GROWTH OF $\text{Al}_x\text{Ga}_{1-x}\text{N}$ THIN FILMS ON SILICON USING SOL-GEL SPIN COATING TECHNIQUE

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UNIVERSITI SAINS MALAYSIA

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GROWTH OF Al$_x$Ga$_{1-x}$N THIN FILMS ON SILICON USING SOL-GEL SPIN COATING TECHNIQUE

by

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LIST OF SYMBOLS

2θ  2-theta

x   Alloy composition

α   Alpha

θ_{hkl}  Bragg angle

D   Crystallite size

β   Full width at half maximum (FWHM)

d_{hkl}  Interplanar spacing between two consecutive scattering planes

a   Lattice constant

c   Lattice constant

\text{c_{AlN}}  Lattice constant of AlN

\text{c_{GaN}}  Lattice constant of GaN

m_{Al}  Mass of aluminum nitrate nonahydrate

m_{Ga}  Mass of gallium nitrate hydrate

h, k, l  Miller indices

w_{Al}  Molecular weight of aluminum nitrate nonahydrate

w_{Ga}  Molecular weight of gallium nitrate nonahydrate

n_{Al}  Number of moles of aluminum nitrate nonahydrate

n_{Ga}  Number of moles of gallium nitrate hydrate

ω-2θ  Omega-2theta

n   Order of reflection

K   Shape factor

θ   Theta

λ   Wavelength
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<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DEA</td>
<td>Diethanolamine</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
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<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standards</td>
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<td>LO</td>
<td>Longitudinal optic</td>
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<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
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<tr>
<td>MOCVD</td>
<td>Metal-organic chemical vapor deposition</td>
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<td>PL</td>
<td>Photoluminescence</td>
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<td>RF</td>
<td>Radio frequency</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
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<tr>
<td>TO</td>
<td>Transverse optic</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VIS</td>
<td>Visible</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<td>XRD-RC</td>
<td>X-ray diffraction rocking curve</td>
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PENUMBUHAN FILEM NIPIS Al\textsubscript{x}Ga\textsubscript{1-x}N ATAS SILIKON DENGAN MENGGUNAKAN TEKNIK PENYALUTAN PUTARAN SOL-GEL

ABSTRAK

Kumpulan III-nitrida seperti aluminum nitride (AlN) dan aluminum gallium nitride (AlGaN) mempunyai aplikasi yang berpotensi untuk pemancar ultra-ungu dan peranti berkuasa tinggi. Pada masa kini, teknik pertumbuhan yang canggih dan mahal digunakan untuk sintesis filem nipis tersebut. Oleh itu, kaedah alternatif yang dikenali salutan putaran sol-gel yang agak mudah dan murah serta kurang diterokai digunakan untuk menumbuhkan filem nipis AlN dan AlGaN. Dalam kerja ini, pertumbuhan dan percirian filem nipis AlN ke atas substrat silikon (Si) melalui kaedah salutan putaran sol-gel di bawah pelbagai parameter nitridasi seperti suhu nitridasi, tempoh nitridasi, dan kadar aliran ammonia (NH\textsubscript{3}) telah diselidiki. Untuk suhu nitridasi yang berbeza, didapati bahawa lebar penuh pada separuh maksimum (FWHM) puncak pembelauan AlN(002) daripada pembelauan sinar-X-ray dan puncak E\textsubscript{2}(tinggi) Raman spektra menunjukkan bahawa apabila suhu nitridasi meningkat daripada 1100 kepada 1150°C, ini menunjukkan peningkatan kualiti kristal AlN. FWHM kedua-dua XRD dan Raman meningkat apabila suhu nitridasi meningkat kepada 1200°C. Ini menunjukkan kemerosotan kualiti kristal AlN. Selain itu, mikroskop elektron pengimbasan pancaran medan (FESEM) bagi sampel pada suhu nitridasi 1150°C menunjukkan bahawa permukaan licin dan seragam dengan bijian yang lebih besar dan padat berbanding sampel yang dinitridasi pada 1100°C. Bagi tempoh nitridasi, XRD menunjukkan peningkatan kualiti kristal AlN dengan peningkatan
tempoh nitridasi dari 45 hingga 60 min. Walau bagaimanapun, kualiti kristal AlN menurun apabila tempoh nitridasi meningkat kepada 75 min disebabkan oleh penyerapan nitrogen yang mungkin berlaku, dengan itu menyekat pembentukan AlN. Hasil FESEM menunjukkan bahawa bijian padat dengan permukaan licin dan seragam terbentuk apabila tempoh nitridasi meningkat kepada 60 min. Walau bagaimanapun, permukaan dengan bijian tidak padat dan berterabur telah terbentuk apabila tempoh nitridasi meningkat sehingga 75 min. Bagi kadar aliran NH$_3$ yang berbeza, keputusan XRD dan Raman menunjukkan bahawa kualiti kristal AlN bertambah apabila aliran NH$_3$ bertambah daripada 300 kepada 400 sccm. Walaubagaimanapun, kualiti kristal AlN menurun apabila kadar aliran NH$_3$ meningkat kepada 500 sccm. Keputusan menunjukkan bahawa suhu nitridasi, tempoh nitridasi, dan kadar aliran NH$_3$ yang paling berkesan dan optimum bagi pertumbuhan filem nipis AlN masing-masing adalah 1150°C, 60 min, dan 400 sccm.

Untuk pertumbuhan filem nipis Al$_x$Ga$_{1-x}$N pada substrat Si(111), AlN digunakan sebagai lapisan penampan. Template komersil AlN/Si(111) dengan ketebalan 25 nm adalah lapisan penampan yang sesuai untuk filem nipis Al$_x$Ga$_{1-x}$N. Filem nipis Al$_x$Ga$_{1-x}$N dengan pelbagai komposisi Al telah ditumbuhkan di atas template komersil AlN/Si(111). Hasil XRD menunjukkan bahawa filem nipis AlGaN (GaN) dengan orientasi pertumbuhan pilihan AlGaN(002) [GaN(002)] telah berjaya ditumbuhkan. Walau bagaimanapun, kualiti kristal filem nipis menurun apabila komposisi Al meningkat. Secara keseluruhan, hasilnya menunjukkan bahawa filem nipis AlN dan AlGaN berjaya ditumbuhkan dengan kaedah salutan putaran sol-gel. Akhirnya, kajian ini dapat menyediakan satu rangka kerja baru bagi pertumbuhan kos rendah filem nipis AlN and AlGaN dengan kaedah salutan putaran sol-gel.
GROWTH OF Al$_{x}$Ga$_{1-x}$N THIN FILMS ON SILICON USING SOL-GEL SPIN COATING TECHNIQUE

ABSTRACT

Group-III nitrides such as aluminum nitride (AlN) and aluminum gallium nitride (AlGaN) have potential applications for ultraviolet light emitting devices and high power devices. Nowadays, sophisticated and expensive growth techniques are used to synthesize these thin films. Thus, an alternative method known as sol-gel spin coating method which is relatively cheap and simple as well as less explored was used to grow AlN and AlGaN thin films. In this work, the growth and characterization of AlN thin films on silicon (Si) substrate by sol-gel spin coating method under various nitridation parameters such as nitridation temperatures, nitridation durations, and ammonia (NH$_3$) gas flow rates were investigated. For different nitridation temperatures, it was found that the full width at half maximum (FWHM) of AlN(002) diffraction peak of X-ray diffraction (XRD) and the E$_2$(high) peak of Raman decreased, as the nitridation temperature increases from 1100 to 1150°C, which indicates the improvement of AlN crystal quality. The FWHM of both XRD and Raman increases when the nitridation temperature increased to 1200°C. This implied the degradation of AlN crystal. Moreover, the field-emission scanning electron microscopy (FESEM) image of sample nitridated at 1150°C showed a smooth and uniform surface with slightly bigger and densely packed grains as compared with that nitridated at 1100°C. As for nitridation durations, XRD showed the improvement of crystalline quality of AlN with increasing nitridation duration from 45 to 60 min.
However, the crystalline quality of AlN degraded as the nitridation duration increases to 75 min due to nitrogen desorption might have occurred, thus restrict the formation of AlN. FESEM results showed that the grains are densely packed with a smooth and uniform surface was formed as the nitridation duration increases to 60 min. However, surface with unpacked and scattered grains was formed when the nitridation duration increases to 75 min. As for different NH$_3$ flow rates, XRD and Raman results showed that the crystalline quality of AlN increases as the NH$_3$ flow rate increases from 300 to 400 sccm. However, the AlN crystal quality degraded, as the NH$_3$ flow rate increases to 500 sccm. The results revealed that the effective and optimum nitridation temperatures, nitridation durations, and NH$_3$ flow rates for the growth of AlN thin films was 1150°C, 60 min, and 400 sccm, respectively. For the growth of Al$_x$Ga$_{1-x}$N thin films on Si(111) substrate, AlN is used as buffer layer. The commercial AlN/Si(111) templates with 25 nm thickness is well-suited buffer layer for Al$_x$Ga$_{1-x}$N thin films. Al$_x$Ga$_{1-x}$N thin films with various Al composition were grown on the commercial AlN/Si(111) templates. XRD results showed that wurtzite AlGaN (GaN) thin films with preferred growth orientation of AlGaN(002) [GaN(002)] were successfully grown. However, the crystalline quality of the thin films degraded as Al composition increases. Overall, the results revealed that AlN and AlGaN thin films were successfully grown by sol-gel spin coating method. Eventually, these works may provide a new framework for the low-cost growth of AlN and AlGaN thin films by sol-gel spin coating method.
CHAPTER 1

INTRODUCTION

1.1 Introduction

Group III-nitrides such as gallium nitride (GaN), aluminum nitride (AlN), indium nitride (InN) and their alloys have received intense research interest among scientific community. In the past few years, many researchers have reported the band gap energy of AlN thin films in the range of 5.0-6.2 eV (Pat et al., 2010; Choudhary et al., 2013). As for results from their wide direct band gap energy, AlN have potential applications for optoelectronics (Tsai et al., 2013), surface acoustic wave (Zhou et al., 2015) and sensing devices (Yarar et al., 2016) which can operate under harsh environment conditions. Besides that, AlN has unique material properties such as high thermal conductivity (Duquenne et al., 2012) and chemical stability (Liu et al., 2017) as well as can sustain and stable at high temperature. This makes the AlN a promising material for applications in high power electronics.

Owing to their direct and tune able band gap energy (ranging from 3.4 to 6.2 eV), group III-nitride ternary alloys, particularly aluminum gallium nitride (AlGaN) have been widely applied in the fabrication of optoelectronic devices operating in blue and violet regions of the spectrum and semiconductors light emitting device (Biyikli et al., 2002; Liu et al., 2008; Sawyer et al., 2008). Moreover, it also has the capacity to cover the spectrum from visible (VIS) to deep ultraviolet (UV) spectral range. These are strongly driven by their superior physical properties such as excellent thermal, mechanical and chemical stability. Although, it has potential in semiconductors devices, there are few difficulties to produce high quality of AlGaN thin films. From their work, Kamiyama et al. (2001)
mentioned that the crystalline quality AlGaN alloys degrades with the increasing of AlN molar fraction.

Nowadays, silicon (Si) substrate shows its potential as a suitable substrate for the growth of AlN thin films. Si substrate is the most widely used material in semiconductors device technology such as complementary metal-oxide-semiconductor, due to its good physical properties such as high crystal quality, large size area, easy to handle and low-cost manufacturing. Si is being investigated intensively in order to make Si a competitor of III/V semiconductors materials. The growth of III-nitride materials on Si substrate is capable in producing high-voltage power device such as high electrons mobility transistors and diodes. Thus, Si is a well suited substrate for the growth of AlN and AlGaN thin films.

Up to date, most common growth techniques used for growing AlN and AlGaN thin films are molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD). Although these methods can produce high quality of AlN and AlGaN thin films, however, these methods involved sophisticated technologies with complicated setup and relatively expensive. For instance, MBE systems operates in ultra-high vacuum environment. Thus, relatively high in production costs are needed in order to maintain a good high vacuum environment. Meanwhile, MOCVD system used volatile metal-organic compounds in films deposition process, therefore, highly disposal cost and precaution are absolutely necessary.

A method with ability to produce good quality AlN and AlGaN thin films at a significant lower cost is necessary. Thus, sol-gel spin coating method is one of promising method, in which it is relatively cheap and simple as compared to the aforementioned methods. The sol-gel spin coating method is an effective method in producing
homogeneous film’s surface and can control film’s thickness by varying synthesis parameters. It is well known technique for depositing metal oxide materials (Natsume et al., 2000; Kamaruddin et al., 2010; Nadzirah et al., 2013). Recently, this technique has successfully been applied to grow GaN (Fong et al., 2014) and InN (Lee et al., 2017). Consequently, the sol-gel spin coating could be an alternative method to grow the AlN and AlGaN thin films. Up to now, little is known about the growth of AlN and AlGaN thin films using sol-gel spin coating method.

Nano-sized crystal AlN were grown on Si(100) substrate under various annealing temperatures (Mohd Amin et al., 2015). However, the nitridation conditions for the growth of AlN thin films are remain unclear. In 2014, Sutanto et al. investigated the effects of electrical properties of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films grown on Si(111) by sol-gel spin coating method under nitrogen gas ambient at 900°C for 2h. However, they reported only electrical properties but the structural, surface morphologies and optical properties of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films were not discussed. As a result, many growth issues and material’s properties still remain unclear. From the fundamental and potential application point of views, in-depth studies on the sol-gel spin coating growth of AlN and AlGaN thin films are needed.

