การหาโครงสร้างผลึกของ GaN บนวัสดุฐานรอง GaAs ที่มีผิวระนาบ (110) ที่ปลูกผลึกด้วย MOVPE

นายพิชญา พรายแก้ว

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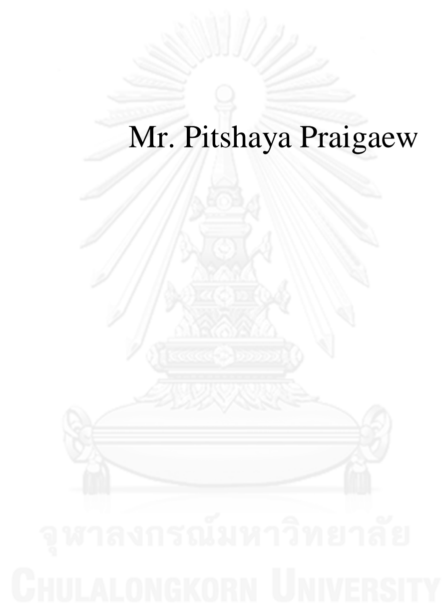
CRYSTAL STRUCTURE DETERMINATION OF GaN ON GaAs (110) SUBSTRATE GROWN BY MOVPE



Mr. Pitshaya Praigaew

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พิชญา พรายแก้ว : การหาโครงสร้างผลึกของ GaN บนวัสดุฐานรอง GaAs ที่มีผิวระนาบ (110) ที่ปลูกผลึกด้วย MOVPE (CRYSTAL STRUCTURE DETERMINATION OF GaN ON GaAs (110) SUBSTRATE GROWN BY MOVPE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. สกุลธรรม เสนาะพิมพ์, 55 หน้า.

โครงผลึกของฟิล์มแกลเลียมไนไตรด์ที่ปลูกบนวัสดุฐานรองแกลเลี่ยมอาเซไนด์ที่มีผิวระนาบ (110) ด้วยวิธีเมทัลออแกนิกเวเพอร์เฟสอิพิแทกซีได้ถูกตรวจสอบด้วยไมโครรามานสเปคโตรสโคปีที่มีความยาวคลื่นเลเซอร์ 473 514 532 และ 633 นาโนเมตร และการเลี้ยวเบนด้วยรังสีเอ็กส์ ผลการทดลองจากการกระเจิงแบบรามานแสดงให้เห็นถึงโหมดการสั่นที่เกี่ยวกับทั้งโครงผลึกคิวบิกและเฮกซะโกนัล นอกจากนี้ผลการทดลองด้วยการเลี้ยวเบนรังสีเอ็กส์แสดงถึงโครงผลึกแบบเฮกซะโกนอลระนาบ (10-13) เป็นโครงผลึกหลักและถูกแทรกตัวด้วยโครงผลึกแบบคิวบิกระนาบ (110) ภายในฟิล์มแกลเลียมไนไตรด์ ผลการทดลองแสดงให้เห็นว่าฟิล์มแกลเลียมไนไตรด์ประพฤติตัวเป็นโครงสร้างแบบคิวบิกในบริเวณใกล้รอยต่อระหว่างวัสดุฐานรองและประพฤติตัวเป็นโครงสร้างแบบเฮกซะโกนัลเมื่อปลูกฟิล์มหนามากกว่า 0.8 ไมครอน จากการคำนวนแสกงให้เห็นว่ามีความไม่เข้ากันของโครงผลึกระหว่างคิวบิกแกลเลียมไนไตรด์ระนาบ (110) และเอกซะโกนัลแกลเลียมไนไตรด์ระนาบ (10-13) เพียง 0.06 % เท่านั้น ดังนั้น ความไม่เข้ากันของโครงผลึกที่มีน้อยมากนี้เองที่ทำให้เกิดการสร้างโครงสร้างเฮกซะโกนัล (10-13) จากผลการตรวจสอบยังแสดงให้เห็นว่าเซมิโพลาร์แกลเลียมไนไตรด์ผิวหน้าระนาบ (10-13) นั้นสามารถปลูกบนวัสดุฐานรองแกลเลียมอาเซไนด์ผิวหน้าระนาบ (110) ได้

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PITSHAYA PRAIGAEW: CRYSTAL STRUCTURE DETERMINATION OF GaN ON GaAs (110) SUBSTRATE GROWN BY MOVPE. ADVISOR: ASST. PROF. SAKUNTAM SANORPIM, Ph.D., 55 pp.

Structural phases of GaN films grown on the GaAs (110) oriented substrates by MOVPE were investigated by μ-Raman spectroscopy with the excitation wavelengths of 473, 514, 532 and 633 nm and XRD. Raman scattering results showed both of cubic and hexagonal phases related phonons. XRD results showed h - GaN (10-13) is the main crystal structure with the c-GaN (110) inclusion in the grown GaN films on GaAs (110). With increasing layer thinness, the results showed GaN film exhibit to cubic structure at the region near to the interface and exhibit to hexagonal structure when the layer thickness increased more than 0.8 μm. The calculation showed only 0.06 % of lattice mismatch between c - GaN (110) and h - GaN (10-13). Thus, the lattice-mismatch significantly involves to construction of the h - GaN (10-13) film on GaAs (110). This investigation showed that a semi-polar GaN (10-13) film was successfully grown on GaAs (110) oriented substrate.

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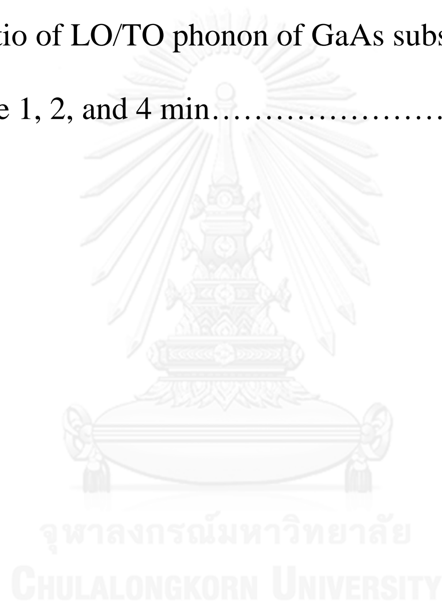
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CHAPTER I
INTRODUCTION

1.1 What is Gallium Nitride?

Gallium Nitride (GaN) is a promising semiconductor materials to produce optoelectronic devices operating in a region of ultra-violet wavelengths [1]. Its alloys such as InGaN is used to produce the blue-green light emitting diode (LEDs) and laser diodes (LDs) [2-4].

GaN crystalizes in both of cubic structure (zincblend structure) and hexagonal structure (wirtzite structure), which are named c-GaN and h-GaN, respectively. It is known that c-GaN and h-GaN are wide band gap of 3.2 eV and 3.4 eV, respectively. Since, the h-GaN crystal is thermodynamically stable, while c-GaN is meta-stable phase. Commonly, then, h-GaN is usually heteroepitaxially grown on hexagonal substrates such as sapphire [5] and Si (111) [6]. On the other hand, c-GaN with cubic phase purity of 85% has been successfully grown on cubic substrate such as GaAs (001) [7]. c-GaN is suitable to produce optoelectronic device cause of high symmetry involves low phonon scattering and high mobility. However, the c-GaN grown film is usually contained with h-GaN in form of stacking faults due to damage at interface of GaN/GaAs (001) by high temperature growth in ramping period of growth process, as figure 1.1, which are

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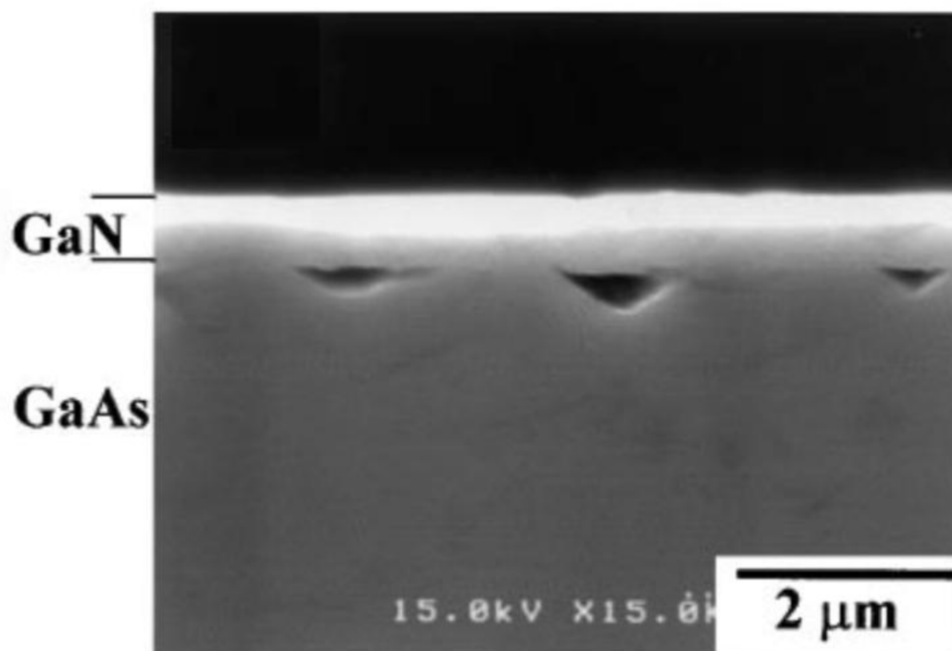


