GROWTH OF $Al_xGa_{1-x}N$ THIN FILMS ON SILICON USING SOL-GEL SPIN COATING TECHNIQUE

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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
c_{AlN}	Lattice constant of AlN
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

LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
DC	Direct current
DEA	Diethanolamine
EDX	Energy dispersive X-ray
FESEM	Field emission scanning electron microscopy
FWHM	Full width at half maximum
IR	Infrared
JCPDS	Joint Committee on Powder Diffraction Standards
LO	Longitudinal optic
MBE	Molecular beam epitaxy
MOCVD	Metal-organic chemical vapor deposition
PL	Photoluminescence
RF	Radio frequency
SEM	Scanning electron microscopy
TEM	Transmission electron microscope
TO	Transverse optic
UV	Ultraviolet
VIS	Visible
XRD	X-ray diffraction
XRD-RC	X-ray diffraction rocking curve

PENUMBUHAN FILEM NIPIS $Al_xGa_{1-x}N$ 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 unuk 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_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_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 $Al_xGa_{1-x}N$ 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 $Al_xGa_{1-x}N$. Filem nipis $Al_xGa_{1-x}N$ 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 $Al_xGa_{1-x}N$ 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 $Al_xGa_{1-x}N$ 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 $Al_xGa_{1-x}N$ thin films. $Al_xGa_{1-x}N$ 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 $Al_xGa_{1-x}N$ 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 $Al_xGa_{1-x}N$ 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 $Al_xGa_{1-x}N$ 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 $Al_xGa_{1-x}N$ 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.

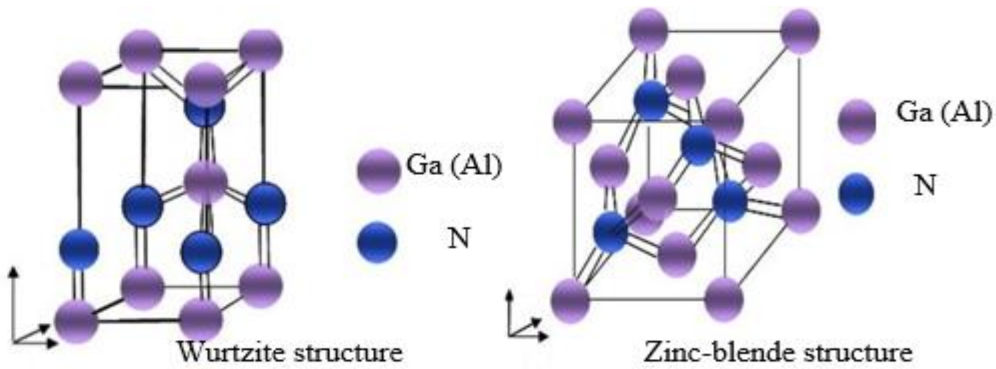

Fig. 2.1: Schematic diagram for wurtzite and zinc-blende structures of AlN crystal structures. (Adapted from Wu, 2010).

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:

$$d_{hkl} = \frac{\lambda}{2 \sin \theta_{hkl}} \tag{2.1}$$

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

$$a_{Al_xGa_{1-x}N} = xa_{AlN} + (1-x)a_{GaN} \tag{2.2}$$

$$c_{Al_xGa_{1-x}N} = xc_{AlN} + (1-x)c_{GaN} \tag{2.3}$$

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:

$$x = \frac{c - c_{GaN}}{c_{AlN} - c_{GaN}}. \quad (2.4)$$

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.