1.2 Problem statement

AlN and AlGaN thin films have been grown by various methods such as MBE and MOCVD. However, these advanced methods involved sophisticated technologies with complicated setup and high cost. Thus, a simple, low cost and safer method is highly desirable, in which it can be obtained from sol-gel spin coating method. The sol-gel spin
coating method is an environment-friendly approach in which it can produce thin and uniform films on substrate.

There are little studies on the sol-gel spin coating growth of AlN and AlGaN thin films. For AlN thin films, growth temperature usually higher than 1000°C (Liu et al., 2016; Pons et al., 2017) is needed as compared with GaN, which around 700°C to 1000°C (Fong et al., 2014; Ghazali et al., 2014) and InN, around 500°C to 700°C (Khan et al., 2008; Briot et al., 2009; Lee et al., 2017) thin films. This is due to the Al atoms are less mobile than Ga atoms (Chen et al., 2008). Besides that, it is quite difficult to grow high quality AlN thin films, in which it requires a high purity source and an oxygen-free environment due to high reactivity of aluminum. As for AlGaN, the growth of high Al compositions with high crystalline quality of AlGaN alloys is difficult too. The crystalline quality of AlGaN thin films degraded as the Al composition increases. Thus, in this work, in-depth investigation on the sol-gel spin coating growth of AlN and AlGaN (with low Al compositions) were carried out.

There are many factors that influencing the growth of AlN and AlGaN thin films via sol-gel spin coating technique. For instance, the difficulties in choosing the well-suited substrate (Si and sapphire) and the buffer layer for AlGaN thin films as well as the nitridation condition to produce the nitride films. Therefore, an in-depth investigation on these subjects are necessarily needed in order to synthesis good crystallinity AlN and AlGaN thin films via sol-gel spin coating technique.

1.3 Research Objectives

The main objectives of this project are:
I. To investigate AlN thin films growth deposited under nitridation temperatures, nitridation durations, and ammonia (NH$_3$) flow rates via sol-gel spin coating method.

II. To explore the growth of Al$_x$Ga$_{1-x}$N thin films with different Al compositions by using AlN buffer layer on Si (111) substrate [AlN/Si (111)] via sol-gel spin coating method.

1.4 Originality of the research work

The primary originality of this work is the growth of AlN and AlGaN thin films using sol-gel spin coating method which is relatively simple and cheaper as compared with aforementioned growth techniques. Nowadays, sol-gel spin coating method has been practically used to grow numerous materials including III-nitrides materials. However, the growth of AlN and AlGaN thin films by sol-gel spin coating method are still rarely reported and explored. Consequently, the relevant growth processes and issues as well as the material’s properties still remain unclear. Through in-depth investigation on the effects of the nitridation temperatures, the nitridation durations and the ammonia gas flow rates on the growth and properties of the AlN thin films, a better insight on the above subject were obtained.

Apart from that, the NH$_3$ gas is used as nitrogen source instead of nitrogen gas (N$_2$) for nitridation process due to the difficulties in breaking the strong and stable triple bond in N$_2$ gas for temperature below than 1000°C. Besides that, the structural, surface morphologies and optical properties of the AlGaN thin films prepared by sol-gel spin
coating method was reported for the first time where the growth of AlGaN thin films with different Al compositions was demonstrated.

1.5 Organization of dissertation

This dissertation consists of 6 chapters. **Chapter 1** gives an introduction on the research work, the problem statement, the research objectives, and the originality of the research work.

**Chapter 2** present the fundamental properties of AlN and AlGaN. An overview of the growth techniques for AlN and AlGaN thin films are given. Next, the basic principle of sol-gel spin coating method is described. The literature reviews on the growth of AlN and AlGaN thin films by using sol-gel spin coating method are given. Then, the factors that influencing the growth of AlN and AlGaN thin films grown via sol-gel spin coating technique are presented.

**Chapter 3** devotes to the experimental procedure. The growth parameters used to grow AlN and AlGaN thin films with different Al compositions are described. Apart from that, the experimental details about the characterization measurements such as settings, measurement parameters, operating condition, and resolution of instrument are also presented.

In **chapter 4**, the results and discussion of the growth of AlN thin films are presented. This chapter is divided into three sections, i.e., (i) the effects of nitridation temperatures on the growth of AlN thin films, (ii) the effects of nitridation durations on
the growth of AlN thin films and (iii) the growth and characterization of AlN thin films under different ammonia gas flow rates.

Chapter 5 devotes to the results and discussion of sol-gel spin coating growth of Al$_x$Ga$_{1-x}$N thin films. A comparison of structural and morphology properties of the deposited thin films grown on AlN/Si substrate and commercial AlN/Si template grown by plasma vapor deposition nano-columns (PVDNC). The summary of this study is included at the end of this chapter.

Finally, Chapter 6 is the conclusion of the research work. Some recommendations for future research are also included.
CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

In this chapter, fundamental properties of AlN and AlGaN will be given. Next, an overview of the growth techniques for the AlN and AlGaN thin films will be presented. After that, basic principle of sol-gel spin coating method will be given. Then, details of the literature reviews on the sol-gel spin coating growth technique will be discussed. The factors that influence the growth of AlN and AlGaN thin films grown by sol-gel spin coating technique will be given. At the end of this chapter, a concluding remark of these literature reviews are presented.

2.2 Fundamental properties of AlN and AlGaN

AlN can be crystallize in two different crystal structures which are hexagonal wurtzite and cubic zinc-blende structure. At room temperature, hexagonal wurtzite AlN is thermodynamically stable. It is in contrast with cubic zinc-blende where it is said to be in metastable or less-stable depending on its growth condition and substrate orientation. The lattice constants of hexagonal wurtzite AlN are given by \( a = 3.112 \) Å and \( c = 4.982 \) Å (Vurgaftman et al., 2001). The hexagonal wurtzite structure of AlN consists of hexagonal unit cell while cubic zinc-blende structure consists of cubic unit cell with four nitrogen atoms. Fig. 2.1 shows the schematic diagram of crystal structure for both hexagonal wurtzite and cubic zinc-blende structure.
AlN possess large direct bandgap of around 6.2 eV and has unique materials properties such as high conductivity (Duquenne et al., 2012) and high breakdown field strength (An et al., 2005). Due to these unique properties, AlN is suitable for high power electronics application which can operate under harsh environment conditions. Apart from that, AlN also is a promising piezoelectric materials which highly suitable for sensing devices and surface acoustic wave (Zhou et al., 2015) under high temperature environment.

AlN crystallize preferentially in hexagonal wurtzite structure, which also applied to GaN material. AlGaN is a III-V nitrides semiconductor ternary alloy. It also can exist in two different crystal structures, namely hexagonal and cubic. However, like its parents, AlGaN possess a stable hexagonal wurtzite structure. In alloys, properties of materials are dependence on the composition of alloy. Nowadays, much attention has been focused from III-V binary compound, however, the information on the fundamental properties of III-V alloys are still rather scarce. AlGaN alloys is one of the important materials in optoelectronic devices especially for light emitting diodes and laser diode, which the
direct energy band gap can be tuned according to the Al composition within the range of UV spectral region 200 nm to 365 nm (Iwaya et al., 2002).

To estimate the Al composition, the lattice spacing \( d_{hkl} \) and the constant \( c \) need to be calculated. Considering the first order reflection \( (n=1) \), the \( d_{hkl} \) can be calculated by:

\[
d_{hkl} = \frac{\lambda}{2 \sin \theta_{hkl}}
\]

(2.1)

where \( \lambda \) is the wavelength of X-ray source (\( \lambda = 1.5406 \, \text{Å} \)) and \( \theta_{hkl} \) is the Bragg angle which is estimated from the diffraction peak. The lattice parameters, \( a \) and \( c \) for Al\(_x\)Ga\(_{1-x}\)N ternary alloy, must obey Vegard’s Law, which the lattice constant is vary linearly on the alloys composition. According to Vegard’s Law, the lattice constants of Al\(_x\)Ga\(_{1-x}\)N as a function of Al composition of, \( x \), can be calculated approximately using the following formula (Kadir et al., 2015):

\[
a_{Al_xGa_{1-x}N} = xa_{AlN} + (1-x)a_{GaN}
\]

(2.2)

\[
c_{Al_xGa_{1-x}N} = xc_{AlN} + (1-x)c_{GaN}
\]

(2.3)

where \( a_{AlN} \) (\( c_{AlN} \)) and \( a_{GaN} \) (\( c_{GaN} \)) are the lattice constant of \( a \) (\( c \)) of AlN and GaN, respectively. Based on Vegard’s Law, by controlling the composition of alloy, \( x \), the lattice constants \( a \) and \( c \) of III-V nitrides semiconductor can be controlled. Moreover, the variation of the lattice constant \( c \) between GaN and AlN is linearly proportional to the Al composition (Vegard, 1921). By arranging Eq. (2.3), the \( x \) can be calculated by:
\[ x = \frac{c - c_{GaN}}{c_{AlN} - c_{GaN}}. \] (2.4)

2.3 Overview of the growth techniques of AlN thin films

Tremendous efforts have been applied to grow epitaxial AlN thin films. Traditionally, metal-organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE) and radio frequency (RF) or direct current (DC) magnetron sputtering were employed as the preferred manufacturing technology for growing the epitaxial AlN thin films. Despite having numerous methods for growing AlN thin films, high quality of AlN thin films are still remain challenging. Apparently, high synthesis temperature is needed to produce larger cohesive of AlN in order to promote good chemical and atomic migration on the substrate surface (Huang et al., 2017).

2.3.1 Metal organic chemical vapor deposition (MOCVD)

MOCVD is one of well-known techniques in growing III-nitrides thin films including AlN thin films. A lot of researchers reported on the effects of growth parameters on the properties of AlN thin films such as growth temperature, gas flow rate, layer thickness and etc. In 1996, Ohba et al. have been successfully grown AlN on sapphire substrate and the effects of growth temperatures (varies from 900°C to 1300°C) on sapphire substrate were investigated. Fig. 2.2 showed the XRD peak intensity and full-width at half-maximum (FWHM) value of AlN(0002) and (0006) for sapphire substrate as a function of growth temperature. They found that the peak intensity of AlN increased and the FWHM become narrower as the growth temperature increases. They observed that
the AlN epitaxial layer becomes rougher as the temperature increase over 1100°C. At temperature higher than 1100°C, they found that the surface roughness of AlN improved as the III/V ratio reduced. Ever since the smooth morphologies of AlN thin films was obtained by Ohba et al., (1996), many researchers have intensively pursued the research in order to obtain high quality of AlN thin films. In year 2017, Huang et al. reported on the growth of high quality AlN thin films at temperature below 1200°C. They successfully grown high quality AlN at substrate temperature of 1180°C.

![Dependences of XRD peak intensity and FWHM on growth temperature for both AlN epitaxial layer and sapphire substrate.](Adapted from Ohba et al, 1996)

In 2012, Çörekçi et al. reported on the effects of ammonia (NH₃) flow rate and the layer thickness on the properties of AlN layers. They concluded that reducing the NH₃ flow rate improved the symmetric AlN(0002) crystalline quality. Moreover, Fig. 2.3 shows the plain-view of SEM micrographs. They observed that sample A (340 nm, 125 sccm) displayed the hillock-like surface whereas samples B (550 nm, 70 sccm) and C (750 sccm) displayed...
nm, 70 sccm) showed mirror-like surface with no cracks were observed. MOCVD has been widely establish method in synthesizing semiconductor thin films. Nonetheless, this technique has its disadvantages. Metal-organics compounds used such as trimethylaluminum (TMAI) are highly in cost compared with inorganic compounds. Besides, MOCVD requires the use of hazardous gas during films deposition process, thus, highly disposal costs and precaution are needed.

Fig. 2.3: Plain-view SEM micrographs of samples: (a) A, (b) B, and (c) C. (Adapted from Çörekçi et al., 2012)

2.3.2 Molecular beam epitaxy (MBE)

In 2017, Tamariz et al. investigated the growth of AlN on Si(111) by ammonia-MBE in the temperature range of 900°C to 1200°C with the flow of 100 sccm of NH₃ (Tamariz et al., 2017). They found that the peak position of E₂(high) from micro-Raman spectroscopy for all samples were below than the reported unstrained value of AlN, as shown in Fig. 2.4. As the temperature increases, the tensile strain was increased, with 1100°C showed the highest tensile strain, which is induced by grain coalescence. They also found that AlN thin films at 1100°C showed the smoothest surface as compared to other samples. They concluded that the most optimum growth temperature, in which
showed the lowest root-means-square (rms) was 1100°C. Moreover, they have proven the sensitivity of AlN growth to surface stoichiometry.

Fig. 2.4: Raman shift of $E_2^{\text{high}}$ phonon line and the corresponding amount of strain in the layer, the dashed line is position of the $E_2^{\text{high}}$ phonon line for unstrained AlN and the black curve is the calculated thermal strain assuming relaxed layers during growth. (Adapted from Tamariz et al., 2017)

Low temperature (<600°C) MBE growth of AlN thin films by MBE has not yet been explored. Preferably higher temperature (above 700°C) is needed to grow high quality single crystal AlN films by using MOCVD or MBE. However, in 2015, Faria et al. have been successfully grown AlN thin films on GaN substrate using low temperature growth via MBE. Fig. 2.5 showed the XRD patterns of AlN grown under different temperature. They found that the FWHM of the AlN(002) peak increases with decreasing growth temperature. From the AFM results, they found that as temperature increases from 470°C to 800°C, the film cracks. However, no crack was found for AlN grown at 250°C and room temperature. Since MBE systems operates in ultra-high vacuum environment (< $10^{-10}$ Torr), thus, it is relatively crucial to maintain a good high vacuum environment.
to ensure the quality of epitaxy layers, therefore, this technique is relatively high in production cost. In addition, the MBE set up is much complicated and the operation conditions must accurately be controlled precisely.