Figure 1.3 SEM image showing voids at interface of GaN film grown on GaAs (001) substrate without an intermediat layer [7]

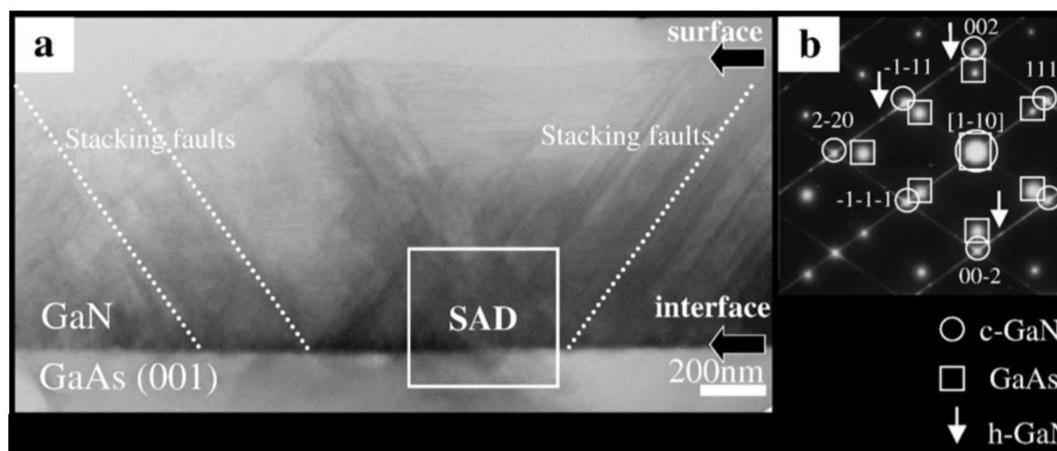


Figure 1.4 Sectional TEM micrograph of the c-GaN layers grown on GaAs(001) substrates at different growth temperatures of (a) 900 °C and (b) Corresponding selected area diffraction (SAD) patterns taken near the 〈1□10〉 zone axis. [9]

constructed on (111) surface during the growth [8], as figure 1.2 . This hexagonal phase inclusion significantly effects on structural phase purity of the grown films [9] .

To reduce a hexagonal phase inclusion, we have considered two hypothesis. First, reduced ramping time from 4 min, then GaN films have been grown before the As atoms decomposed from the GaAs (001) substrate surface. Second, used the GaAs (110) surface as substrate surface. With higher step density, it is purposed to be a substrate for c-GaN. To analyze structural phase purity in GaN films on GaAs (110) substrates, μ-Raman spectroscopy with the excitation wavelengths of 473, 514, 532 and 633 nm were used. Surface and interface morphologies have been investigated by scanning electron microscopy (SEM) and atomic force microscope (AFM).

To improve the quality of cubic GaN films grown on GaAs substrates with higher cubic phase purity and smooth interface, crystal structure transformation and improvement of growth morphology due to a use of GaAs (110) surface, ramping time and layer thickness were systematically studied. The goals of this work as following.

1. **A reduction of planar defects along the <111> directions.**

   Thermal decomposition of GaAs substrate surface resulted from high growth temperature is considered. Decreasing ramping time is expected to protect the GaN/GaAs interfaces.

2. **A reduction of an amount of h-GaN/c-GaN mixed structures in GaN on GaAs**.

   the smooth GaN/GaAs interface is an important key. The GaAs (110) substrate with higher step density is expected to grow a film with smooth

interface at relatively high growth temperature. The GaN film grown on the GaAs (110) substrate is expected to have a cubic structure as main structure with optimum ramping time. However, in fact, the GaN crystal crystalizes in both cubic and hexagonal structures.

1.2 Objectives

In this thesis, we have studied GaN film on GaAs (001)- and (110)-oriented substrate surfaces grown by metal organic vapor phase epitaxy (MOVPE) with various growth conditions such as, ramping time and growth time. Structural properties were investigated by Raman scattering and X-Ray diffraction techniques. Objectives of this work are as following.

1. To Investigate crystal structures of GaN grown on GaAs (110)
2. To Identify an influences of growth parameters such as ramping times, substrate surface orientation, films thickness, which relate to quality of interface and crystal structure of GaN/GaAs films.

1.3 Organization of the thesis

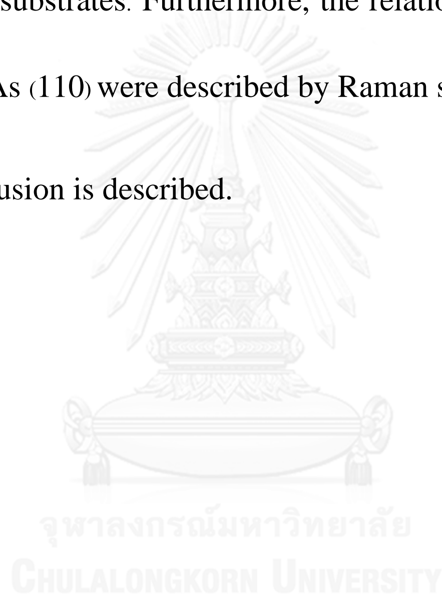
The thesis organized as following:

CHAPTER II : Polytypes of GaN films grown on GaAs (001) substrate were described, this due to stacking fault and hexagonal-cubic mixed structure. Additional, Raman scattering and X-Ray diffraction phenomena were described in this chapter

CHAPTER III: We inform the specimen's details of GaN/GaAs (001)- and (110)-oriented substrate surface with different growth conditions, which are ramping time and growth time. Raman spectroscopy and X-Ray diffraction setup were also described.

CHAPTER IV: Optimum growth condition of GaN/GaAs (001)- and (110)- orientations were described by SEM, AFM and Raman scattering result. Raman scattering results gave the best excitation wavelength condition for using Raman spectroscopy on GaN film grown on GaAs substrates. Furthermore, the relation of structural properties and thickness of GaN/GaAs (110) were described by Raman scattering and XRD results.

CHAPTER VI: Conclusion is described.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CHAPTER II
BACKGROUND

It is important to discuss about background knowledge, which lead to problem/hypothesis of this work and how to solve that problems by a systematic investigations. It is also included the polytypes of GaN for the material problems. Raman scattering and X-Ray Diffraction theory for the experiments for characterization of all structural phases in GaN film are described.

2.1 Polytypes of GaN

GaN can be crystalized both of cubic and hexagonal phase namely c – GaN and h – GaN. Impure GaN film has long been discovered [10-13]. Metastable c – GaN were successfully grown on GaAs substrate, with more than 85% of cubic crystal inside by MOVPE, however, there are some hexagonal inclusion in the c – GaN crystal. Thermal damage such as void at interface have been observed as shown in previous chapter (figure1.1). The previous research of some of structural defect such as stacking fault and hexagonal GaN inclusion in c – GaN grown on GaAs (0 0 1) were discussed due to the stacking fault parallel to {111} plane. These atomic defects have been grown from this void and involve to atomic alignment during growth mechanism.