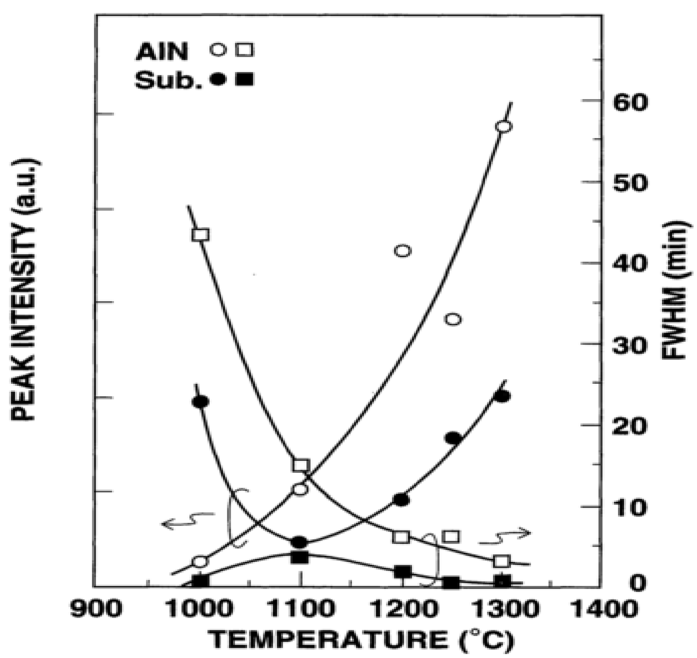

Fig. 2.2: Dependences of XRD peak intensity and FWHM on growth temperature for both AlN epitaxial layer and sapphire substrate. (Adapted from Ohba et al, 1996)

In 2012, Çörekçi et al. reported on the effects of ammonia (NH_3) flow rate and the layer thickness on the properties of AlN layers. They concluded that reducing the NH_3 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 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 (TMAl) 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.

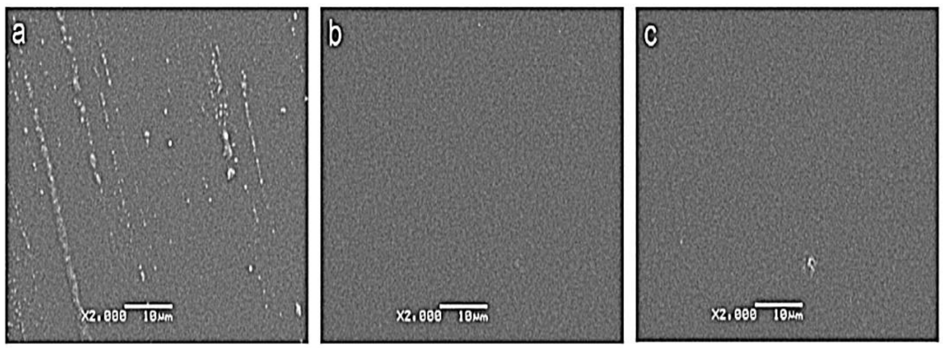

Fig. 2.3: Plain-view SEM micrographs of samples: (a) A, (b) B, and (c) C. (Adapted from Çörekçi et al., 2012)

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 NH_3 (Tamariz et al., 2017). They found that the peak position of E_2(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.

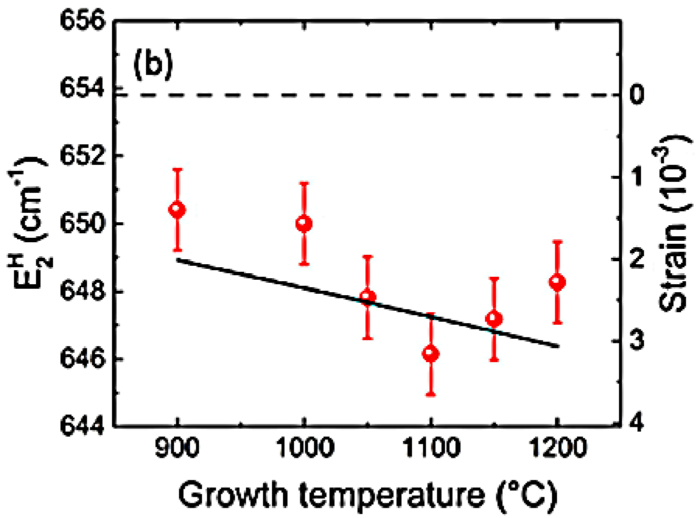

Fig. 2.4: Raman shift of E_2(high) phonon line and the corresponding amount of strain in the layer, the dashed line is position of the E_2(high) phonon line for unstrained AlN and the black curve is the calculated thermal strain assuming relaxed layers during growth. (Adapted from Tamariz et al., 2017)

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.