![Graph](image)

Fig. 2.5: ω-2θ scan along the 002 reflections for the series of 5 samples show peak for 15 nm AlN on GaN substrate grown at different temperatures. (Adapted from Faria et al., 2015)

### 2.3.3 Magnetron sputtering

As compared with the other two conventional methods mentioned above, sputtering method is simple, low temperature operation and has ability to grow high quality of thin films (Kar et al., 2005). Typically, RF and DC sputtering approaches were used to grow AlN thin films. In order to obtain high quality of AlN thin films by sputtering techniques, a few researchers used different growth parameters such as growth temperature, sputtering power and gas pressure as well as nitrogen/argon (N₂/Ar) flow ratio. Cheng et al. (1996) reported the growth of AlN thin films by RF sputtering with
various N₂/Ar flow ratios, RF powers and sputtering pressures (Cheng et al., 1996). From the XRD results, they found that AlN thin films exhibit a strong AlN(002) preferential orientation for 75% of N₂ concentration, as shown in Fig. 2.6. However, as the N₂ concentration decreases, the (002) intensity also decreased with the presence of AlN(100) and AlN(101) peaks. They also found that the lattice constant c for all the samples was lower than that of the reported lattice constant.

Moreover, Khan et al. (2015) also have investigated the growth of AlN thin films by DC sputtering under different substrate temperature (300°C to 600°C) and N₂/Ar flow ratios. They found that the AlN thin films exhibit (002) preferential orientation with 2θ = 36.023°, which is slightly lower that AlN powder data (~36.04°). This result implies that

Fig. 2.6: XRD patterns of AlN thin films deposited at various N₂ concentrations (a) 25%, (b) 37.5%, (c) 50%, (d) 62.5% and (e) 75%, with a sputtering pressure of 7.5 mTorr, substrate temperature 350°C and RF power 300 W. (Adapted from Cheng et al., 1996).
the samples exhibit residual compressive stress, as shown in Fig. 2.7. For sample grown under different substrate temperatures, as the temperature increases to 500°C, the FWHM was decreased and started to increase as temperature increase to 600°C. For the 30% N₂ fraction, the crystallite size obtained was slightly higher as compared with the other sample conditions. They found that the optimum substrate temperature and percentage of N₂ fraction were 500°C and 60%, respectively. From Raman spectroscopy, peaks with correspond to E₂(high) and A₁(LO) modes were detected at 659 cm⁻¹ and 892 cm⁻¹, respectively, as shown in Fig. 2.8.

Fig. 2.7: XRD patterns of the AlN films prepared at various (a) substrate temperatures and (b) nitrogen conditions. (Adapted from Khan et al., 2015).
2.4 Overview of the growth techniques of AlGaN thin films

Up to date, there are numerous methods used to grow Al\textsubscript{x}Ga\textsubscript{1-x}N thin films such as MOCVD and MBE. However, the in-depth investigation on the properties of Al\textsubscript{x}Ga\textsubscript{1-x}N thin films still relatively scarce. In 1997, Stutzmann et al. reported the growth of AlGaN epitaxial films on sapphire substrate with (0 ≤ x ≤ 1). Fig. 2.9 shows the XRD patterns of Al\textsubscript{x}Ga\textsubscript{1-x}N with (0 ≤ x ≤ 1). They found that as the x value increases, the width of 002 was increased from 50 arcsec (GaN) to about 200 arcsec (AlN), with a significantly larger width for alloys with an Al content of about 80%, indicating a reduced structural quality in this alloy range. Besides, they found that A\textsubscript{1}(LO) mode exhibits one-mode behavior while E\textsubscript{2}(high) exhibits two-mode behavior, as shown in Fig. 2.10.
Fig. 2.9: High resolution XRD patterns of MBE grown AlGaN alloy films with different composition. (Adapted from Stutzmann et al., 1997)

Fig. 2.10: Raman spectra of AlGaN showing the dependence of the (a) $A_1$(TO) and the $E_2$ mode and (b) of the $A_1$(LO) mode on the Al content. (Adapted from Stutzmann et al., 1997)
Over the years, using high temperature (HT)-AlN/GaN buffer on sapphire substrate, Al$_x$Ga$_{1-x}$N were successfully grown by MOCVD. Liu et al., (2008) indicated that as the Al composition increases from $x = 0.13$ to 0.54, the FWHM of AlGaN (002) and (102) were decreased. However, as for the $x = 0.8$, the crystalline quality degraded. They concluded that $x = 0.54$ has the best crystal quality and surface morphologies among the other samples.

2.5 Basic principle of sol-gel spin coating method

Basically, sol-gel process is a process which producing a final product in the formed of a solid or material from a solution (Giordano et al., 2011). Sol-gel method is a method used in fabrication of thin films, nanomaterials, nanostructures, or ceramic nanopowders. Apart from having a simple and economical method, the sol-gel method is a low temperature method and possible to produce a high quality as well as a uniform nanostructures coating. Sol-gel method can be divided into a few groups include the two-basic coating; spin coating and dip coating. Both spin and dip coating involve the deposition of solution onto the flat surface.

Sol-gel spin coating method involves the deposition of a solution onto the center of substrate and the solution is spread on the substrate by centrifugal forces. This method usually used to produce a uniform and homogenous thin film with nanoscale thicknesses onto the surface substrate. This coating method is simple, low-cost, and efficient in manufacturing thin films.
2.5.1 Overview of sol-gel spin coating growth

Sol-gel method is one of the alternative methods that capable to produce high quality III nitrides thin films at low manufacturing cost. The first research using sol-gel method is involving metal oxide coatings and it were performed by Geffcken and Berger in 1939. Spin coating method is well-known method to form highly uniform thin films (Haas et al., 2000) using sol-gels. Zinc oxide is one of the famous oxide materials deposited using sol-gel spin coating method (Natsume et al., 2000; Nagarani et al., 2013; Znaiidi et al., 2016). Nowadays, sol-gel spin coating method has also been applied to deposit III-nitrides materials. GaN thin films has been successfully grown on Si substrate by sol-gel spin coating method (Fong et al., 2014). Meanwhile, Lee et al., (2017) have successfully grown InN thin films via the same method.

Investigations on the sol-gel spin coating growth of GaN thin films under various nitridation temperatures and durations were reported by Fong et al. (2013, 2014). From the reported results, they found that 950°C and 75 min, respectively, are the optimum nitridation temperature and duration, where GaN thin films with highest quality were synthesized, as shown in Figs. 2.11 and 2.12. Apart from that, Lee et al. (2017), also reported the effects of nitridation duration on the growth of InN thin films grown using same approach. As reported previously by Fong et al. and Lee et al., the nitridation temperatures and durations have significant effects on the growth of III-nitrides thin films.
Fig. 2.11: XRD patterns of the GaN thin films deposited under various temperatures: (a) 750°C, (b) 850°C, (c) 950°C and (d) 1050°C. (Adapted from Fong et al., 2013).

Fig. 2.12: XRD patterns of the GaN thin films under various nitridation durations: (a) 15 min, (b) 45 min, (c) 75 min and (d) 105 min. Inset is the XRD-RC of the GaN(002) peak measured in the omega scan mode. (Adapted from Fong et al., 2014).
Nevertheless, this approach on III-nitrides materials is still need in-depth investigation especially on AlN thin films. Previously, nano-sized crystal grains AlN have been grown on Si(100) substrate under various annealing temperatures (Mohd Amin et al., 2015). From this study, the optimum annealing temperature was 650°C, in which the sample exhibits AlN(100) preferential orientation, as shown in Fig. 2.13. Even though the growth of AlN thin films by sol-gel spin coating method was successful, further optimization on the growth parameters of AlN is necessary in order to improve quality of deposited thin films. Besides, the growth of AlN thin films via sol-gel spin coating method is still relatively scarce.

![XRD patterns of AlN thin films with various annealing temperatures](image)

**Fig. 2.13:** XRD patterns of AlN thin films with various annealing temperatures: (a) 250°C, (b) 450°C, (c) 650°C and (d) 850°C. (Adapted from Mohd Amin et al., 2015).

Up to date, the growth of AlGaN thin films by sol-gel spin coating method are limited. Previously, in 2014, Sutanto et al. have investigated the effects of electrical
properties on Al<sub>x</sub>Ga<sub>1-x</sub>N thin films grown on Si(111) by sol-gel spin coating method. In their study, AlGaN thin films were grown under 120 sccm of N<sub>2</sub> at temperature of 900°C for 2 hours. From the Hall effects measurement, they found that the Al<sub>x</sub>Ga<sub>1-x</sub>N thin films have n-type condition. However, the structural, surface morphologies and optical properties of Al<sub>x</sub>Ga<sub>1-x</sub>N thin films were not discussed in the study. With only a few researchers reporting on the growth of Al<sub>x</sub>Ga<sub>1-x</sub>N thin film using sol-gel spin coating method, therefore, many information related to the growth process and material’s properties remain unclear. From the fundamental point of view, the investigation on the sol-gel spin coating growth of Al<sub>x</sub>Ga<sub>1-x</sub>N thin films is needed.

2.6 Factors influencing the sol-gel spin coating growth of AlN and AlGaN thin films

There are many factors that influence the sol-gel spin coating growth of AlN and AlGaN thin films via sol-gel spin coating method. These factors include well-suited substrate, buffer layer for the growth of AlGaN thin films, nitrogen source, etc. In order to obtain good quality of AlN and AlGaN thin films, all these factors must be taken into consideration.

2.6.1 Choice of substrate

A well-suited substrate is needed in producing a good quality of III-nitrides semiconductors. In the past years, there were numerous studies on the growth of AlN thin films on various substrate such as sapphire, Si and silicon carbide (SiC) substrates (Morita et al., 1981; Ohba et al., 2000; Chen et al., 2008). Among these substrates, Si substrate shows its potential as a suitable substrate for the growth of AlN thin films due to its good
physical properties such as high crystal quality, large size area, easy to handle and low-cost manufacturing. While the sapphire and SiC substrates are costly as compared with Si, therefore, Si substrate is highly desirable in conjunction with low cost sol-gel spin coating method.

Over the years, AlN thin films have been grown on Si substrate with orientations i.e., (100) and (111). In year 2005, Zhang et al. stated that the FWHM of AlN(002) diffraction peak of AlN films deposited on Si(111) substrate was smaller than that deposited on Si(100) substrate. The growth of AlN thin films on Si(100) substrate is quite challenging due to its large lattice mismatch and the different in crystallographic symmetry to hexagonal wurtzite AlN(002) (Jose et al., 2012). Besides, Pandey et al. (2017), mentioned that the residual stress of AlN films grown on Si(111) substrate was lower as compared with AlN grown on Si with orientations of (100) and (110).

### 2.6.2 Buffer layer for AlGaN thin films

For AlGaN alloys, the literature review on their structural, optical and electrical properties have been reported by Wetzel et al. (1995) and Steude et al. (1998). The capability of AlGaN alloys to change the band gap from 3.4 eV to 6.2 eV makes this material a suitable candidate for LEDs and detectors operating in blue and near ultraviolet regions. In 1999, Al$_x$Ga$_{1-x}$N layers have been grown on thin buffer layer of GaN on sapphire substrate (Davydov et al., 1999). However, according to Yan et al. (2009), GaN template is not suitable for Al$_x$Ga$_{1-x}$N films with high Al compositions. This mainly due to the lattice parameter of AlGaN alloy is smaller than the GaN template, in which the
AlGaN layer is under biaxial tensile strain and easily induces cracks. Moreover, the GaN template is quite expensive.

Even though Si substrate is most promising heteroepitaxy, however it is difficult to grow Al$_x$Ga$_{1-x}$N directly on the Si substrate due to the large lattice mismatch between AlGaN (i.e., $x=0$) and Si substrate, which is around 17% (Watanabe et al., 1993) and large thermal expansion. Hence, an intermediate or buffer layer such as AlN is used to reduce the lattice mismatch. Therefore, in year 2002, Al$_x$Ga$_{1-x}$N alloys were grown on AlN buffer layer on Si substrate (Xi et al., 2002). Apart from that, AlN has comparable lattice constants to that of GaN [lattice constants, $a = 0.3189$ nm and $c = 0.5185$ nm (Kukushkin et al., 2008)], therefore, epitaxial AlN layers are widely used as a buffer layer for 2-dimension (2D) growth of GaN (Vispute et al., 1997) as well as AlGaN layers.

Thickness of the buffer layer is also one of the factors that needs to be considered. The properties of the deposited Al$_x$Ga$_{1-x}$N thin films will be affected by the thickness of buffer layer. Previously, the effects of AlN buffer layer thickness (i.e., varied 20 to 45 nm) on the properties of GaN epilayer has studied (Zhang et al., 2004). They have found that the lateral grain size reached maximum when the buffer layer thickness was 36 and 28 nm for samples grown on single-polishing and double-polishing sapphire, respectively. As the buffer layer thickness exceeded 30 nm and 20 nm, for single-polishing and double-polishing sapphire substrate, respectively, the strain of the epilayer decreased. In year 2008, Lin et al., reported on the influence of AlN buffer layer thickness (i.e., from 9 nm to 72 nm) on the growth of GaN grown on Si(111) by MBE. They found that the optimum thickness for best surface morphology and crystal quality is 36 nm. The device performance of AlGaN/GaN high electron mobility transistors grown on Si substrate with
AlN buffer layers with thickness of 200 and 300 nm were also studied (Arulkumaran et al., 2005). The results showed that the defects reduced with the increases of AlN buffer layer thickness.