2.1.1 Stacking fault

Two types of GaN crystal structures subdivide to Cubic GaN (c-GaN) and Hexagonal GaN (h-GaN).Commonly, c-GaN has been successful grown with hexagonal

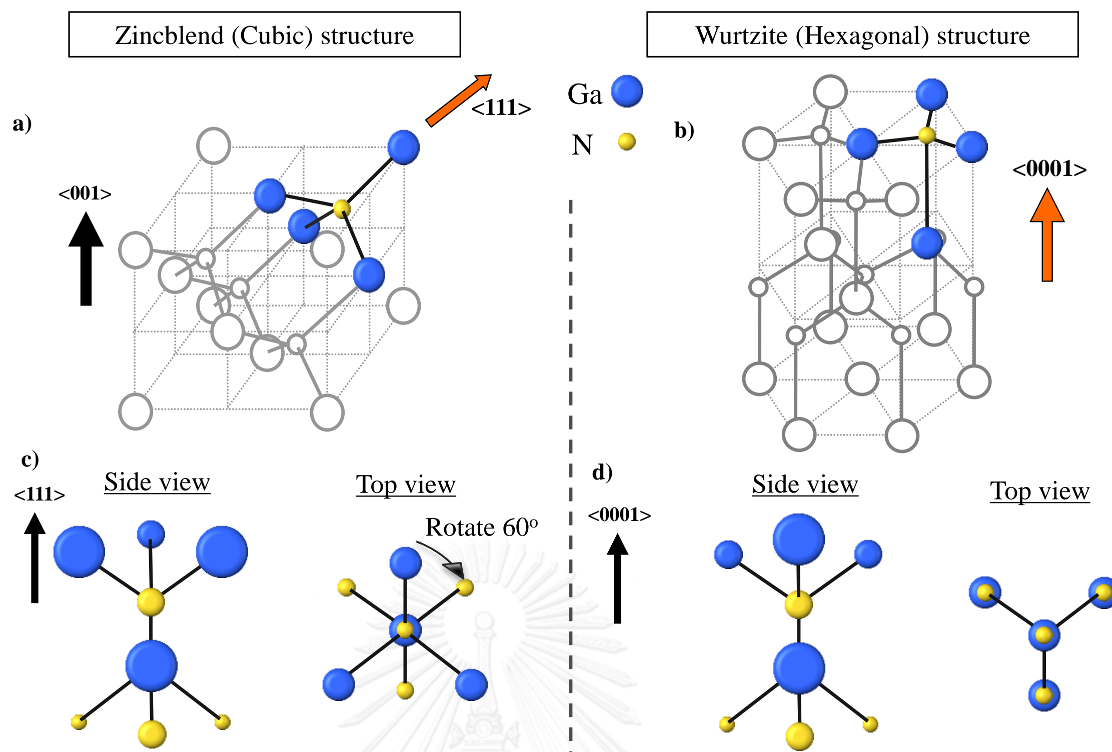

Figure 2.1 Ga atom and N atom contacted with tetrahedral bond for a) c - GaN and b) h - GaN , c) and d) mechanism of bond rotation

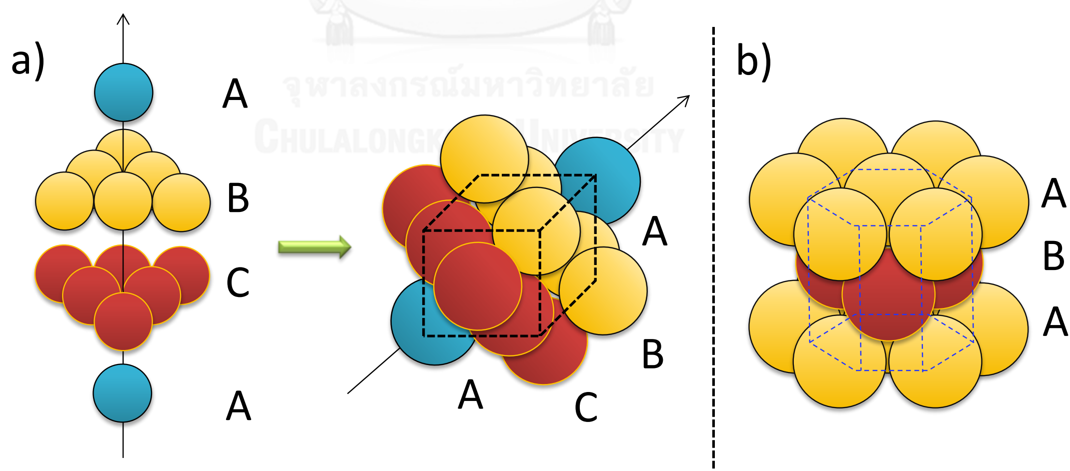

Figure 2.2 Atomic alignment patterns, a) ABCABC, with cubic unit cell and b) ABAB with hexagonal cell.

inclusion [14, 15]. This phenomena explained by the tetrahedral bond of Ga and N atoms in cubic and hexagonal unit cell, as shown on figure 2.1 (a) and (b) respectively. Generally, an atom in cubic structure of c – GaN crystal places in order of ABCABC. Stacking fault (SFs) is the disoriented of atomic alignment. Tetrahedral molecular lie to {111 direction has been bended 60° from previous, as figure 2.1 (c). One of mono layer has interrupted alignment from ABCABC to ABABAB, as shown in figure 2.2 a) and b), respectively. The crystal structure has been exhibited like <111> parallel to <0001> in hexagonal system. This phenomena called phase transformation [16].

In previous research, Siripen Suandon et,al. were discussed that TEM image of the region containing the pyramid-like structure for GaN layer near to the interface of GaN/GaAs. The SFs become a seed of the h – GaN structure and then, generate to cubic/hexagonal mixed structure when grown longer. Another evidence is that h – GaN is easily to generated from the planar defect lied on (111) face of GaN/GaAs (111) were investigated These result shown that defective at an interface of GaN/GaAs is to reason to generates hexagonal inclusion in GaN films grown on GaAs

2.1.2 Hexagonal - Cubic mixed structure

For macroscopic crystal structure, hexagonal inclusion has been generated from planar defect lie on (111) face. Figure 2.3 shown that the hexagonal inclusion in cubic GaN crystal structure, this due to the stacking fault from previous section. From the

result c – GaN with does not has 100% purities can called cubic-hexagonal mixed structure. This problem leading to nonradiative results [17-20] and makes the device malfunction.

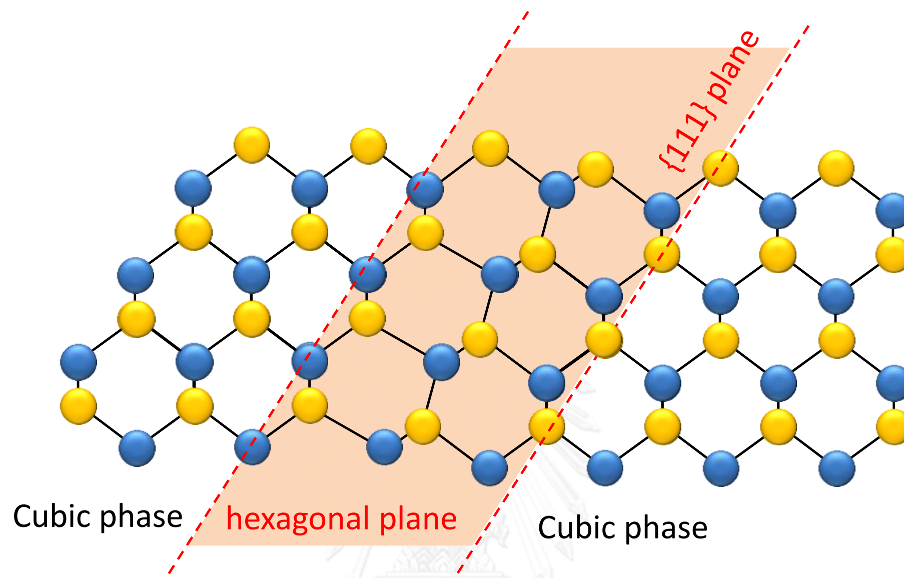

Figure 2.3 Hexagonal phase inclusion called hexagonal/cubic mixed structure. This due to stacking fault lie on (111) plane

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2.2 Raman Scattering

Inelastic light scattering of molecules described by C.V. Raman. His name refer to the light scattering, which create vibrational mode or phonon when excited the specimen by laser with coherent visible wavelength. This technique were used for investigate the phonon which for particular crystal structure.

Raman scattering is the inelastic light scattering which subdivided into two types, Stroke scattering and anti – Stroke scattering. Figure.2.4 shows Stroke scattering

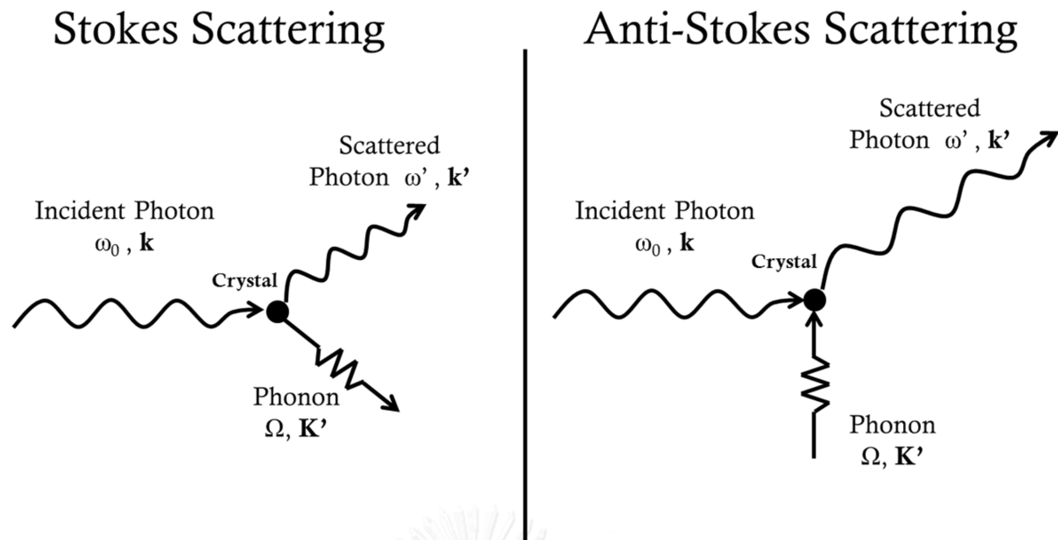

Figure 2.4 Illustration of conservation of energy and momentum corresponds the interaction that: (a) Stroke scattering (b) Anti-Stroke scattering processes

is correspond to phonon creation with energy of scattered light is less than incident laser energy. Loses energy absorbed by crystal. It makes the vibrational mode and quantized to be a particular particle called phonon in the crystal. In opposite way anti-Stroke is correspond to phonon annihilation. For the crystal structure which had some of phonon in system, for the specimen in high temperature. The scattered light with more energy than incident excited laser due to absorbed from phonon annihilation in specimen.