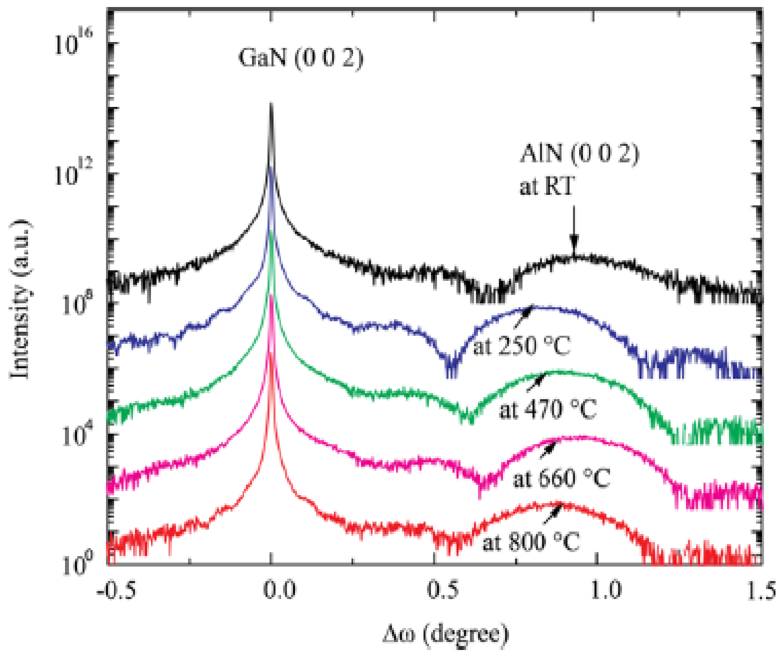

Fig. 2.5: ω-2θ scan along the 002 reflections for the series of 5 samples show peak for 15 nm AlN on GaN substrate grown at different temperatures. (Adapted from Faria et al., 2015)

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 (N_2/Ar) flow ratio. Cheng et al. (1996) reported the growth of AlN thin films by RF sputtering with various N_2/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 N_2 concentration, as shown in Fig. 2.6. However, as the N_2 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.

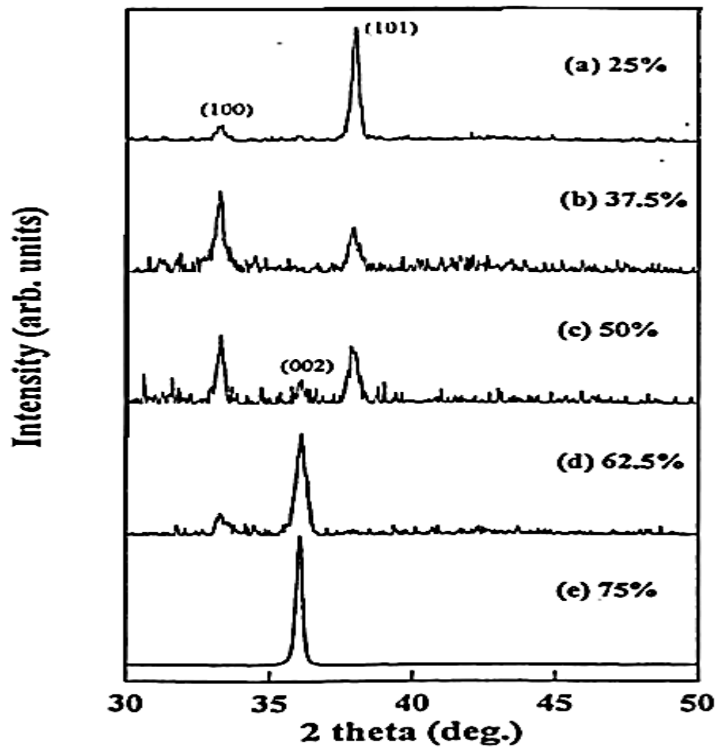

Fig. 2.6: XRD patterns of AlN thin films deposited at various N_2 concentrations (a) 25%, (b) 37.5%, (c) 50%, (d) 62.5% and (e) 75%, with a sputtering pressure of 7.5 mTorr, substrate temperature 350°C and RF power 300 W. (Adapted from Cheng et al., 1996).

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 N_2/Ar flow ratios. They found that the AlN thin films exhibit (002) preferential orientation with $2\theta =$ 36.023°, which is slightly lower that AlN powder data (~36.04°). This result implies that 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% N_2 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 N_2 fraction were 500°C and 60%, respectively. From Raman spectroscopy, peaks with correspond to E_2(high) and A_1(LO) modes were detected at 659 cm^{-1} and 892 cm^{-1}, respectively, as shown in Fig. 2.8.