2.6.3 Nitrogen source for nitridation process

For sol-gel spin coating growth of III-nitrides, nitridation process is an important step in order to transform the deposited thin film into nitrides thin film. Generally, the nitridation process can be performed under N\textsubscript{2} or NH\textsubscript{3} gas ambient. In 1861, Briegleb and Geuther were the first endeavored the synthesized of AlN by heating aluminum fillings under N\textsubscript{2} gas flow (Wang et al., 2017). They concluded that Al and N had reacted to form AlN. In 1970s, Slack et al. have proved the improvement of chemically pure AlN by replaced N\textsubscript{2} gas with NH\textsubscript{3} gas (Slack, 1979). After all these chemical synthesis reaction, Nakamura et al. (1998) finally discovered the use of NH\textsubscript{3} as a nitrogen source to form AlN thin films.

Over the years, many researchers have started to use NH\textsubscript{3} gas as a nitrogen source instead of N\textsubscript{2} gas. This is mainly due to the difficulties in breaking the strong and stable triple bond in N\textsubscript{2} gas for temperature below than 1000\textdegree{}C. Recently, in 2011, Kim et al. proved that the interaction of alumina with NH\textsubscript{3} gas to form AlN. Besides that, Mohd Amin et al., (2015) used NH\textsubscript{3} gas as nitrogen source in producing AlN thin films grown via sol-gel spin coating method. They able to produce AlN thin films with NH\textsubscript{3} flow rates of 500 sccm.
2.7 Summary

In this chapter, fundamental properties of AlN and AlGaN were given. Brief review on the research background of AlN and AlGaN thin films were presented. Moreover, a few growth techniques used for the deposition of AlN and AlGaN thin films were discussed. Principle of sol-gel spin coating method were also given. Next, an overview of the sol-gel spin coating growth method was discussed. Lastly, the factors that influence the growth of AlN and AlGaN thin films was given.
CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Introduction

In this chapter, methodology and instrumentation used in this study will be described. First, the sample preparations will be presented. Next, the basic deposition parameters used for the growth of AlN thin films are given. The growth of AlGaN thin films with different Al compositions will be discussed. After that, the instrumentation used to access the material’s properties will also be presented. This include the measurement setting, parameters, resolution of the characterization tools, etc. Finally, a summary will be given. The research flow chart is shown in Fig 3.8 at the end of this chapter.

3.2 Sample preparations

In this study, p-type (boron doped with resistivities: 1-10 ohm-cm) Si(111) wafer was used as substrate for deposition AlN thin films. Firstly, the 4 inch Si(111) wafer was cleaved into 1 cm × 1 cm. Prior to the spin coating process, the Si substrate is undergoing cleaning process. The Si substrate was immersed in acetone and undergone sonication for 5 min. Then, Si substrate was subjected into chemical solution of hydrofluoric acid: distilled water (HF: H2O) in ratio 1:50 for 1 min to remove the oxide from the films. Since HF is a highly corrosive and has high reactivity towards glass, the use of plastic containers is compulsory. Next, the Si substrate was rinsed using distilled water before was dried using nitrogen (N2) gas. Upon the cleaning process, the Si was subjected to plasma
treatment (Nano-tech Plasmaprep 100). The plasma treatment is a treatment where the surface of films will be converted from native hydrophobic to more hydrophilic surface in order to enhance the wetting problem. The plasma treatment process was carried out for 15 min at 60 W.

For the subsequent growth of AlGaN thin films, commercial AlN (thickness of 25 nm) on p-type Si(111) [AlN/Si (111)] was used as substrate. The AlN/Si(111) substrate was used to grow the AlGaN thin films due to the large lattice mismatch and the difference in thermal expansion between the AlGaN (as well as the GaN) layer with the Si substrate. The substrate undergoing the same method of cleaning process as for Si(111).

3.3 Methodology

3.3.1 Sol-gel spin coating of AlN thin films with different nitridation temperatures, durations, and ammonia flow rates

The precursor used in this study is aluminum nitrate nonahydrate (Al(NO$_3$)$_3$.9H$_2$O, Acros Organics) (purity 99.999%) powder. First, the Al(NO$_3$)$_3$.9H$_2$O powder was added into ethanol (purity 99.7%) and undergone sonication for 2 hours until the powder was completely dissolved. Next, diethanolamine was added. After that, the precursor remain under sonication until transparent precursor was obtained. The spin coating process was done by dropping the resulting precursor onto the Si substrate with spin rate of 2500 rpm for 30 s in ambient condition. After every spin coating process, the deposited film was left to dry on hot plate (WiseSTIR MSH-20D) for 5 min at 80°C. The spin process was carried
out for few times to obtain the homogeneous surface. The spin coater (Smart coater 110-B) and its schematic diagram used for depositing the films is shown in Fig 3.1.

![Spin coater system and its schematic diagram for films deposition process.](image)

Fig. 3.1: Spin coater system and its schematic diagram for films deposition process.

After that, thin films were undergone annealing process under N\(_2\) gas flow at 650°C for 15 min in tube furnace (Carbolite and Nabertherm) in order to dry and refine the surface of films, as shown in Fig. 3.2. Next, nitridation process were carried out to transform the deposited films into AlN and the process were carried out using the same tube furnace. The coated film undergone nitridation process with the continuous flow of NH\(_3\) gas (purity 99.98%) with 400 sccm flow rate. After reaction complete, the NH\(_3\) gas was switched off and the tube furnace was cool down with the flow of N\(_2\) gas. A blue yellowish color deposited layer was form on the surface of Si substrate. For the formation of AlN, the chemical routes can be summarized as follows:

\[
2\text{NH}_3(g) \rightarrow \text{N}_2 + 3\text{H}_2(g) \quad (3.1)
\]

\[
\text{NH}_3(g) \rightarrow \text{H} + \text{NH}_2 \quad (3.2)
\]

\[
\text{Al}_2\text{O}_3(s) + 2\text{NH}_3 \rightarrow 2\text{AlN}(_{g,s}) + 3\text{H}_2\text{O}(g) \quad (3.3)
\]
The NH\textsubscript{3} gradually decomposes into N\textsubscript{2} and H\textsubscript{2} species. Apart from N\textsubscript{2} and H\textsubscript{2} species, the other species such as, N, NH or NH\textsubscript{2} are also produced during the thermal decomposition of NH\textsubscript{3}. The Al\textsubscript{2}O\textsubscript{3} will react with NH\textsubscript{3} to produce AlN and water vapor. Table 3.1 summarizes the deposition parameters of the sol-gel spin coating growth of AlN thin films under various nitridation temperatures and durations.

![Fig. 3.2: Tube furnace used for both annealing and nitridation process with its schematic diagram.](image)

For more understanding of the nitridation process, time-temperature chart in furnace for nitridation process is shown in Fig. 3.3. There were four stages in nitridation process. The first stage (a), was the stage where the furnace was switched on and the temperature was ramped up with heating rate of 10°C/min until the desired temperature was achieved. The second stage (b) takes place when the desired temperature was achieved. During this stage, the N\textsubscript{2} gas was flowed through the furnace around 20 min to remove the excess oxygen before the sample was placed in the furnace. Next, the sample was placed in the furnace and N\textsubscript{2} gas was then switched off and NH\textsubscript{3} gas was continuously flowed under a constant desired flow rate. The NH\textsubscript{3} gas was continuously flowed until the
desired nitridation duration was achieved. In the third stage (c), the furnace was allowed to cool down naturally to room temperature. During the cooling process, NH₃ gas was switched off and N₂ gas was flowed to remove the excess NH₃ gas. In the last stage (d), the sample was taken out after the furnace was cool down under N₂ gas ambient for around 45 min. Then, N₂ gas was switched off as well as the furnace.

![Time-temperature chart for nitridation process.](image)

Fig. 3.3: Time-temperature chart for nitridation process.

Table 3.1: Deposition parameters of the sol-gel spin coating growth of AlN thin films under various nitridation temperatures, nitridation durations, and ammonia flow rates.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Nitridation temperature (°C)</th>
<th>Nitridation duration (min)</th>
<th>NH₃ flow rate (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1050</td>
<td>60</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>60</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>60</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>60</td>
<td>400</td>
</tr>
<tr>
<td>2</td>
<td>1150</td>
<td>45</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>60</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>75</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>1150</td>
<td>60</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>60</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>60</td>
<td>500</td>
</tr>
</tbody>
</table>
3.4 Sol-gel spin coating growth of Al\textsubscript{x}Ga\textsubscript{1-x}N thin films

In this study, the lattice mismatch between GaN or AlGaN layers with the Si substrates was overcome by using AlN buffer layer. The commercial AlN templates with thickness of 25 nm and grown on p-type Si(111) substrates were purchased from Kyma Technologies. This commercial AlN templates were grown by PVDNC method. The growth of Al\textsubscript{x}Ga\textsubscript{1-x}N with different Al compositions, i.e., 0, 0.1, and 0.2, thin films on commercial AlN/Si (111) substrate via sol-gel spin coating technique was carried out. Three types of precursors were prepared. Gallium nitrate hydrate [Ga(NO\textsubscript{3})\textsubscript{3}.\times\textsubscript{H\textsubscript{2}O}] (purity 99.999%, Sigma Aldrich) powder was mixed with aluminum nitrate nonahydrate (Al(NO\textsubscript{3})\textsubscript{3}.9\textsubscript{H\textsubscript{2}O}) (purity 99.999%, Acros Organics) powder with different Al concentrations (0, 0.1, and 0.2). The powders were dissolved in ethanol (purity 99.7%) and undergone ultrasonication until completely dissolved. Then, a few drops of diethanolamine were slowly added into solution and lastly, a transparent solution was obtained.

To obtain the precursor with different Al compositions, different masses of Ga(NO\textsubscript{3})\textsubscript{3}.\times\textsubscript{H\textsubscript{2}O} and Al(NO\textsubscript{3})\textsubscript{3}.9\textsubscript{H\textsubscript{2}O} powder were needed to obtain the precursor with different Al compositions. The mass of the powder needed can be calculated using (Callister et al., 1997):

\[ n_{Ga} = \frac{m_{Ga}}{w_{Ga}} \]  \hspace{1cm} (3.4)

\[ x_{Al} = \frac{n_{Al}}{n_{Al} + n_{Ga}} \times 100 \]  \hspace{1cm} (3.5)
where \( n_{Ga} \) and \( n_{Al} \) denote the number of moles of gallium nitrate hydrate and aluminum nitrate nonahydrate powders, respectively. The \( m_{Ga} \) and \( m_{Al} \) represent the mass of the gallium nitrate hydrate and aluminum nitrate nonahydrate powders, respectively. The \( w_{Ga} \) and \( w_{Al} \) denote the molecular weight for gallium nitrate hydrate (255.74 g/mol) and aluminum nitrate hydrate (375.13 g/mol) powders; and \( x_{Al} \) is the composition of Al used. The masses of the powders used to prepare precursors with different Al compositions are listed in Table 3.2.

Table 3.2: \( \text{Al}_{x}\text{Ga}_{1-x}\text{N} \) thin films with different Al compositions grown on AlN/Si(111) substrate.

<table>
<thead>
<tr>
<th>Al compositions, ( x )</th>
<th>Mass gallium nitrate hydrate powder (g)</th>
<th>Mass aluminum nitrate nonahydrate (g)</th>
<th>DEA (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.5</td>
<td>-</td>
<td>0.75</td>
</tr>
<tr>
<td>0.1</td>
<td>2.25</td>
<td>0.37</td>
<td>0.75</td>
</tr>
<tr>
<td>0.2</td>
<td>2.0</td>
<td>0.73</td>
<td>0.75</td>
</tr>
</tbody>
</table>

The spin process was performed at 2500 rpm for 25 s. The deposition and spin coating process were repeated for 10 times to obtain homogeneous surface. After every spin coating process, the deposited film was dried on hot plate at 100°C for 5 min. To refine and dry the deposited films, the thin film was undergone annealing process under \( \text{N}_2 \) ambient at 950°C for 15 min. Lastly, the nitridation process was conducted to transform the film into GaN (or AlGaN) at 950°C for 75 min under the flow of \( \text{NH}_3 \) gas at 400 sccm. The furnace was cooled down after nitridation process and the sample was then collected.
for characterization. The summary of deposition conditions for the deposition of AlGaN thin films with different Al compositions are listed in Table 3.3.

Table 3.3: Summary of the deposition conditions for the deposition of AlGaN thin films with different Al compositions grown on AlN/Si(111) substrate via sol-gel spin coating technique.

<table>
<thead>
<tr>
<th>Al composition, x</th>
<th>Nitridation temperature (°C)</th>
<th>Nitridation duration (min)</th>
<th>NH₃ flow rate (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>950</td>
<td>75</td>
<td>400</td>
</tr>
<tr>
<td>0.1</td>
<td>950</td>
<td>75</td>
<td>400</td>
</tr>
<tr>
<td>0.2</td>
<td>950</td>
<td>75</td>
<td>400</td>
</tr>
</tbody>
</table>

3.5 Characterizations

In this section, the details of characterization tools are described. These include the parameters, operating conditions and the resolution of the instrumentations required for measurements. The surface morphology, structural and optical properties for all the deposited samples were characterized by using XRD, FESEM, EDX and Raman spectroscopy.

3.5.1 XRD measurements

XRD is a powerful non-destructive method to determine the crystalline quality, crystallite size, strain and the preferred orientation of polycrystalline materials as well as chemical composition (Wolgamott et al., 2017). It has limitless possibilities in measuring for all type of samples such as thin films, powders, nano materials and others.