$$\omega' = \omega_0 \pm \Omega, \tag{2.1}$$

$$\vec{k}' = \vec{k}_i \pm \vec{K} \quad , \tag{2.2}$$

Where ω and $\vec{k}$ are frequency and wave vector of light, respectively. Subscribe i represent to incident light, Ω and $\vec{K}$ are the phonon frequency and wavevector, respectively. The + sign correspond the phonon emission (Stroke scattering) and – sign for absorption (anti-Stroke scattering). We called phonon frequency that "Raman shift" for the observed in the spectra. Raman spectra plotted in term of intensity of scattering phonon, with the "a.u." unit versus Raman shifted in wave number unit "cm^{-1}".

The scattering geometry written as $\vec{k}_i$ (e_i,e_s) $\vec{k'}$ called Portó notation [21] , where as $\vec{k}_i$ and $\vec{k'}$ are the direction of incident and scattered photon ; i and s are the polarizations of incident and scattered photon, respectively. For specimen which has (0 0 1) surface, backscattering is the simplest scattering geometry, with [0 0 1] direction of incident photon respect to [*x y z*] direction system. In opposite way [0 0 $\bar{1}$] is the direction of backscattered photon. LO phonon is longitudinal optical phonon respect to incident direction and TO phonon is transverse optical phonon polarized in x-y plane. Thus, the backscattering geometries of (0 0 1) can be written to $z(x,y)\bar{z}$ or $z(y,x)\bar{z}$ also.

The optical penetration depth of excited laser energy is depend on absorption coefficient α [22, 23], which is

$$d = \frac{1}{\alpha} \quad , \qquad (2.3)$$

; α : absorption coefficient of GaN

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For example, 514 nm of excited wavelength has penetration depth 109 nm. For different excited wavelength can be collects the signal in different depth from the surface.

Recently publication, H. Yaguchi et al. [24] has used Raman scattering experiment to classified cubic and hexagonal phonons in GaN layer grown on 3C-SiC substrate with (001) surface. This results detects cubic phase to hexagonal phase related phonons in GaN film grown on cubic substrate. H.siegle et al. [25] was published a wave number related to cubic and hexagonal phonons in GaN film, which different scattering geometries, as shown in table 2.1. These showed the position of Raman shift which corresponded to phonons in GaN crystal. For hexagonal structure which have atom with complicated alignment, there are particular name for specific vibrational, as shown in figure 2.5 [26] .Raman scattering phenomena is the effective tool to investigate the structural of GaN crystal [27].

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Film	Phonon mode	Raman shift (cm^{-1}) [25,26]
GaAs	LO	268
	TO	290
c-GaN	TO	552
	LO	739
h-GaN	A_1(TO)	535
	E_2-high	569
	A_1(LO)	735

Table 2.1 Raman shifted corresponding to the GaAs ,c-GaN and h-GaN related phonons

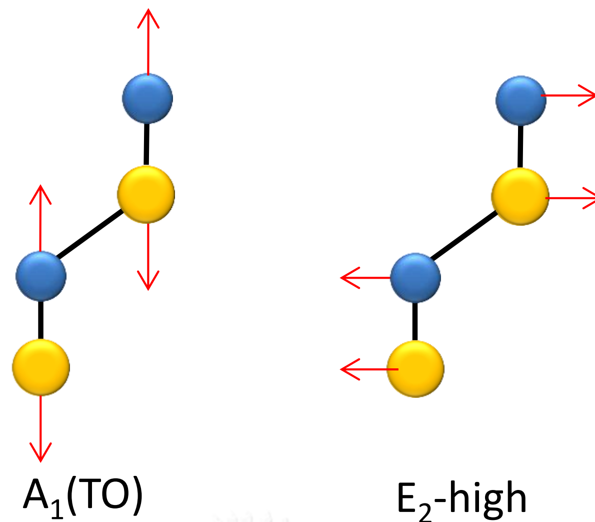

Figure 2.5 Specific vibrational modes of A_1(TO) and E_2–high, which corresponding to hexagonal phonon.

2.3 X-Ray Diffraction (XRD)

X-ray diffraction phenomena were used as a tool to investigate the crystal information in GaN epitaxial film [28, 29]. This application using Cu X-Ray source generated $K_{\alpha 1}$ (λ = 1.5406 Å) which radiated from electron transition from 2P orbital called "L" shell (n = 2 , l = 1/2) to ground state "K" shell (n = 1) , then incident to the specimen and finally, reach to the detector as figure 2.7. The X-Ray Diffraction phenomena exhibit on the role of "Bragg's law" as

$$2d_{hkl} \sin \theta_B = \lambda \quad , \qquad (2.4)$$

Where, d_{hkl} is the lattice plane spacing of the (h k l) plane called d-spacing of each crystal structure correspond to particular diffraction angle, θ_B is Bragg's angle and λ is the wave length of X-ray.

d – spacing of tetragonal structure can be calculate by:

$$\frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \quad , \quad (2.5)$$

and for hexagonal structure: $$\frac{1}{d_{hkl}^2} = \left(\frac{4}{3}\right)\frac{h^2+hk \;\; + k^2}{a^2} + \frac{l^2}{c^2} \quad , \quad (2.6)$$

, which using to calculate Blagg's condition for particular crystal structure.

The spectrum which detected is called "Diffraction profile", with the relation of intensity

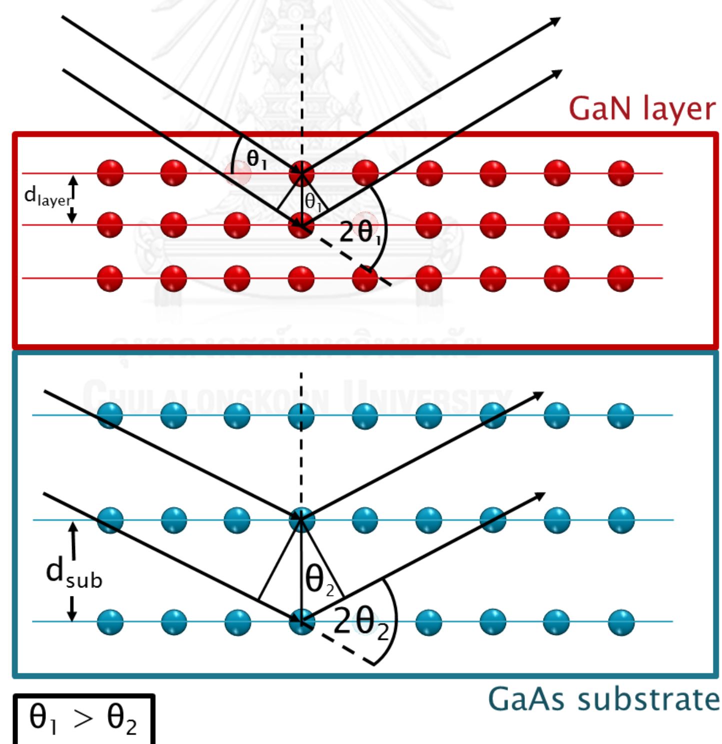

Figure 2.6 Illustration of X-ray diffraction phenomena on GaN/GaAs layer which have different d-spacing d_{layer} , d_{sub} corresponding to different diffraction angle θ_1 and θ_2 , respectively.

versus the angle which incline the specimen surface, for 2θ/ω mode. This mode show that the orientation of the film which diffracted. This technique is the most popular to estimate the crystal quality. However, we must know that Bragg's condition which suitable for each plane which X-Ray

Crystal	**(h k l)**	**2θ**
GaAs	(2 2 0)	45.349 °
	(4 4 0)	100.836 °
c-GaN	(2 2 0)	57.875 °
h-GaN	(1 0 -1 3)	63.449 °
	(2 1 -1 0)	95.119 °

Table 2.2 A candidate peaks position obtained from XRD on GaN film investigated with 2θ/ω mode

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CHAPTER III
EXPERIMENT

3.1 GaN film grown on GaAs substrate by MOVPE

3.1.1 What is MOVPE?

Metal organic vapor phase epitaxy (MOVPE) is considered as grown technique for crystalline epitaxial growth. It uses compound as a precursor and chemical reaction vapor phase to growth crystal on substrate. This technique has many advantages such as high growth rate, which suitable for commercial system, different material can be growth in the same system and precision in deposition thickness and possible sharp interfaces growth thus, it is very suitable for hetero-structures.