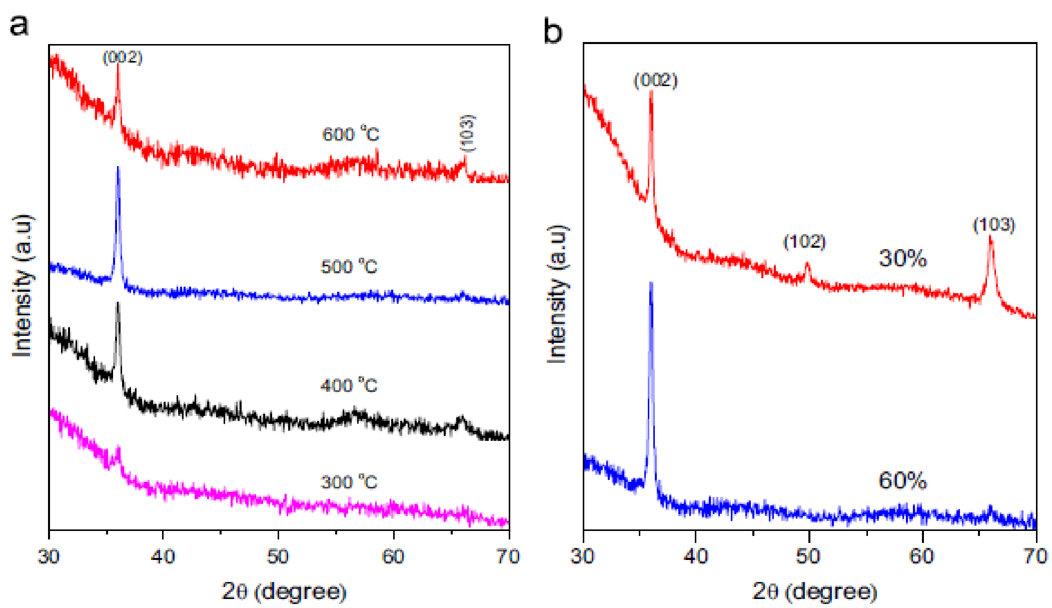

Fig. 2.7: XRD patterns of the AlN films prepared at various (a) substrate temperatures and (b) nitrogen conditions. (Adapted from Khan et al., 2015).

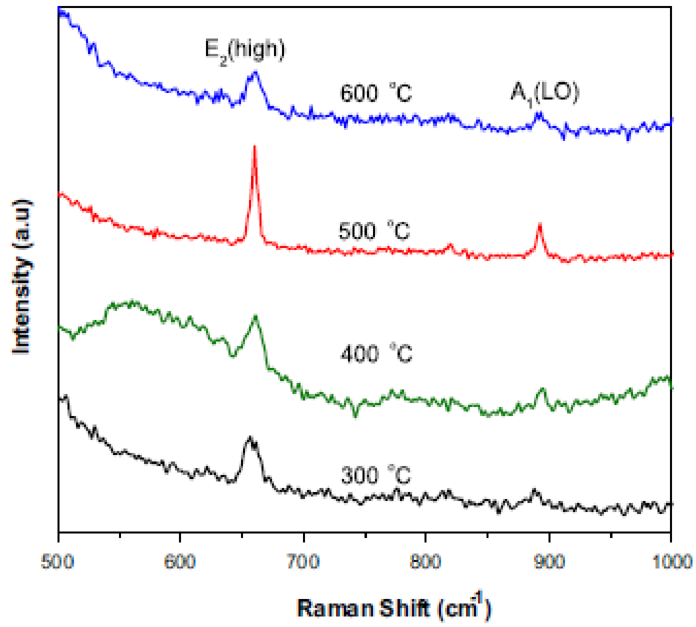

Fig. 2.8: Raman spectra of AlN grown at different growth temperatures. (Adapted from Khan et al., 2015).

2.4 Overview of the growth techniques of AlGaN thin films

Up to date, there are numerous methods used to grow $Al_xGa_{1-x}N$ thin films such as MOCVD and MBE. However, the in-depth investigation on the properties of $Al_xGa_{1-x}N$ thin films still relatively scarce. In 1997, Stutzmann et al. reported the growth of AlGaN epitaxial films on sapphire substrate with ($0 \leq x \leq 1$). Fig. 2.9 shows the XRD patterns of $Al_xGa_{1-x}N$ with ($0 \leq x \leq 1$). 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_1(LO) mode exhibits one-mode behavior while E_2(high) exhibits two-mode behavior, as shown in Fig. 2.10.

