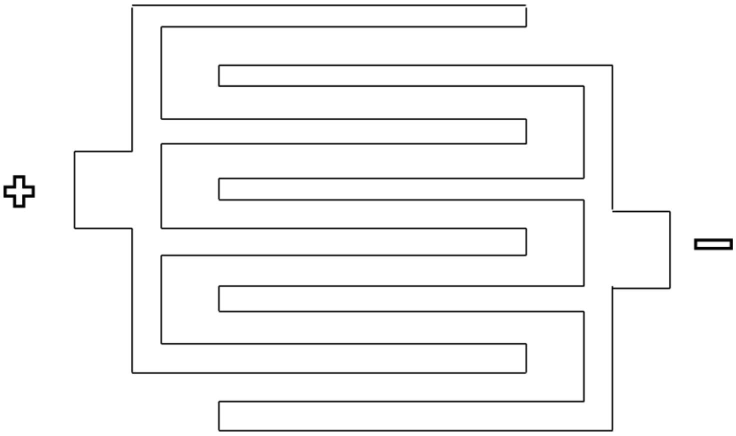

Fig. 2.3: Schematic top view of MSM structure with two interdigitated contact pads connected back to back.

Fabrication of UV photodetectors by using GaN material system has been the main focus in research and industrial community. Its wide direct band gap and high thermal stability make it suitable for various UV detection applications such as biological and chemical sensors, flame detector (Wang et al., 2003), and UV astronomy (Ghusoon and Chakrabarti, 2010). The UV region of electromagnetic radiation occupies a section of wavelengths ranging from 10 to 400 nm. It is