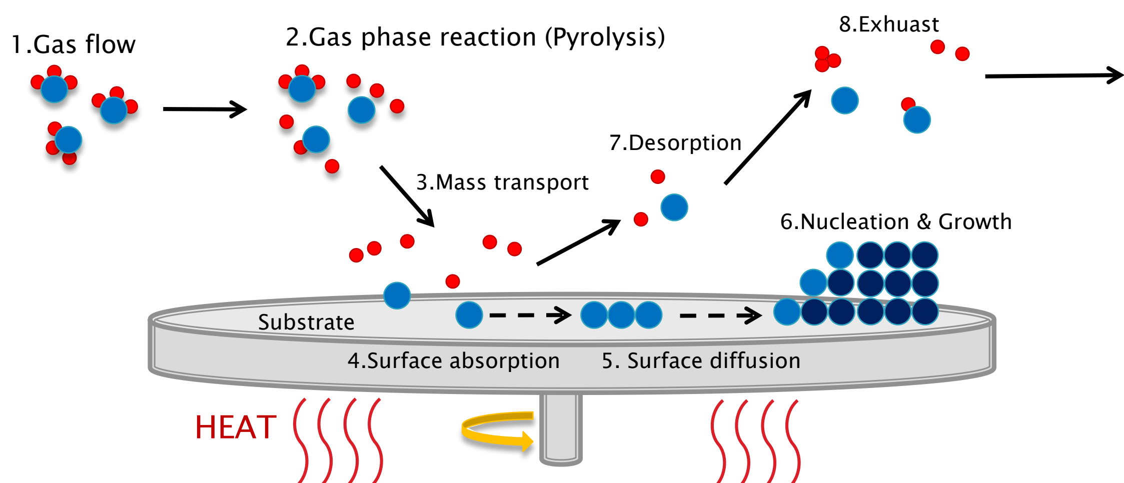


Figure 3.1 Chemical reaction in MOVPE system during growth process.

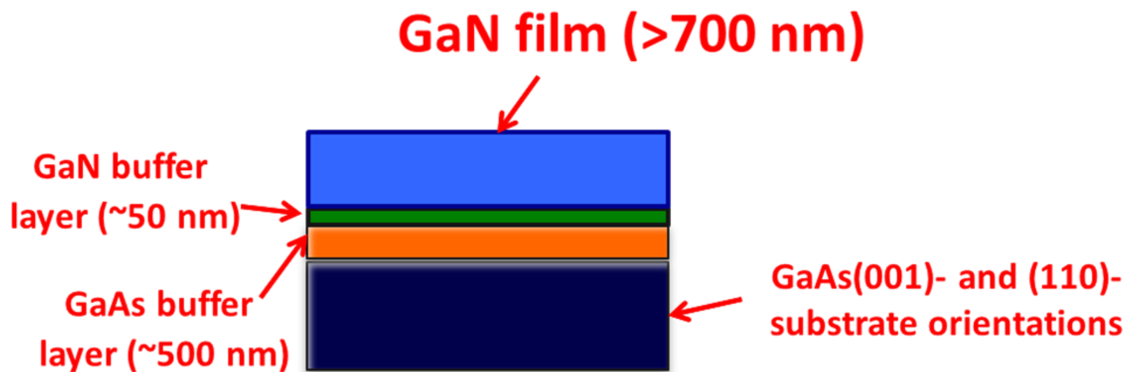


Figure 3.2 Illustration of the GaN film's structure grown on GaAs (001) – and (110) – substrate orientations

Figure 3.1 illustrates the growth mechanism in MOVPE. First, the precursor in gas phase has been flow in the system. Second, Chemical reaction will by absorb some of energy to extract an atom from compound, this phenomenon called Pyrolysis. Next, mass transport to the substrate surface which spin and obtain some energy form heat, this technique give surface absorption and diffusion phenomena. Then, Ga and N atom construct the bond and growth crystal structure.

In the thesis, GaN films were grown on GaAs (001)- and (110)-oriented substrates at 900°C by metal organic vapor phase epitaxy (MOVPE). Trimethylgallium (TMGa), thertiarybutylarsine (TBAs) and dimethylhydrazine (DMHy) were used as the Ga, As and N precursors, respectively. Figure 3.2 illustrate GaN film grown on GaAs substrate which has GaAs buffer layer 500 nm and GaN buffer layer 50 nm.

From section 1.1, GaN grown on GaAs (001) with 4 min of ramping time [30, 31] has been reviewed. The growth process of this film has been shown on figure 3.3.

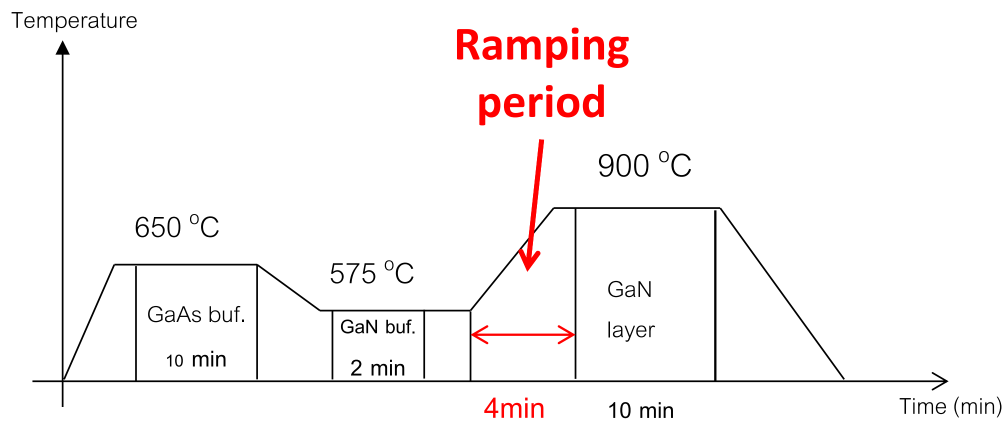


Figure 3.3 Growth process diagram of the GaN film on GaAs (001) substrate with using 4 min of ramping time.

Thermal damage at interface due to As atom decomposition. In this experiment, we have two hypothesis which protect GaAs substrate surface from high temperature growth.

3.1.2 Reducing of ramping time

In this experiment, 3 specimens of GaN films grown on GaAs (001) substrates with different ramping times of 4 ,2 and 1 min, as shown on Figure 3.4 .These films has been grown for 10 min which have 700 nm of averages thickness.

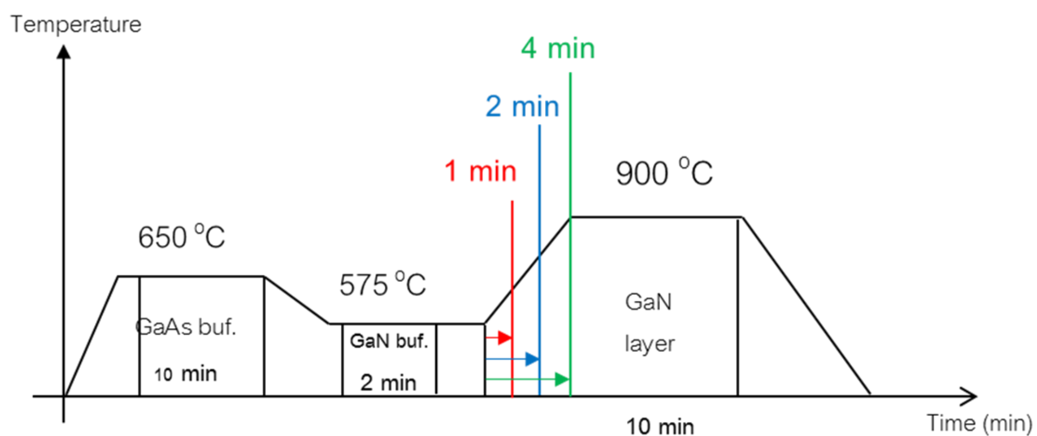


Figure 3.4 The modified growth process by reducing Ramping time, we disregards the growth temperature and start growth process when the ramping time at 2 and 1 min.