For XRD measurement, a beam of X-rays with wavelength λ is directed onto a sample at a specific angle of θ. The X-rays are scattered (or diffracted) in all direction by
electrons present in the material (see Fig. 3.4). The scattered rays must be scattered coherently and occurs at an angle of $\theta$ to the planes. This geometric condition is known as Bragg’s Law:

$$n\lambda = 2d_{hkl}\sin\theta_{hkl} \tag{3.7}$$

where $n$ is the order number of reflection which in integer form, $\lambda$ is the wavelength of x-ray radiation source, $d_{hkl}$ is the interplanar spacing between two consecutive diffracting planes, $\theta_{hkl}$ is the Bragg angle which is the incident and diffraction angle.

The most common crystalline structure for AlN is cubic or hexagonal structure. The value of $d_{hkl}$ for both cubic and hexagonal structure can be calculated using following relations (Cho, 2009):

Cubic structure:

$$d_{hkl}^2 = \frac{a^2}{\sqrt{h^2 + k^2 + l^2}} \tag{3.8}$$

Hexagonal structure:

$$d_{hkl} = \frac{1}{\sqrt{\frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right)}} \tag{3.9}$$

where $a$ and $c$ are the lattice constants in-plane and out-of-plane, respectively. The lattice constant of $a$ and $c$ can be calculated using Eqs. (3.5) and (3.6).
Fig. 3.4: Schematic diagram of diffraction of X-rays in a crystalline materials under Bragg condition (Callister et al., 1997).

The sharp of the diffraction peak provides the details whether the layer is crystalline or amorphous in nature (Wolgamott et al., 2017). The intensity, width and the position of the peak will provide the crystallite size of the materials. In order to calculate the crystallite size, the Scherrer’s formula is used.

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

(3.10)

where \( D \) is the crystallite size in the direction to the lattice planes \( hkl \), \( K \) is the shape constant factor with typical value of 0.9, \( \lambda \) is the wavelength of CuK\( \alpha \) (\( \lambda = 1.5406\text{Å} \)), \( \beta \) is the FWHM in radians and \( \theta \) is Bragg’s angle.

High-resolution (HR) X-ray diffractometer (PANalytical X’Pert Pro MRD) radiation source (\( \lambda = 1.5406\text{Å} \)) with Cu-K\( \alpha_1 \), is used to obtain the crystallinity and quality of the samples, as shown in Fig. 3.5. XRD phase analysis with absolute scan of 2theta-
omega (2θ-ω) is utilized to measure the crystalline quality of the thin films in range of 20° to 80°. The accelerating voltage and current used are 40 kV and 30 mA, respectively. After the measurement, the data will be analyzed using PANalytical X’Pert Highscore Plus. The structural properties of the thin films such as the peak orientation, FWHM, lattice parameter and crystalline quality of the samples were determine using this software.

Fig. 3.5: XRD system (PANalytical X’Pert PRO MRD PW3040) and its schematic diagram used for structural characterization.

3.5.2 Field-emission scanning electron microscopy (FESEM)

FESEM is a type of electron microscope which is used to obtain the surface morphology and the cross sectional of films. It uses with electron instead of light to produce high magnifications up to 300,000× images of the sample. Unlike the conventional scanning electron microscope (SEM), FESEM can produce clearer images and smaller structure on the sample’s surface where as small as 1 nanometer can be observed.
Basically, to generate FESEM image of specimen, a focus beam of electron is used. The details of working principal of FESEM are discussed as follows. An electron beam is bombarded from field emission source with high energy that can be reach up to 50 keV on the specimen’s surface. These electrons are focused in high vacuum condition and were deflected by electromagnetic lenses which are condenser lens and objective lens. Condenser lens is used to control the diameter of the beams. While, objective lens used to focus the electron beam onto the specimen. The electron beam that strikes onto the specimen will then interact with the atoms on the specimen’s surface thus, produces secondary electrons. Finally, detector will collect the secondary electrons and produces an electron signal. This electron signal is amplified and transformed into a high resolution image.

Fig. 3.6 shows the FESEM (Model FEI Nova NanoSEM 450) system and its schematic diagram that employed to examine the surface and the cross-sectional morphologies of the sample. The measurements were scanned at 10,000× and 100,000× magnifications for surface morphology. While 150,000× magnifications for cross-sectional thickness of the samples. For the cross-sectional thickness measurements, the backside of the sample was cleaved into half using diamond scriber. The sample is scanned using accelerating voltage of 10 kV for both measurements.
3.5.3 Energy dispersive X-ray (EDX)

EDX system is a non-destructive method that is widely used to identify the elements present and to investigate the elemental composition of the sample. EDX system is usually used in conjunction with FESEM (see Fig. 3.7) or transmission electron microscopy (TEM) instruments. When a high energy beam of X-ray is impinged on the sample, an electron is ejected from the shell thus creating an electron hole. This atom is in unstable state and thus, an electron from the outer shell, which situated at higher energy level will then fill up the vacancy. The electron loses its energy in the form of an X-ray photon. The energy of X-rays is equal to the potential energy different between the higher energy shell and the lower energy shell. The potential energy differences between those two shells and the atomic structure of the element from which they were emitted allows the elemental composition of the specimen to be measured. The EDX system measure the intensity of emitted X-rays versus their X-ray energy. From the EDX spectrum, the energy
of X-ray represents a characteristic of the element form which the X-ray is emitted, while the intensity of the peak represents the concentration of the element in the specimen.

EDX is a system that attached to FESEM was utilized in order to analyze the elementary composition of the samples. For this measurement, EDX (MaxN Silicon Drift Detector with 50 mm$^2$) was used in conjunction of FESEM system. The measurements are performed at 10,000× magnification with accelerating voltage of 10 kV.

### 3.5.4 Raman spectroscopy

Raman spectroscopy is a non-destructive technique that used to examine the lattice vibrational and rotational modes of the materials. It is a scattering technique that were based on the inelastic scattering of monochromatic radiation of light. In Raman scattering, a monochromatic light from an excitation source which is laser is incident onto a sample then, a beam of light interacts with matter. The light in terms of photons might be absorbed or scattered. During this process, some energy is transmitted that causes the transition of electron from ground state level to virtual state level. The virtual or excited state level are relatively unstable and will causes instantaneously decay to the ground state by scattering process.

Generally, Raman spectroscopy system is made up of three important components: an excitation source (typically a laser), spectrometer and detector. The most dominant process in Raman spectroscopy is elastic scattering which is Rayleigh scattering. While Raman scattering is considered as an extremely weak process which approximately 1 in $10^7$ of photon are inelastically scattered. Therefore, a monochromatic and highly intense light source (laser) is needed. A spectrometer used filter to produce a very narrow range
sample region. The detector which is charge-coupled device detector is used to detect the Raman shifted radiation. Raman intensity of the inelastic scattered light as a function of the frequency difference in wavenumber from the incident radiation represents a Raman spectrum. This difference is known as Raman shift. The Raman shift is independent of the frequency of the incident radiation. The Raman bandwidth is related to the structure crystallinity of the materials (Kuball, 2001).

Generally, hexagonal wurtzite AlN crystal has six first-order Raman active modes namely $A_1$(TO), $A_1$(LO), $E_1$(TO), $E_1$(LO), $E_2$(high) and $E_2$(low) (Liu et al., 2016). Both $E_2$ modes are Raman active and the $A_1$ and $E_1$ modes are both Raman and infrared active (Kuo et al., 2008). Two Raman active modes which are $E_2$(high) and $A_1$(LO) phonons are commonly used to monitor the crystallinity quality and the free carrier concentration of the deposited films, respectively (Xi et al., 2009). As for Al$_x$Ga$_{1-x}$N thin films, the $A_1$(LO) phonon mode exhibits one-mode behavior and as the Al composition increases, the frequency of GaN $A_1$(LO) mode continuously increases to AlN $A_1$(LO) mode, with frequency dependence given by equation (Kuball, 2001):

$$\omega A_1(LO) = 746 + 169.5x + 11.7x^2 - 36.6x^3$$

(3.11)

where $\omega A_1(LO)$ is the frequency of $A_1$(LO) mode in units of cm$^{-1}$ (valid for $x > 0.05$) for unstrained Al$_x$Ga$_{1-x}$N.

Raman measurements are performed by Horiba Jobin Yvon HR800UV at room temperature, as shown in Fig 3.7. An argon ion laser operates at 514.5 nm with 20 mW incident laser power was used to perform the Raman measurements. A ×50 LW of microscope objective lens is used to focus the laser on the sample. The Raman
measurements are carried out in range of 200 to 1000 cm\(^{-1}\). The accumulation and acquisition time used throughout the measurements are 2 and 2 s, respectively. Before the measurements, the Raman system is calibrated using bare Si sample where the zone-centre Raman mode for Si is located at 520 cm\(^{-1}\).

For Raman scattering, the measurements are carried out in the \(z\) (x, unpolarized) \(\tilde{z}\) scattering configuration, where \(z\) and \(\tilde{z}\) are the directions of propagation of the incident laser and the scattered Raman light, respectively.

Fig. 3.7: Raman system (Horiba Jobin Yvon HR800UV) and its schematic diagram (Adapted from Gouadec et al., 2007) used for this work.

### 3.6 Summary

In this chapter, the sample preparation includes the details of experimental set up and the deposition parameter used in this study have been presented. Apart from that, the characterization tools, the measurement parameters and conditions have been discussed.
Fig. 3.8: Research flow chart of the study.
CHAPTER 4

THE EFFECTS OF NITRIDATION TEMPERATURES, DURATIONS AND AMMONIA GAS FLOW RATES ON THE SYNTHESIS OF AlN THIN FILMS

4.1 Introduction

In this chapter, the growth and characterization of AlN thin films grown by sol-gel spin coating method will be discussed. Firstly, the effects of nitridation temperatures and durations on the synthesis of AlN thin films will be investigated. Next, the growth and characterization of AlN thin films with different ammonia gas flow rates will be studied. In these studies, the p-type Si(111) substrate was used. The crystalline structure, surface morphology and optical properties of the AlN thin films were analyzed using various characterization tools. At the end of this chapter, the remarks of all the investigation will be presented.

4.2 Effects of nitridation temperature on the growth of AlN thin films prepared by sol-gel spin coating method

Fig. 4.1 shows the sample’s image before and after nitridation process grown by sol-gel spin coating method. For sample before nitridation (annealing) process, a smooth and rainbow color on the deposited thin film can be observed, as shown in Fig. 4.1(a). Fig. 4.1(b) shows the image of the sample nitridated at temperature of 1150°C for 60 min. Since all the samples look alike after nitridation process regardless grown under different nitridation temperatures, nitridation durations, and ammonia flow rates, thus only one sample’s image is displayed. A blue and yellowish can be seen from the sample after
nitridation process. From both images, edge beads can be observed at the edge of the samples. The edge beads are due to the formation of excess fluid that remain after the spin coating process. This edge bead is normally seen for rectangular substrate.

![Fig. 4.1: Images of sample (a) before and (b) after nitridation process.](image)

### 4.2.1 Crystalline structure

Fig. 4.2 displays the XRD patterns of AlN thin films grown under different nitridation temperatures via sol-gel spin coating method. Fig. 4.2(a) shows the XRD pattern of the deposited thin film nitridated at 1050°C. It can be seen that only one diffraction peak corresponds to Si(111) peak can be observed at 28.4°. This result revealed that amorphous thin film may be formed at this temperature (will be proven later in Raman results). Figs. 4.2(b)-(d) show the XRD patterns of thin films after nitridation process at 1100°C, 1150°C, and 1200°C, respectively. For sample nitridated at 1100°C, apart from the Si(111) peak, diffraction peak that corresponds to AlN(002) can be observed at ~36.0°. All the diffraction peaks were ascribed to the formation of hexagonal wurtzite structure AlN (with reference to JCPDS 00-008-0262). At 1100°C, the conversion of the Al₂O₃ to AlN started to occur. Further increment of nitridation temperature to 1150°C, the intensity of diffraction peak of AlN(002) increases. However, for sample nitridated at 1200°C, the diffraction peak intensity of AlN(002) decreases. Therefore, sample nitridated at 1150°C has the highest intensity among all the samples.
Fig. 4.2: XRD patterns of deposited thin films under different nitridation temperatures: (a) 1050°C, (b) 1100°C, (c) 1150°C, and (d) 1200°C.

The obtained FWHM and crystallite size, are displayed in Table 4.1. It can be clearly seen that as the nitridation temperature increases from 1100°C to 1150°C, the FWHM decreases while crystallite size increases, which indicates an improvement of structural quality of AlN. However, as the nitridation temperature increases to 1200°C, the FWHM increases while the crystallite size decreases, which implied the degradation of AlN crystal quality. Generally, high temperature tend to provoke more NH$_3$ decomposition and reduces its yield (Elagin et al., 2013), thus resulting in lower AlN crystal quality. As compared to the reported work by Imura et al. (2008) (that is, experiments with reaction temperature up to 1600°C), the conversion of Al$_2$O$_3$ to AlN can be produced at lower temperature.
Table 4.1: FWHM and crystallite size of AlN thin films extracted from AlN(002) diffraction peak deposition under various nitridation temperatures: (a) 1050°C, (b) 1100°C, (c) 1150°C, and (d) 1200°C.