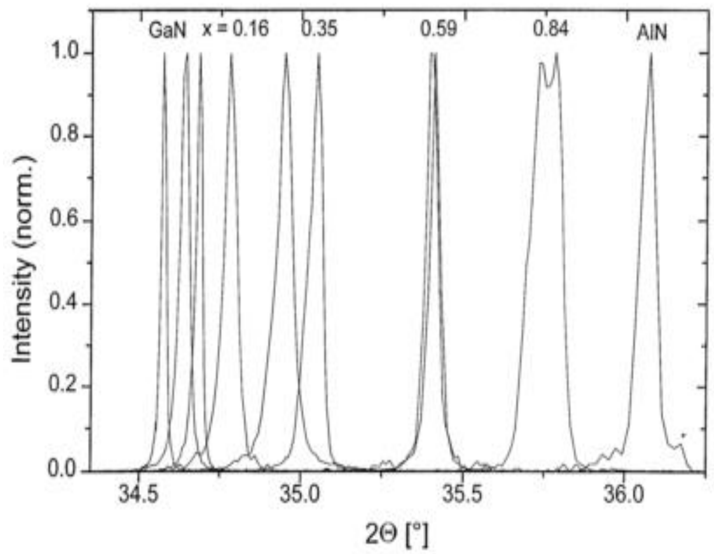

Fig. 2.9: High resolution XRD patterns of MBE grown AlGaN alloy films with different composition. (Adapted from Stutzmann et al., 1997)

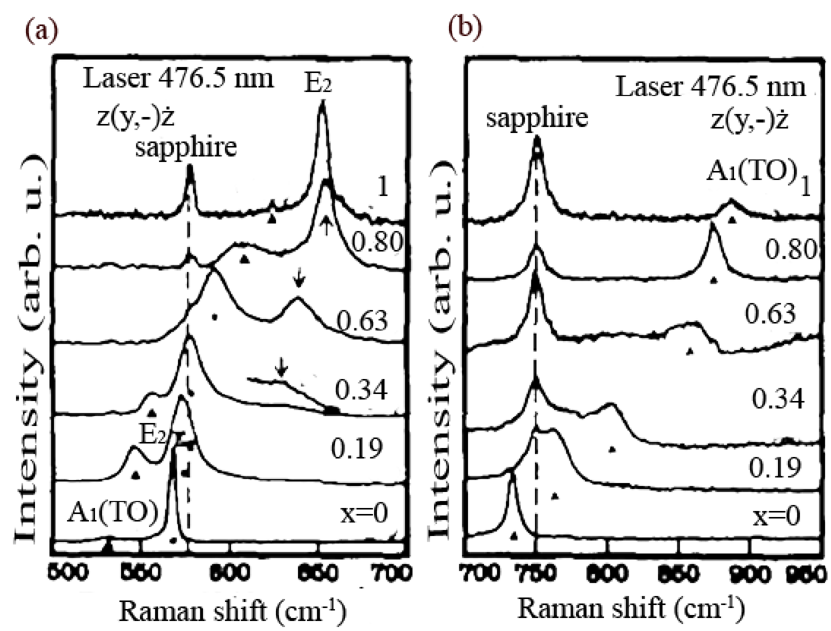

Fig. 2.10: Raman spectra of AlGaN showing the dependence of the (a) A_1(TO) and the E_2 mode and (b) of the A_1(LO) mode on the Al content. (Adapted from Stutzmann et al., 1997)

Over the years, using high temperature (HT)-AlN/GaN buffer on sapphire substrate, $Al_xGa_{1-x}N$ 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; Znaidi 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.

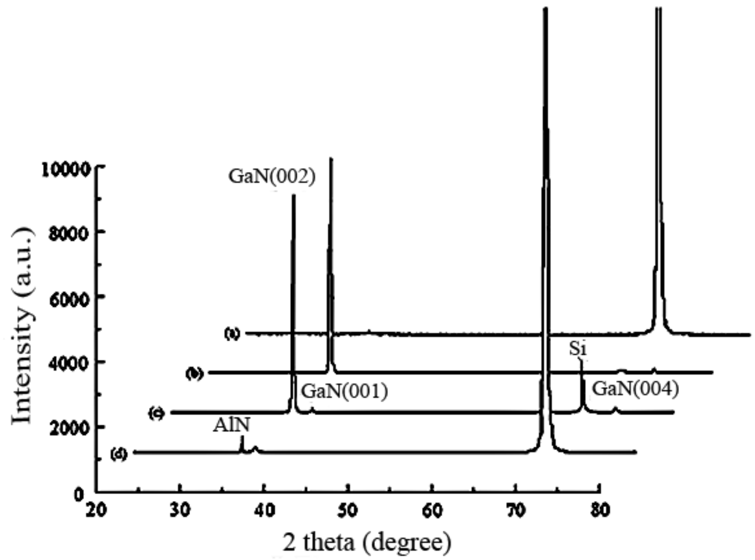

Fig. 2.11: XRD patterns of the GaN thin films deposited under various temperatures: (a) 750°C, (b) 850°C, (c) 950°C and (d) 1050°C. (Adapted from Fong et al., 2013).