3.1.3 The higher Step density GaAs (110) substrate orientation

Another hypothesis for protect substrate surface from thermal decomposition is increase nucleation for substrate surface. GaAs (110) surface [32] which higher step density [33] has been use as substrate in this experiment. Figure 3.5 shown (110) surface which label the step of (110) to the red line. This show that (110) surface have atomic step more than (001) surface. This involve to higher nucleation rate also. In this experiment, GaN have been grown on GaAs (110) substrate surface orientations with same condition of ramping time as previous section 3.1.2 for 3 specimens. Moreover, We have considered GaN/GaAs (110) which have different thickness that are grown for

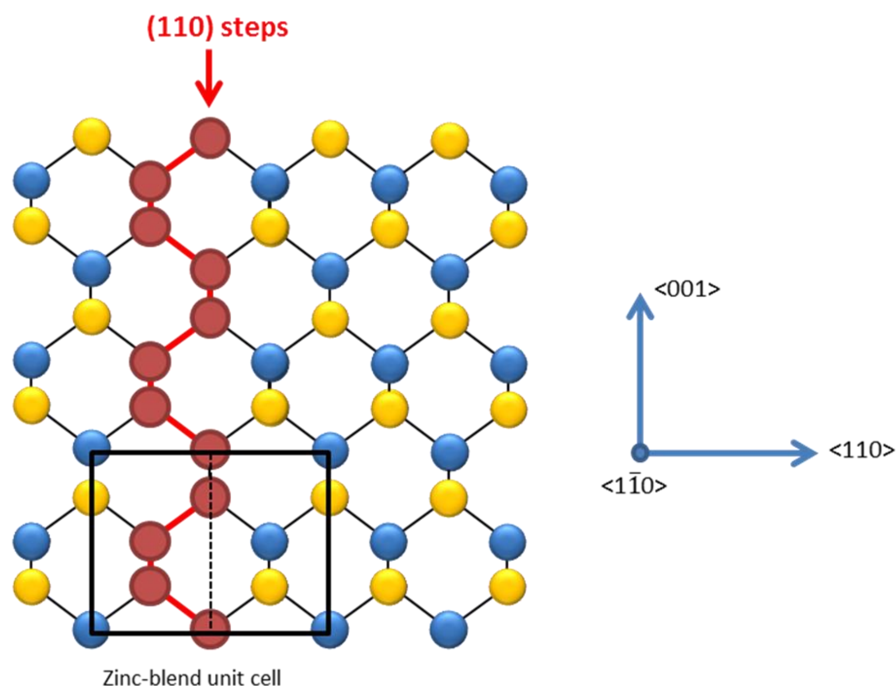


Figure 3.5 Cross-sectional of 2-dimensional GaN crystal in the <1$\bar{1}$0> direction showing step density on the (110) plane

10, 30, 60 and 120 min as condition on figure 3.6 for 4 specimens, which have thickness as table 3.1

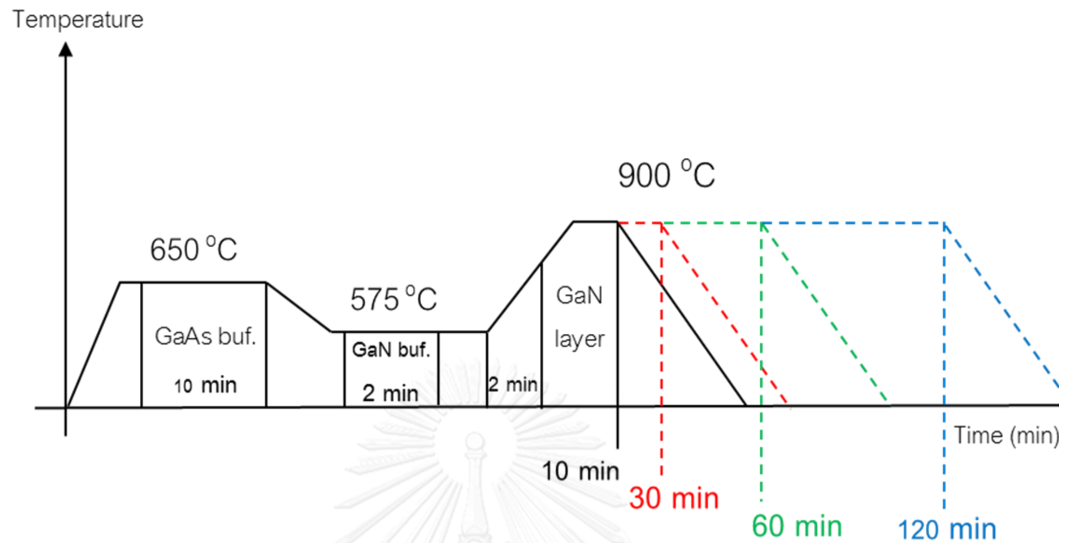


Figure 3.6 The modified growth process diagram of GaN film grown on GaAs(110) substrate. We have expanded the growth time to 30, 60 and 120 min.

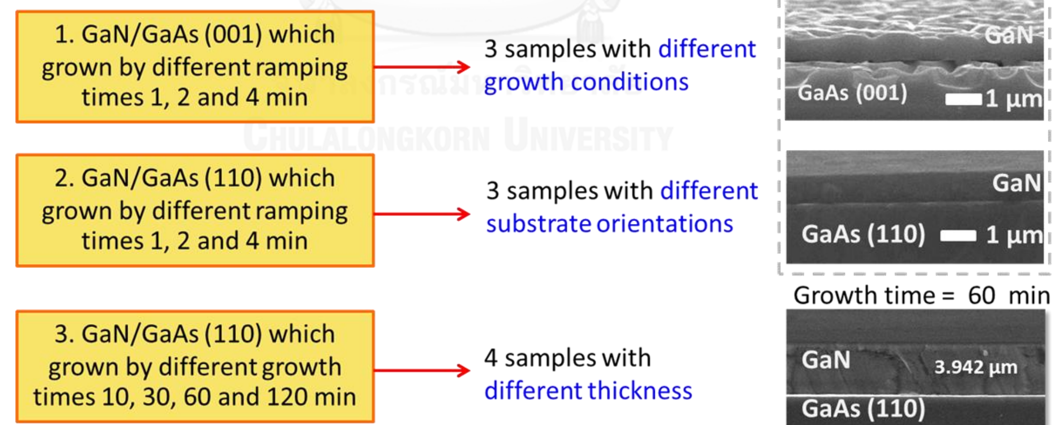


Figure 3.7 SEM images of 10 specimens of GaN films grown on GaAs substrates with different growth conditions, subdivided to 3 series. There are series of different ramping time, different substrate orientations and different thickness.

Growth time (min)	Thickness (μm)
10	0.8
30	2.7
60	3.9
120	8.4

Table 3.1 GaN films grown on GaAs (110) substrates with ramping time of 2 min, showing a relation between growth time and thickness.

3.2 Raman Spectroscopy setup

Crystal structures of the GaN grown films were investigated by μ-Raman spectroscopy with 10mW of power, different excitation wavelengths of diode pumped solid state (DPSS) lasers 473, Ar^+ 532 and He-Ne 633 nm, which expected for information from different penetration depths (the depth which electro-magnetic wave travel in the medium and decreasing intensity to 37%) of GaN as table 3.2.

The experimental apparatus used to record Raman spectra is shown in figure 3.8 and 3.9. The specimen has been excited by coherent laser which 2μm radius of spot, then scattered to monochromator and finally, reach to multi-channel change couple device (CCD) as, the photon-counting detector.

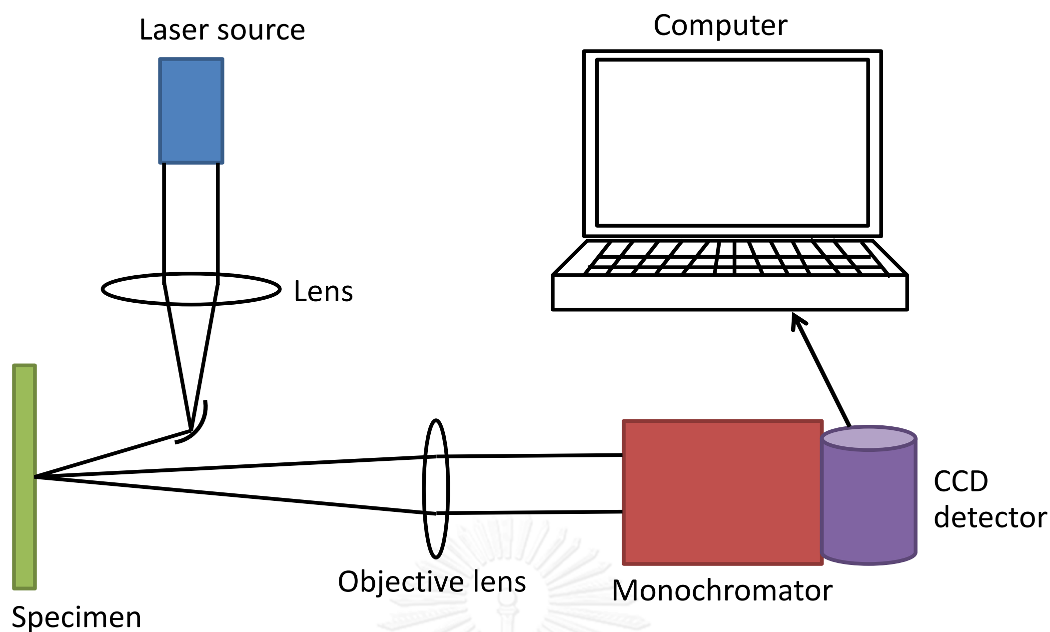


Figure 3.8 Schematic drawing of Raman spectroscopy system.