<table>
<thead>
<tr>
<th>Nitridation temperature (°C)</th>
<th>FWHM (°)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1050</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1100</td>
<td>0.67</td>
<td>12.47</td>
</tr>
<tr>
<td>1150</td>
<td>0.59</td>
<td>14.32</td>
</tr>
<tr>
<td>1200</td>
<td>0.66</td>
<td>12.66</td>
</tr>
</tbody>
</table>

4.2.2 Surface morphology

FESEM images of deposited thin films grown under various nitridation temperatures are shown in Fig. 4.3. Different types of surface features can be seen from all the samples. This implied that the nitridation temperature has significant effects on the surface morphologies of the deposited AlN thin films. From Fig. 4.3(a), the surface morphology of the deposited films shows a relative smooth and homogeneous surface throughout all the Si(111) substrate. There are irregular shaped grains formed on the surface. This may be due to the formation of the amorphous thin films as reported in XRD result previously, in which no AlN peak was detected at 1050°C. At nitridation temperature of 1100°C, the surface of AlN thin films exhibits densely packed grains with the present of pinholes. It is worthy to point out that nitrogen atoms have successfully replaced the oxygen atoms to form AlN. Further extension of nitridation temperature to 1150°C, resulted in smooth and uniform surface with slightly bigger and densely packed grains as compared with sample nitridated at 1100°C. This phenomenon is most likely due to the increment formation of AlN particles was increases where atoms have enough energy to occupy the correct site (Al and N site) of the crystal lattice (Kim et al., 2004) at higher temperature. However, as the nitridation temperature increases to 1200°C, the
grains start to agglomerate and form larger particles, in which its scattered around the substrate. These findings indicated that the nitridation temperature has significant effects on the surface morphologies of AlN thin films.

The inset of Fig. 4.3 shows the FESEM cross-sectional images of the samples. The thickness of the deposited film nitridated at 1050°C was 176 nm. As the nitridation temperature increases, the thickness of the deposited AlN thin films was gradually decreased. The decrement of the film’s thickness most probably due to the thermal etching effects induced from the increment of partial pressure of H₂ (Lee et al., 2017). This phenomenon tends to wash off the deposited films, and thus led to the decrease of the film’s thickness. From these findings, the thickness of AlN thin films grown by sol-gel spin coating method closely depends on the nitridation temperature.

![FESEM images](image)

Fig. 4.3: High-magnification (×100 K) FESEM images of the deposited films under various nitridation temperatures: (a) 1050°C, (b) 1100°C, (c) 1150°C, and (d) 1200°C. The inset shows the cross-sectional FESEM images captured at higher magnification (×150 K).
Fig. 4.4 shows the EDX results of the deposited films grown under various nitridation temperatures. At nitridation temperature of 1050°C, the oxygen component in the films is dominant as compared with Al and N elements. According to Brien and Pigeat (2008), higher oxygen contents led to higher defects density, thus producing an amorphous phase. This result is in good agreement in XRD results previously, in which the amorphous thin films were formed at this temperature. As the nitridation process takes place, the oxygen component in amorphous AlN started to reduce by the reducing agent of NH₃, thus transforming the films into crystalline AlN. At nitridation temperature of 1100°C, the atomic percentage of oxygen component decreases with the presence of nitrogen component. At this stage, the deposited film has started to transform into AlN thin film, i.e., as evidenced from XRD results that were discussed previously. As the temperature increases to 1150°C, the presence of nitrogen composition was further increased while the oxygen composition exhibits the opposite trends, as shown in Fig 4.4(c). These results implied that higher nitridation temperature is needed in order for the aluminum atoms to react with nitrogen atom from NH₃ to form AlN. The high atomic percentage of oxygen contents (~10%) is most likely due to the oxidation during the cooling process, in which the sample was cooled under the atmospheric ambient. At higher temperature of 1200°C, it was found that the composition of the nitrogen and aluminum components were decreased. This is most likely due to the desorption of nitrogen and thermal etching effects. This analysis is consistent with the cross-sectional images, in which the thickness of the deposited films was decreased as the nitridation temperature increases.
4.2.3 Optical properties

Fig. 4.5 shows the Raman scattering spectra of AlN thin films. A very strong Raman band located at ~521 cm$^{-1}$ was originate from the Si(111) substrate. The scale intensity of Raman spectra has been magnified several times to reveal low intensity of Raman phonon modes. A Raman diffraction peak which corresponds to E$_2$(high) mode of wurtzite structure AlN can be seen. This phonon mode was comparable to the values reported for bulk AlN at 659 cm$^{-1}$ (Song et al., 2006) and for unstrained AlN at 657 cm$^{-1}$ (Kuball et al., 2001). Raman spectrum with broad scattering regions reflects the shape of phonon density state function of amorphous or nanocrystalline, thus determine the films are amorphous or nanocrystalline (Hobert et al., 1999). From Fig. 4.6(a), a very weak and broad E$_2$(high) is observed at 662 cm$^{-1}$. This weak and broad peak is due to the amorphous phase, in which it is proven in XRD results previously, where no diffraction peak of AlN was observed. The intensity of E$_2$(high) mode increases as the nitridation temperature increases to 1150$^\circ$C and then, it starts to decrease at 1200$^\circ$C. For samples nitridated at temperatures
of 1050°C, 1100 °C, 1150°C, and 1200°C, the obtained FWHM are 41.14 cm⁻¹, 39.28 cm⁻¹, 26.04 cm⁻¹, and 29.43 cm⁻¹, respectively. From the obtained FWHM, as the nitridation temperature increases to 1150°C, the FWHM decreases. This indicates an improvement of AlN crystal quality. However, as the nitridation increases to 1200°C, the FWHM also increases and this implied the degradation of AlN crystal quality. This is due to the higher decomposition of NH₃ occurred at higher temperature, thus reduces the crystallinity of AlN thin films. The A₁(LO) phonon mode is related to the presence free carrier charge (Gaspar et al., 2017) in the sample. Thus, the free carrier for all the samples were too low, therefore, no A₁(LO) mode is detected. Generally, A₁(LO) mode is very weak in nature. The damping in the AlN thin films samples were too high and hence, intensity is very low.

Fig. 4.5: Raman spectra thin films deposited under various nitridation temperatures: (a) 1050°C (b) 1100°C, (c) 1150°C, and (d) 1200°C.

Apart from investigate the optical phonon mode, Raman spectroscopy is also used to study the stress information. A shift of Raman phonon frequency can be induced by
internal and external parameters including stress (Oliveira et al., 2001). To analyze the stress state of the samples, $E_2$(high) is normally used as it is highly sensitive to stress (Kuo et al., 2008). In order to detect the stress in AlN thin films, the stress-free AlN of $E_2$(high) at 657.4 cm$^{-1}$ was used as reference (Prokofyeva et al., 2001). Note that, if the value of AlN $E_2$(high) phonon mode is larger than 657.4 cm$^{-1}$, the AlN samples might having some compressive stress, on the other hand, the AlN samples might developed some tensile stress if the value of $E_2$(high) is smaller than that. The peak position of $E_2$(high) phonon mode of samples nitridated at 1050°C, 1100°C, 1150°C and 1200°C are 664.1 cm$^{-1}$, 664.1 cm$^{-1}$, 659.8 cm$^{-1}$, and 659.8 cm$^{-1}$, respectively. From the detected peaks position, it is clearly found that all the AlN samples were subjected to compressive stress.

4.3 Effects of nitridation duration on the growth of AlN thin films prepared by sol-gel spin coating method

4.3.1 Crystalline structure

Fig. 4.6 shows the XRD patterns of AlN thin films deposited under various nitridation durations (45, 60, and 75 min) at 1150°C in NH$_3$ ambient. For all samples, two diffraction peaks which correspond to Si(111) and AlN(002) are observed at around 28.4° and 34.0°, respectively. From Fig. 4.6, it can be observed that as the nitridation duration increases from 45 to 60 min, the intensity of diffraction peak AlN(002) increases. The XRD patterns shows the hexagonal wurtzite structure and comparable with the JCPDS 00-008-0262. According to Lee et al, (2017), longer nitridation duration tends to promote a higher decomposition rate of NH$_3$, thus providing sufficient duration for the diffusion of
N atoms into the deposited thin films and producing a better crystal quality of AlN. However, as the nitridation is prolong to 75 min, the intensity of the AlN(002) diffraction peak decreases. At this temperature, the nitrogen desorption might have occurred, thus, restrict the formation of AlN (Lee et al., 2017). As compared to the previous studies using different growth techniques (Lee et al., 2002; Lee et al., 2005), the nitridation duration for the sol-gel spin coating growth of AlN requires shorter nitridation duration to produce AlN as compared with the reported duration of more than 2 hours.

Fig. 4.6: XRD patterns of AlN thin films deposited under various nitridation durations: (a) 45 min, (b) 60 min, and (c) 75 min.

The obtained FWHM and crystallite size are displayed in Fig. 4.7. It can be clearly seen that as the nitridation increases to 60 min, the FWHM increases whereas the crystallite size shows the opposite trends. Sample nitridated for 60 min has the biggest
crystallite size (smallest FWHM), which indicates an improvement of structural quality of AlN. However, as the nitridation increases to 75 min, the FWHM increases while the crystallite decreases which implied the degradation of AlN crystal quality.

Fig. 4.7: FWHM (■) and crystallite size (▲) of AlN thin films extracted from AlN(002) diffraction peak deposited under various nitridation durations: (a) 45 min, (b) 60 min, and (c) 75 min.

4.3.2 Surface morphology

FESEM images of the AlN thin films grown under various nitridation durations from 45 to 75 min are shown in Fig 4.8. Inset are the cross-sectional images of the sample. For nitridation duration of 45 min, the AlN crystals start to deposit around the substrate with the presence of many pores (represented by dark spots). This phenomenon may be due to the grains were not fully packed. With the increasing of nitridation duration to 60 min, the grains are densely packed (i.e., less dark spots) and a smooth and homogenous surface was formed. However, further increasing the nitridation duration to 75 min, unpacked and scattered grains can be observed as illustrated in Fig. 4.8(c). The FESEM findings were in good agreement with the XRD results, where the intensity of AlN(002)
peak as well as the crystallite size were decreased as nitridation duration increased. In general, the thickness of the AlN thin films gradually decreases as the nitridation durations increases. This may probably due to nitrogen desorption effect (Lee et al., 2017) where the film will become thinner as it expose longer to the NH₃ during nitridation. These findings showed that longer nitridation duration tends to degrade the homogeneity of surface morphology and the thickness of AlN thin films.

Fig. 4.8: High-magnification (×100 K) of FESEM images of AlN thin films deposited under various nitridation durations: (a) 45 min, (b) 60 min, and (c) 75 min. The inset shows the cross-sectional FESEM images captured at higher magnification (×150 K).
Fig. 4.9 displays the EDX analysis results for AlN thin films grown under various nitridation durations. Overall, all the samples except for sample nitridated at 75 min, consist of atomic percentage ratio of 1:1 for aluminum and nitrogen compositions. Sample nitridated for 60 min shows the lowest oxygen composition. For nitridation durations of 45 min and 60 min, the atomic percentages of aluminum and nitrogen were gradually increased; while the atomic percentage of oxygen was reduced. These results suggest that longer nitridation duration (60 min) will provide sufficient time for aluminum atoms to associate with nitrogen atoms to form AlN. However, as nitridation duration increases to 75 min, the aluminum and nitrogen compositions were reduced whereas the oxygen composition was increased. From the EDX results, the optimum nitridation duration was 60 min.

Fig. 4.9: EDX analysis results of the AlN thin films grown under various nitridation durations: (a) 45 min, (b) 60 min, and (d) 75 min.
4.3.3 Optical properties

Fig. 4.10 shows the Raman spectra of AlN thin films deposited under various nitridation durations. A very strong Raman band corresponds to Si(111) substrate was observed at ~521 cm\(^{-1}\). The peak position of \(E_2\) (high) phonon mode for samples nitridated at 45 min, 60 min, and 75 min are 663.0 cm\(^{-1}\), 659.8 cm\(^{-1}\), and 659.8 cm\(^{-1}\), respectively. The peak position of \(E_2\) (high) obtained were compared with the stress-free AlN of \(E_2\) (high) at 657.4 cm\(^{-1}\) (Prokofyeva et al., 2001). It was found that all the AlN samples were subjected to compressive stress. The \(A_1\) (LO) phonon mode is related to the presence free carrier charge (Gaspar et al., 2017) in the sample. Thus, the free carrier for all the samples were too low, therefore, no \(A_1\) (LO) mode is detected. Generally, \(A_1\) (LO) mode is very weak in nature. The damping in the AlN thin films samples were too high and hence, intensity is very low.

![Raman spectra of AlN thin films](image)

Fig. 4.10: Room temperature Raman spectra of AlN thin films deposited under various nitridation durations: (a) 45 min, (b) 60 min, and (c) 75 min.
4.4 Growth and characterization of AlN thin films under different ammonia gas flow rates

4.4.1 Crystalline structure

To obtain good crystal quality of AlN, it is necessary to remove the oxygen content in the films via nitridation process with the flow of NH$_3$. The NH$_3$ is used as a nitrogen source and acts as reducing agent. Al$_2$O$_3$ will react with NH$_3$ to produce AlN and water vapor as shown in Eq. 3.3. It is quiet challenging to remove oxygen content with the NH$_3$ gas treatment (Elagin et al., 2013). However, this can be achieved by using a suitable growth nitridation conditions including suitable NH$_3$ flow rate.