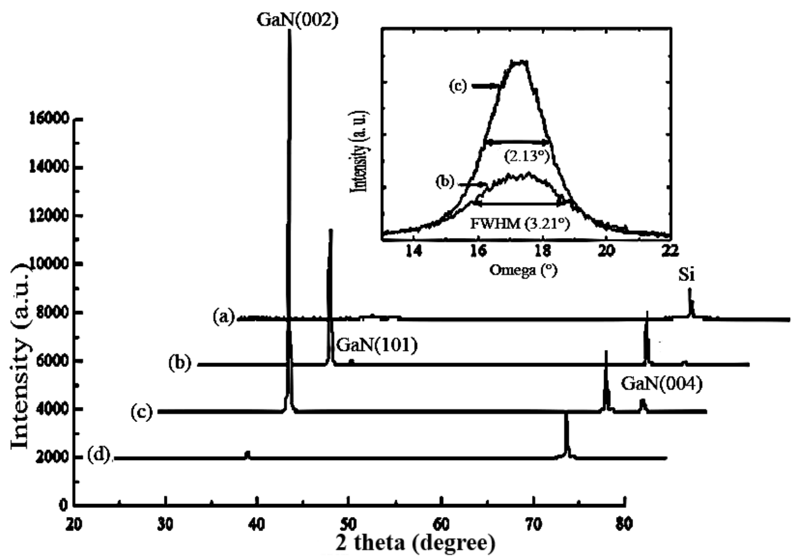

Fig. 2.12: XRD patterns of the GaN thin films under various nitridation durations: (a) 15 min, (b) 45 min, (c) 75 min and (d) 105 min. Inset is the XRD-RC of the GaN(002) peak measured in the omega scan mode. (Adapted from Fong et al., 2014).

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.

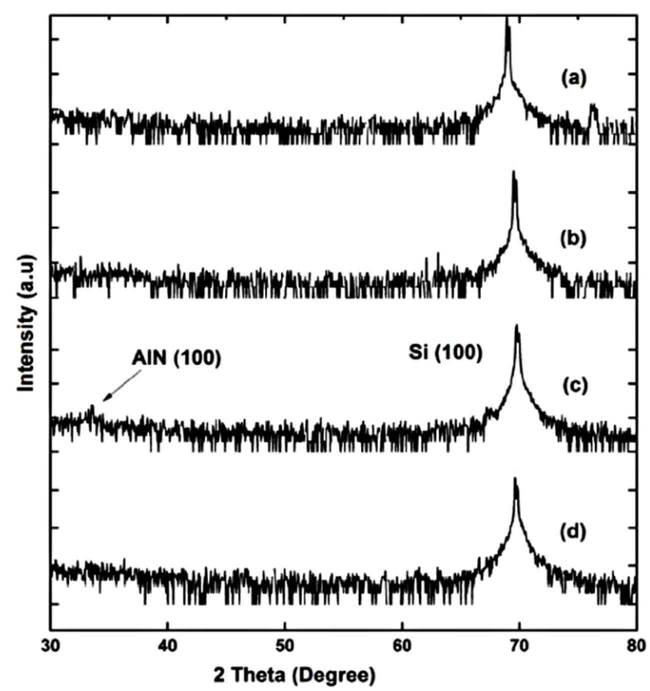

Fig. 2.13: XRD patterns of AlN thin films with various annealing temperatures: (a) 250°C, (b) 450°C, (c) 650°C and (d) 850°C. (Adapted from Mohd Amin et al., 2015).

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 $Al_xGa_{1-x}N$ 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_2 at temperature of 900°C for 2 hours. From the Hall effects measurement, they found that the $Al_xGa_{1-x}N$ thin films have n-type condition. However, the structural, surface morphologies and optical properties of $Al_xGa_{1-x}N$ thin films were not discussed in the study. With only a few researchers reporting on the growth of $Al_xGa_{1-x}N$ 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 $Al_xGa_{1-x}N$ 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, $Al_xGa_{1-x}N$ 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 $Al_xGa_{1-x}N$ films with high Al compositions. This mainly due to the lattice parameter of AlGaN alloy is smaller than the GaN template, in which the