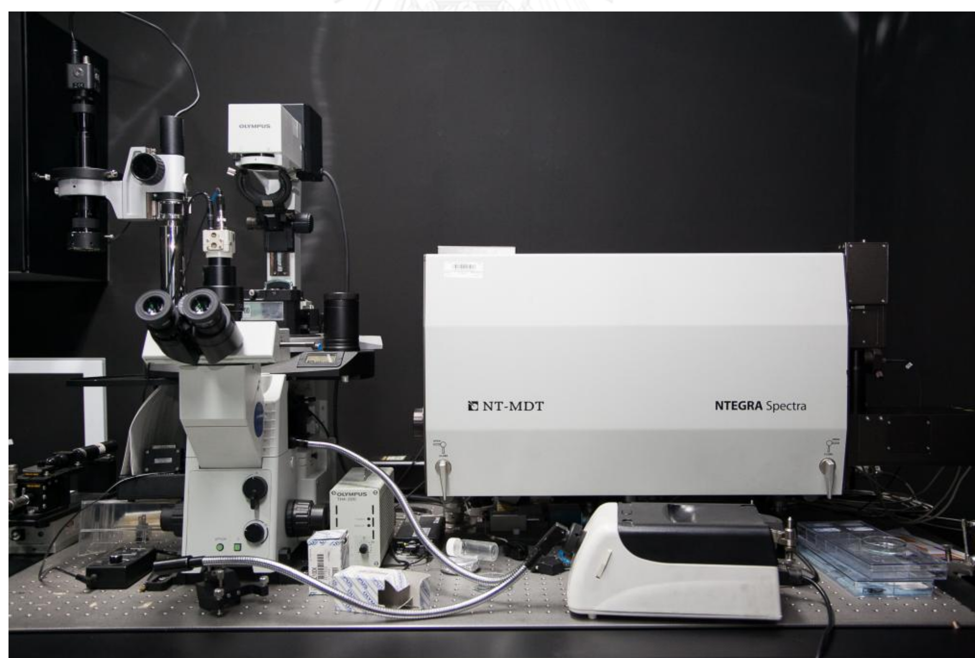


Figure 3.9 Raman spectroscopy setup at National Nanotechnology Center (NANOTEC).

Excited wavelength (nm)	Penetration depth (nm)
473	144.77
514	157.32
532	162.83
633	193.74

Table 3.2 Calculation of penetration depth related to excited wavelength.

3.3 X-Ray Diffraction (XRD) setup

Epitaxial GaN layer exhibits a high degree of crystalline perfection, which crystal information underlying single – crystal substrate. X-ray diffractrometer has a long been use as a tool to investigate the structural phase and crystal quality, interpretation from X-Ray diffraction pattern. Schematic X-ray diffraction apparatus has been shown in figure 3.10 and shows how does it work as figure 3.11. They moves X-ray source and detector while collecting diffracted beam which according to Bragg's condition (eq. 2.4). The 2θ/ω mode gives relation between Intensity of X-ray diffracted and 2θ angle. This mode is using for investigate distribution of crystal plane which diffracted by FWHM of the peak, additional, we can calculate the plane which diffract by position in diffraction profile, then Bragg's condition (eq.2.4) involve to d-spacing equation as equation 2.5 - 2.6 . In this experiment we used the TTRAX III ,powerful diffractometer. Utilizing an 18 kW rotating anode X-ray source in a θ/θ geometry provides the perfect

system for demanding application which using Cu X-Ray source generated Kα1 (λ = 1.5406 Å), as shown in figure 3.12.

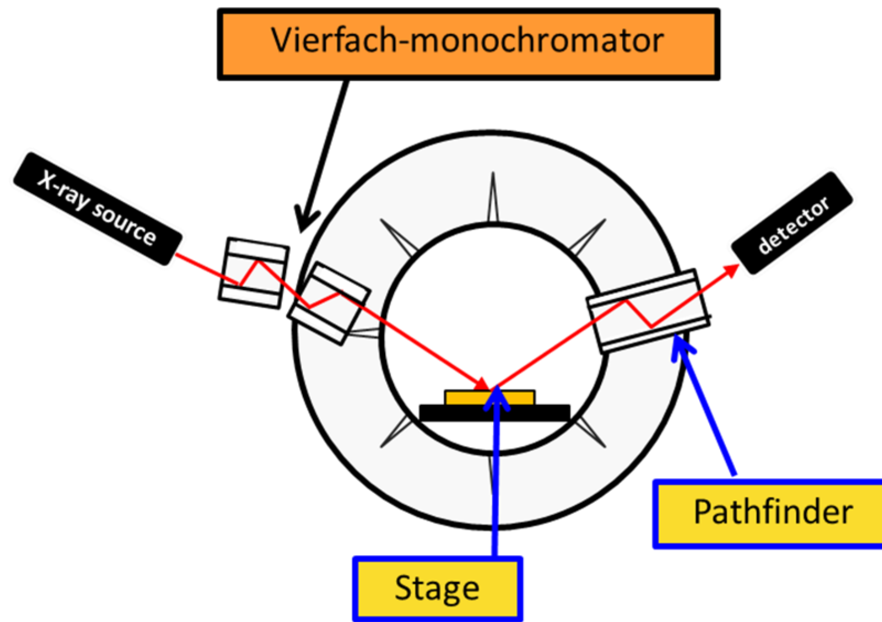


Figure 3.10 Schematic X-Ray diffractometer with alignment.

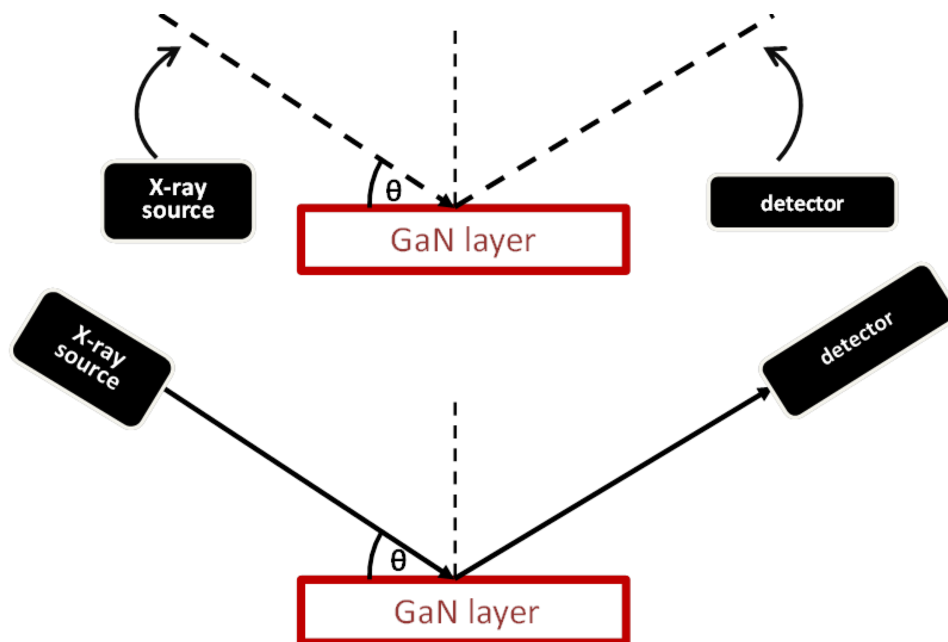


Figure3.11 2θ/ω mode alignment of X-ray diffractometer.