Fig. 4.11 shows the XRD patterns of AlN thin films grown under various NH$_3$ flow rates. The growth mechanism of AlN thin films under different NH$_3$ flow rates for nitridation process at 1150°C for 60 min will be discussed in detail. The previous studies on the optimum nitridation temperature and duration were used in this study. All the samples exhibit a common diffraction peak at 28.4° which originated from the Si(111) peak. Apart from that, a strong diffraction peak around 36.0° which corresponds to AlN(002) was observed. All the diffraction peaks were ascribed to the formation of hexagonal wurtzite structure AlN (with reference to JCPDS 00-008-0262). From Fig. 4.11, no formation of Al$_2$O$_3$ peak was detected. This finding shows that the Al$_2$O$_3$ was successfully transformed into AlN under various nitridation NH$_3$ flow rates. Sample nitridated at 400 sccm has highest AlN(002) peak intensity. At 500 sccm of NH$_3$ flow rate, the peak intensity of AlN(002) decreased. The FWHM of samples nitridated under NH$_3$ flow rates of 300 sccm, 400 sccm, and 500 sccm are 0.57°, 0.51°, and 0.53°, respectively.
From these results, the FWHM decreases as the NH$_3$ flow rates increases to 400 sccm. This implied an improvement of crystalline quality of AlN. However, as the NH$_3$ flow rates increases to 500 sccm, the FWHM increases which implied the degradation of AlN crystal quality. It is known that higher NH$_3$ flow rate will decompose higher N$_2$ and H$_2$ molecules. Thus, at 500 sccm, the growth of AlN take place in N-rich condition, which the excess N adatoms reduce the mobility of Al adatoms (Hsu et al., 2007) and resulting in degraded of AlN crystal quality. From these findings, NH$_3$ flow rate of 400 sccm is the optimum flow rate.

Fig. 4.1: XRD patterns of AlN thin films grown under different NH$_3$ flow rates: (a) 300 sccm, (b) 400 sccm, and (c) 500 sccm.
4.4.2 Surface morphology

Fig. 4.12 displays the FESEM images of the deposited AlN thin films on the Si(111) substrate grown under various NH$_3$ flow rates. For NH$_3$ flow rate of 300 sccm, the AlN crystals start to deposit around the substrate with the presence of pinholes. The present of pinholes is due to the formation of grains not fully packed. As the NH$_3$ flow rate increases to 400 sccm, the grains grew bigger and no pinholes were observed, as shown in Fig. 4.12(b). This is due to the increment formation of AlN particles, in which it can be explained from EDX results (Fig. 4.12(b) which will be discussed later) where the percentage of atomic ratio between aluminum and nitrogen compositions was approximately 1:1. This finding was consistent with the XRD result, in which high crystal quality of AlN with lowest FWHM was obtained at 400 sccm of NH$_3$ flow rate. For NH$_3$ flow rate of 500 sccm, the grains start to agglomerate and form particles in bigger particles. As a result, the surface of AlN thin films becomes rougher.

The inset of Fig. 4.12 is the cross-sectional images of the sample. It can be clearly seen that as the flow of NH$_3$ increases, the thickness of the deposited films decreases. In general, higher flow of NH$_3$ will decompose more N$_2$ and H$_2$ molecules. Higher partial pressure of H$_2$ induces thermal etching effects (Koukitu et al., 1997). Consequently, the deposited films tend to wash off and led to the decrement of film thickness. The obtained results showed that the NH$_3$ flow rate affects the surface morphologies and the thickness of AlN thin films.
Fig. 4.12: High-magnification (×100 K) of FESEM images of deposited AlN thin films under various NH$_3$ flow rates: (a) 300 sccm, (b) 400 sccm, and (c) 500 sccm. The inset shows the cross-sectional FESEM images captured at high-magnification (×150 K).

Fig. 4.13 displays the EDX analysis results of the AlN thin films grown under various NH$_3$ flow rates. Fig. 4.13(b) shows that the ratio of atomic percentage between aluminum and nitrogen composition is approximately 1:1 and with the lowest oxygen composition. The presence of oxygen (less than 13%) most probably during the sample cooling. This finding indicates that optimum formation of AlN thin films under different NH$_3$ flow rate is 400 sccm. This amount of NH$_3$ flow rate during nitridation process is sufficient for fully convert the Al$_2$O$_3$ to AlN. It can be clearly seen that as the NH$_3$ flow rate increases, the aluminum and nitrogen compositions decreased. Generally, higher NH$_3$ flow rate will decompose more N$_2$ and H$_2$. The H$_2$ will act as an etching agent, in which it will restrict the diffusion of nitrogen element into the film.
Fig. 4.14 shows the Raman spectra of AlN thin films grown under different NH$_3$ flow rates measured at room temperature. A very strong band located at $\sim$521 cm$^{-1}$ for all the samples is originated from the Si(111) substrate. Besides that, the $E_2$(high) phonon mode of AlN was observed at 660 cm$^{-1}$. Fig. 4.14(b) shows a narrow AlN $E_2$(high) peak with FWHM of 28.46 cm$^{-1}$. This indicates highest crystal quality of AlN was produced under NH$_3$ gas flow rate of 400 sccm. However, as the NH$_3$ flow rate increases up to 500 sccm, the $E_2$(high) peak becomes weaker with FWHM of 38.55 cm$^{-1}$, resulting in the degraded of AlN crystalline quality. Generally, $A_1$(LO) mode is very weak in nature. The
damping in the AlN thin films samples were too high and hence, intensity is very low. Consequently, no A$_1$(LO) mode was detected for all the samples.

![Graph showing Raman spectra of AlN thin films grown under different NH$_3$ flow rates: (a) 300 sccm, (b) 400 sccm, and (c) 500 sccm.]

**Fig. 4.14:** Raman spectra of AlN thin films grown under different NH$_3$ flow rates: (a) 300 sccm, (b) 400 sccm, and (c) 500 sccm.

### 4.5 Summary

The growth of AlN thin films under various nitridation temperatures in NH$_3$ ambient was studied. The effects of nitridation temperature on the structural, surface morphologies and optical characteristics were discussed. From the obtained results, it was found that both the XRD and the Raman results showed the improvement of crystalline quality of AlN with increasing nitridation temperature from 1050°C to 1150°C, while crystal quality of the films degraded as the nitridation temperature increases to 1200°C. To sum up, the most effective nitridation temperature is at 1150°C.
The influences of nitridation duration on the structural, morphologies and optical properties of AlN thin films were investigated. Based on the obtained results, the nitridation duration has a great impact on the growth of AlN thin films. As the nitridation duration increases to 60 min, the samples showed densely packed grains morphology and the crystalline quality of AlN thin films increased. However, the crystalline quality of the films degraded as the nitridation duration increases to 75 min. Besides that, the Raman results revealed that all the AlN samples were subjected to compressive stress. These findings showed that the most efficient nitridation duration is 60 min.

The growth of AlN thin films on Si(111) substrate under various NH$_3$ flow rates was investigated. Based on the obtained results, it can be deduced that AlN thin films with (002) preferential orientation were successfully grown with different NH$_3$ flow rates. The XRD and Raman results showed that the crystalline quality of AlN thin films was improved as the NH$_3$ flow rate increases from 300 sccm to 400 sccm. However, the crystal quality degraded as the NH$_3$ flow rate increases to 500 sccm. In addition, surface morphology with densely packed grains and without pinholes was observed for AlN film grown with NH$_3$ flow rate of 400 sccm. Overall, the most efficient NH$_3$ flow rate is 400 sccm.
CHAPTER 5

GROWTH OF Al\textsubscript{x}Ga\textsubscript{1-x}N THIN FILMS WITH DIFFERENT Al COMPOSITIONS
BY USING AlN BUFFER LAYER ON Si(111) SUBSTRATE VIA SOL-GEL SPIN COATING METHOD

5.1 Introduction

In this chapter, AlN thin films were grown on the Si(111) substrate and the commercial AlN/Si(111) template. The structural and morphology properties of the deposited thin films were compared as to choose the best and well-suited substrate for growing the Al\textsubscript{x}Ga\textsubscript{1-x}N thin films. Next, the growth of Al\textsubscript{x}Ga\textsubscript{1-x}N thin films on commercial AlN/Si(111) template with different Al compositions by sol-gel spin coating method will be presented. The structural, morphological, and optical properties of the deposited thin films were characterized by using various characterization tools. Finally, a summary will be presented at the end of this chapter.

5.2 Comparison between AlN/Si substrate grown by sol-gel spin coating method and the commercial AlN/Si template grown by PVDNC method

Based on the literature reviews, GaN or AlGaN thin films grown on Si substrate with good quality can be achieved by using a thin AlN buffer layer. In the previous chapter, the effects of nitridation temperatures and durations as well as NH\textsubscript{3} flow rates on the growth of AlN thin films were discussed. In this work, the structural and morphological of AlN/Si(111) thin films grown previously by sol-gel spin coating method
is compared with the commercial AlN/Si(111) template that grown by PVDNC method. Note here that samples with AlN/Si(111) grown by sol-gel spin coating method and commercial AlN/Si(111) template were labelled as S1 (thickness ~160 nm) and S2 (thickness 25 nm), respectively.

Fig. 5.1 shows the XRD patterns of AlN/Si thin films grown using sol-gel spin coating method and commercial AlN/Si template grown by PVDNC method. Both samples exhibits two prominent peaks which correspond to Si(111) and AlN(002). All the diffraction peaks were ascribed to the formation of hexagonal wurtzite structure AlN (with reference to JCPDS 00-008-0262). The diffraction peaks AlN(002) was observed at 36.0° and 36.02° for sample S1 and S2, respectively. The peak position for bulk AlN(002) is 36.04°. The peak position of sample S2 located slightly lower than bulk AlN as compared with sample S1, which indicates that the sample S2 experienced lower stress as compared to sample S1. Table 5.1 shows the data obtained from XRD measurements of AlN thin films for both samples. The lattice constant, $c$ for samples S1 and S2 was 4.985 Å and 4.982 Å, respectively. Sample S2 has lower lattice constant, probably due to the thickness of AlN buffer layer for sample S2 is thinner as compared with sample S1 (Zhang et al., 2004). The FWHM of the AlN(002) diffraction peak for samples S1 and S2 were 0.51° and 0.49°, respectively. Sample S2 has smaller FWHM and bigger crystallite size compared with sample S1, which indicate that sample S2 has higher crystalline quality of AlN. From XRD results, it can be deduced that the S2 is more suitable for the growth of Al$_x$Ga$_{1-x}$N thin films where it can reduce the large lattice mismatch between Si substrate and the Al$_x$Ga$_{1-x}$N thin films.
Fig. 5.1: XRD patterns of (a) AlN/Si substrate using sol-gel spin coating method and (b) commercial AlN/Si template (S2) grown by PVDNC method.

Table 5.1: Data obtained from XRD measurements of AlN/Si substrate (S1) grown using sol-gel spin coating method and commercial AlN/Si template (S2) grown by PVDNC method.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Diffraction peak, 2θ AlN(002) (°)</th>
<th>Lattice constant, c (Å)</th>
<th>FWHM (°)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>36.00</td>
<td>4.985</td>
<td>0.51</td>
<td>16.38</td>
</tr>
<tr>
<td>S2</td>
<td>36.02</td>
<td>4.982</td>
<td>0.49</td>
<td>17.15</td>
</tr>
</tbody>
</table>

FESEM images of the AlN/Si thin films grown by sol-gel spin coating method and commercial AlN/Si template thin films grown by PVDNC method are shown in Fig 5.2. The surface of sample S1 exhibits densely packed grains with the present of small pinholes. As for sample S2, a very densely packed grains with crack-free as well as no pinholes can be observed throughout all the Si(111) substrate. Therefore, a smooth and
uniform Al$_x$Ga$_{1-x}$N thin films is easier to produce on sample S2. Therefore, sample S2 with 25 nm thickness is a better choice as a substrate to grow Al$_x$Ga$_{1-x}$N thin films.

Fig. 5.2: High-magnification (×100 K) FESEM images of the (a) AlN/Si substrate (S1) grown by sol-gel spin coating method and (b) commercial AlN/Si template (S2) grown by PVDNC method.

Fig. 5.3 displays the EDX analysis results of the AlN/Si substrate grown by sol-gel spin coating method and commercial AlN/Si template grown by PVDNC method. Based on Fig. 5.3(a), sample S1 shows highest oxygen composition around 13% as compared with sample S2 with oxygen composition less than 2%. According to Mcneil et al., (1992), the presence of oxygen is associated with the reduction of thermal conductivity of the material, which makes it less attractive for applications which benefit for a high thermal conductivity. For instance, a large presence of oxygen composition is responsible for point defects, stacking faults and secondary phases at the grain boundaries which reduce the thermal conductivity of the material. Moreover, AlN is one of materials that has high thermal conductivity up to 320 W/m K (Junior and Shanafield, 2004). Since sample S2 has much lower oxygen composition as compared with sample S1, this implied that sample S2 is more attractive and better choice for the growth of AlGaN thin films in order to maintain the high benefit of thermal conductivity of AlGaN material.
Fig. 5.3: EDX analysis results of the (a) AlN/Si substrate (S1) grown by sol sol-gel spin coating method and (b) commercial AlN/Si template (S2) grown by PVDNC method.

5.3 Growth and characterizations of Al$_x$Ga$_{1-x}$N thin films grown with different Al compositions via sol-gel spin coating method

Based on the structural and morphology results in previous section, the commercial AlN/Si template grown by PVDNC (sample S2) is a more suitable for the growth of Al$_x$Ga$_{1-x}$N thin films. In this section, Al$_x$Ga$_{1-x}$N thin films with different Al compositions were grown by sol-gel spin coating method.

5.3.1 Crystalline structure

XRD patterns of the deposited Al$_x$Ga$_{1-x}$N prepared by sol-gel spin coating method are shown in Fig. 5.4. The XRD patterns of Al$_x$Ga$_{1-x}$N films on AlN/Si(111) were measured under 2θ-ω scan mode. For sample with $x = 0$, two predominant diffraction peaks correspond to GaN(002) and GaN(004) can be observed at 34.55° and 72.95°, respectively. These diffraction peaks were in good agreement with the bulk GaN of the
Joint committee for Powder Diffraction Standard (JCPDS file No. 05-0792). As the alloy composition increases (i.e., $x = 0.1$ and $0.2$), the diffraction peaks of AlGaN(002) and AlGaN(004) were shifted towards higher angle. Apart from that, diffractions peaks correspond to the AlN(002) and Si(111) can be clearly observed. Based on Eq. 2.4, Al composition, $x$, can be calculated. The calculated Al compositions are listed in Table 5.2.

Based on Fig. 5.4, the XRD results indicate that the deposited Al$_x$Ga$_{1-x}$N thin films have wurtzite structure with (002) preferred orientation. Due to the incorporation of Al contents in the GaN crystal lattice (Kuppulingam et al., 2014), it was found that the diffraction peak of AlGaN(002) was shifted towards higher angle for sample $x = 0.1$ and $x = 0.2$. From Table 5.2, as the Al composition increases, the lattice constant $c$ is decreased due to the incorporation of Al that causes the changes of the lattice structure of GaN. The Al composition obtained from XRD measurement using Eq. 2.4, is lower as compared with the actual Al composition from the $x = 0.1$ and $x = 0.2$ samples, which is 0.073 and 0.142, respectively. This is due to the efficiency of the Al incorporation was strongly dependent on the growth temperature. According to the Parish et al., (2001), the Al mole fraction increases with the increasing of the growth temperature. In this study, the growth temperature (namely the nitridation temperature), used was 950°C which is inadequate for the Al-species to substitute the Ga-species. Generally, higher temperature is needed as to lower the sticking probability of Ga-species on the epitaxial surface (Parish, 2001), thus it is easier for Al-species to replace the Ga-species.

The FWHM value of Al$_x$Ga$_{1-x}$N sample increases as the Al composition increases. This indicates that the crystalline quality of Al$_x$Ga$_{1-x}$N thin films was degraded as the Al composition increases. This is due to the strain-induced dislocation (Huang et al., 2010).
The strain leads to the broadening of the diffraction peaks and also the shifting of the peaks (Kuppulingam et al., 2016). Therefore, in this work, $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films can be grown using sol-gel spin coating method with different Al compositions from 0 to 0.2. Further increment of Al composition will degrade the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ crystal quality.

![XRD diffraction patterns of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films with different Al compositions](image)

**Fig. 5.4:** XRD diffraction patterns of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films with different Al compositions (a) $x = 0$, (b) $x = 0.1$, and (c) $x = 0.2$.

**Table 5.2:** The Al compositions obtained from the XRD results.

<table>
<thead>
<tr>
<th>Sample $x$</th>
<th>Diffraction peak, $2\theta_{(002)}$ ($^\circ$)</th>
<th>Lattice spacing, $d_{(002)}$ (Å)</th>
<th>Lattice constant, $c$ (Å)</th>
<th>Al composition, $x$</th>
<th>FWHM ($^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0$</td>
<td>34.55</td>
<td>2.594</td>
<td>5.188</td>
<td>0</td>
<td>0.24</td>
</tr>
<tr>
<td>$x = 0.1$</td>
<td>34.65</td>
<td>2.587</td>
<td>5.173</td>
<td>0.073</td>
<td>0.29</td>
</tr>
<tr>
<td>$x = 0.2$</td>
<td>34.75</td>
<td>2.579</td>
<td>5.159</td>
<td>0.142</td>
<td>0.72</td>
</tr>
</tbody>
</table>
5.2.2 Surface morphology

FESEM images of the deposited Al\textsubscript{x}Ga\textsubscript{1-x}N thin films on AlN/Si(111) substrate is shown in Fig. 5.5. These FESEM images were taken with magnification of ×10K and ×100K. These FESEM images showed that the Al compositions, \( x \) has a great impact on the morphology of the synthesized Al\textsubscript{x}Ga\textsubscript{1-x}N thin films. All these samples exhibit smooth and uniform surface without any significant crack. At \( x = 0 \), the surface morphology of the films exhibits densely packed grains [Fig. 5.5(a)]. It is in good agreement with the XRD results as discussed early, where GaN(002) diffraction peak with higher intensity was observed for GaN sample as compared with AlGaN samples. The grains started to accumulate and form larger grains at \( x = 0.1 \) and some dark spots (known as pinholes) can also be noticed [Fig. 5.5(b)]. As \( x \) increases up to \( x = 0.2 \), more pinholes are formed. According to Ng (2007), the presence of pinholes may most probably caused by the incomplete coalescence of AlGaN island. Therefore, the different surface morphologies can be induced by the incorporation of Al into the structure of GaN. The overall FESEM results show that the surface morphologies of the synthesized Al\textsubscript{x}Ga\textsubscript{1-x}N thin films were affected by the Al composition \( x \).

Figs. 5.5 (d) to (f) display the cross-sectional FESEM images of the Al\textsubscript{x}Ga\textsubscript{1-x}N thin films grown with different Al compositions. It can be observed that the Al\textsubscript{x}Ga\textsubscript{1-x}N thin films have an average thickness of approximately 556 nm, 504 nm, and 480 nm for sample with Al composition of \( x = 0 \), 0.1, and 0.2, respectively. The thickness of the AlGaN epilayer degraded as the Al composition increases. As discussed in FESEM, as the Al compositions increase, the grains started to accumulate and more pinholes were observed. These pinholes caused by the incomplete coalescence of AlGaN island, in which lower...
the thickness of AlGaN films, i.e., the results obtained are in good agreement with XRD and FESEM.

Fig. 5.5: Top-view of lower magnification (×10K) (left-hand side) and cross-sectional (right-hand side) FESEM images of the Al$_{x}$Ga$_{1-x}$N thin films grown on AlN/Si substrate: (a), (d) $x = 0$; (b), (e) $x = 0.1$; and (c), (f) $x = 0.2$. Inset is FESEM images captured with higher-magnification (×100K).
Fig. 5.6 displays the EDX analysis results of the deposited Al$_x$Ga$_{1-x}$N thin films prepared by sol-gel spin coating method. As $x = 0$, the atomic percentage ratio between Ga and N elements was approximately 1:1. There was a gradual increase of atomic percentage of Al element, while the atomic percentage of Ga element decrease with the increase of Al composition. This shows that the Al element was successfully incorporate into the Ga and N element to form AlGaN.

![EDX analysis results of the Al$_x$Ga$_{1-x}$N thin films deposited under different Al compositions: (a) $x = 0$, (b) $x = 0.1$, and (c) $x = 0.2$.]

**Fig. 5.6: EDX analysis results of the Al$_x$Ga$_{1-x}$N thin films deposited under different Al compositions: (a) $x = 0$, (b) $x = 0.1$, and (c) $x = 0.2$.**

### 5.2.3 Optical properties

Fig. 5.7 displays the Raman scattering spectra of the deposited Al$_x$Ga$_{1-x}$N thin films measured with $z$ ($x$, unpolarized) $\hat{z}$ scattering configuration. A very strong Raman band can be clearly seen located at $\sim 521$ cm$^{-1}$ which was originated from the Si substrate.
From Fig. 5.7(a), [GaN (x = 0) sample], two dominant Raman peaks can be clearly observed at 566 cm\(^{-1}\) and 731 cm\(^{-1}\) which corresponds to the wurtzite GaN of E\(_2\) (high) and A\(_1\) (LO), respectively. These results were comparable with the reported result (Fong et al., 2013). However, there was no additional peak for AlN of E\(_2\) (high) mode from AlN buffer layer. It may be due to the thickness of the AlN buffer layer is relatively too thin. Both E\(_2\) (high) and A\(_1\) (LO) modes were affected by the Al composition in Al\(_x\)Ga\(_{1-x}\)N thin films. Theoretically, the E\(_2\) (high) mode of Al\(_x\)Ga\(_{1-x}\)N thin films displays two-mode behavior, in which two set of phonon modes related to the pure crystal that compose AlGaN alloy, i.e. GaN and AlN (Hong et al., 2006). It was found that, the E\(_2\) (high) modes slightly shift towards higher wavenumber with the increase of Al composition. A blue shift of E\(_2\) (high) mode was observed and it may due to the increasing of the compressive stress as well as the increases of Al content (Zheng et al., 2017). The E\(_2\) (high) mode for x = 0.1 and x = 0.2 was a GaN-like E\(_2\) (high) mode. According to the Wetzel and Akasaki (1998), at x = 0.5, the E\(_2\) (high) mode of Al\(_x\)Ga\(_{1-x}\)N shifted towards higher wavenumber at around 50 cm\(^{-1}\) and thus indicates the appearance of the AlN-like E\(_2\) (high) mode. Since the Al composition used in this study only x ≤ 0.2, thus the E\(_2\) (high) phonon modes were clearly exhibit one-mode behavior.

From eq. 3.11, the estimated of \(\omega A_1(LO)\) for x = 0.1 and x = 0.2 were supposed to be 763.03 and 780.08 cm\(^{-1}\), respectively. However, from this work, x = 0.1 and x = 0.2, the \(\omega A_1(LO)\) are 731 and 735 cm\(^{-1}\), respectively. The discrepancy between the estimated and experimental \(\omega A_1(LO)\) may be due to the different concentration of free carriers of AlGaN epilayers (Davydov et al., 2002). Note that, the present of high carrier concentration, will increase the high frequency shift of A\(_1\) (LO) mode due to the formation
of mixed plasmon-LO-phonon modes (Davydov et al., 2000). Besides, it also may be due to the growth technique applied, the growth parameter and as well as the quality of the GaN epilayer. The obtained $A_1$(LO) mode exhibit one-mode behavior since no extra line was observed for $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys within the range frequency of LO phonons (Davydov et al., 2002). Thus, this findings confirmed the theoretical prediction of one-mode behavior of LO phonons as reported (Cros et al., 1997; Grille et al., 2000).

Fig. 5.7: Raman spectra of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films deposited under different Al compositions (a) $x = 0$, (b) $x = 0.1$, and (c) $x = 0.2$.

5.3 Summary

The commercial AlN/Si(111) template grown by PVDNC method is a well-suited substrate for the growth of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films. In this work, $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films were
successfully grown on commercial AlN/Si(111) template by sol-gel spin coating method. Investigation has been carried out to study the effects of various Al compositions on the crystalline structure, surface morphology and optical properties of the AlGaN thin films. From XRD results, the Al$_x$Ga$_{1-x}$N thin films exhibit wurtzite structure with (002) preferred orientation and the lattice constant $c$ decreases as well as the crystalline quality degraded as Al composition increase. FESEM images showed the smooth and homogenous surface for all the sample. However, as the Al composition increases, pinholes are observed. From the Raman measurements, both $A_1$(LO) and $E_2$(high) of Al$_x$Ga$_{1-x}$N phonon modes exhibit one-mode behavior. Further experiments need to be carried out to grow good crystalline quality of Al$_x$Ga$_{1-x}$N thin films with higher Al composition. Overall, hopefully this study provides new framework into the development of simple and low-cost method for the manufacturing of AlGaN thin films.
In this study, it has been highlighted the growth of AlN and Al\textsubscript{x}Ga\textsubscript{1-x}N thin films by using sol-gel spin coating technique. There are many factors that could affect the growth of AlN thin films via sol-gel spin coating method including the nitridation conditions. Various nitridation conditions such as nitridation temperatures, nitridation durations and NH\textsubscript{3} flow rates are investigated in order to produce good quality of AlN thin films. It was found that the nitridation temperatures and nitridation durations as well as NH\textsubscript{3} flow rates significantly affect the growth of AlN thin films. Generally, high nitridation temperature with suitable nitridation duration as well as good amount of NH\textsubscript{3} flow rates will increase the formation of AlN particles where atoms have enough energy to occupy the correct site of the crystal lattice. Therefore, the most effective and optimum nitridation temperature, nitridation duration, and NH\textsubscript{3} flow rates are 1150°C, 60 min, and 400 sccm, respectively.

The commercial AlN/Si(111) template grown by PVDNC method was used as a substrate for Al\textsubscript{x}Ga\textsubscript{1-x}N thin films. This is due to the quality and the thickness of AlN buffer layer is more suitable and better as compared to home-grown AlN/Si substrate. The preliminary study on the growth of Al\textsubscript{x}Ga\textsubscript{1-x}N thin films under different Al compositions by using AlN/Si(111) template grown via sol-gel spin coating technique were investigated. From the results obtained, the Al compositions affect the quality of Al\textsubscript{x}Ga\textsubscript{1-x}N thin films. The crystalline structure of Al\textsubscript{x}Ga\textsubscript{1-x}N thin films degraded as the Al
compositions increases due to the strain-induced dislocation. Based on the results obtained, both of the research objectives were achieved.

For future studies, instead of nitridation process by using tube furnace, microwave assisted growth for the AlN and AlGaN can be carried out after spin coating process. During nitridation process in tube furnace, higher temperature is needed, therefore, this may easily induce crack on the films and also there are high possibility of oxidation occurred during the cooling process of the sample. Higher oxidation led to higher defects density, thus probably producing an amorphous thin film. The advantages of using microwave assisted growth are (i) it involves shorter growth time, (ii) higher growth temperature, and (iii) it enhances the reaction kinetic. In addition, more uniform heating process takes place and low power level of ignition can be achieved.
REFERENCES


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LIST OF PUBLICATIONS AND SEMINARS

PUBLICATIONS


SEMINARS