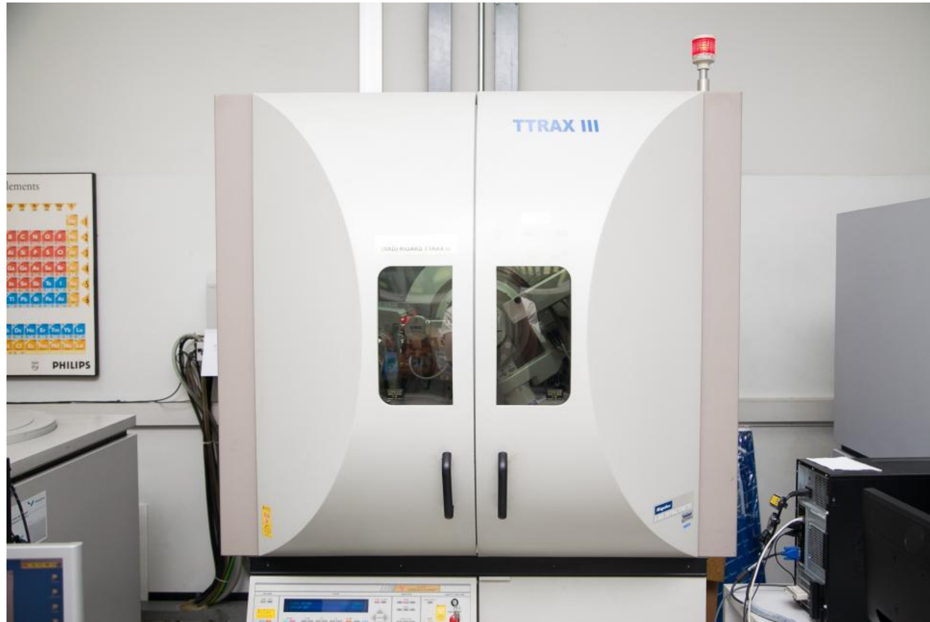


Figure 3.12 the TTRAX III ,X-ray diffractometer. Utilizing an 18 kW rotating anode X-ray source at National Metal and Materials Technology Center (MTEC), Thailand

CHAPTER IV
RESULT AND DISCUSSION

In this chapter, the investigational results of structural properties of GaN films grown on GaAs (001)– and (110)– substrate orientations by SEM, Raman scattering and X-Ray diffraction phenomena are reported. The GaN films grown on the GaAs (001) substrates were used as a reference to compared with the films grown on the GaAs (110) substrates. The results involve to the optimum conditions for growth condition such as different ramping times, growth time and Raman scattering measurement condition were described.

4.1 Effects of Ramping time and GaAs (110) substrate orientation

SEM and AFM images show the interface and surface morphologies of GaN films on GaAs (001) grown with different ramping times of 4, 2 and 1 min, as figure 4.1. GaN film on GaAs (001) with using ramping time of 4 min show voids due to the thermal damage as figure 4.1 (a), while no voids observe for GaN film grown by ramping time less than 4 min. Figure 4.1 (b) and (c) shows SEM images of GaN film on GaAs (001) substrates with grown by using ramping times for 2 and 1 min, respectively. The smoother interface for GaN/GaAs (001) showed that a reduced ramping time of 2 min suppressed the thermal decomposition at interface. As reduced ramping time, we obtained smoother surface confirmed by AFM images as shown in Figure 4.1 (d), (e) and (c) for the GaN films grown using ramping times for 4, 2 and 1 min, respectively.

However, GaN films grown on GaAs (001) substrates does not flat, they are still rough and ineligible for make semiconductor devices. For GaN films grown on GaAs (110)-oriented substrates, SEM images are shown, as figure 4.2 (a) - (c), SEM images shows smooth interface for GaN films grown on GaAs (110) substrate for all ramping time. This interpreted that higher step density can protected GaAs layer form high temperature growth. For GaN films, AFM images shows flat surface with root mean square roughness (rms) around 8.6 – 13.3 nm, as shown on figure4.2 (d) – (f). This results showed GaAs (110) substrate surface give GaN films with smooth interface and surface for all ramping time. However, figure 4.2 (f) shows AFM image of GaN surface, with the contrast like grain. This shows GaN film with used ramping time for 1 min exhibit to poly crystals on the top of the film.

Crystal structure have been interpreted by Raman scattering results. For GaAs (001) substrate, Raman spectra shows TO and LO phonons at 267 and 291 cm^{-1} which corresponded to 514 nm of excitation wavelength. GaAs wafer with no growth any film, grown by used ramping time for 4, 2 and 1 min represents by green, red, blue and black spectrums, respectively. Compared spectrums of 4 specimens are shown, as figure 4.3 (a). For GaAs (001) with refer the green spectrum to phonons corresponded from no damage GaAs surface. Raman spectra shows TO/LO integrated intensity ratio with changed respects to different ramping times, as table 4.1. This results showed GaAs phonons are sensitive with ramping time condition and corresponded to the thermal damages at interface. This claim that Raman scattering has been used as a tool to

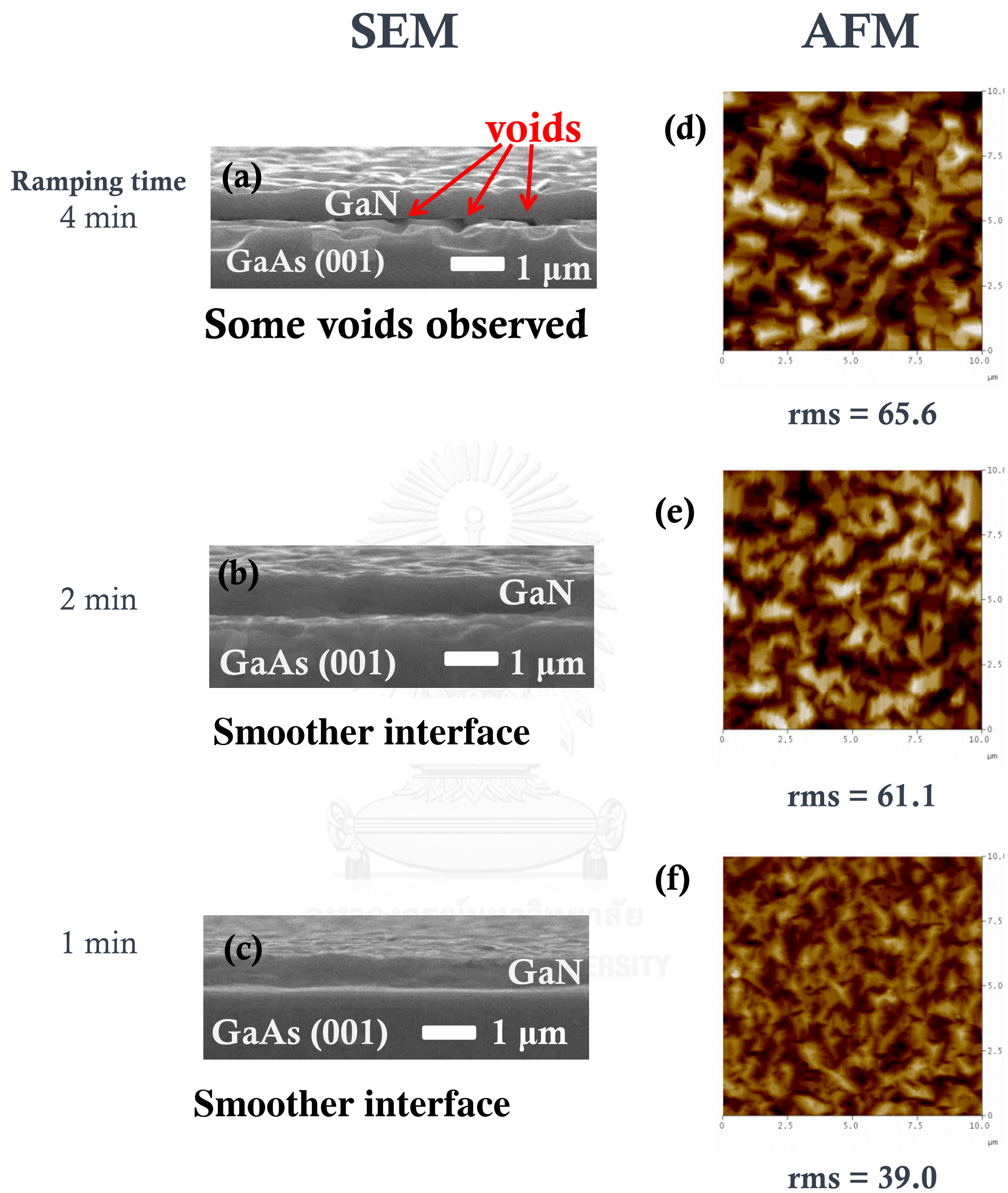


Figure 4.1 SEM images of GaN film grown on GaAs (001) which ramping time of (a) 4 min, (b) 2 min, (c) 1 min and AFM images which are (d) 4 min (e) 2 min (f) 1 min

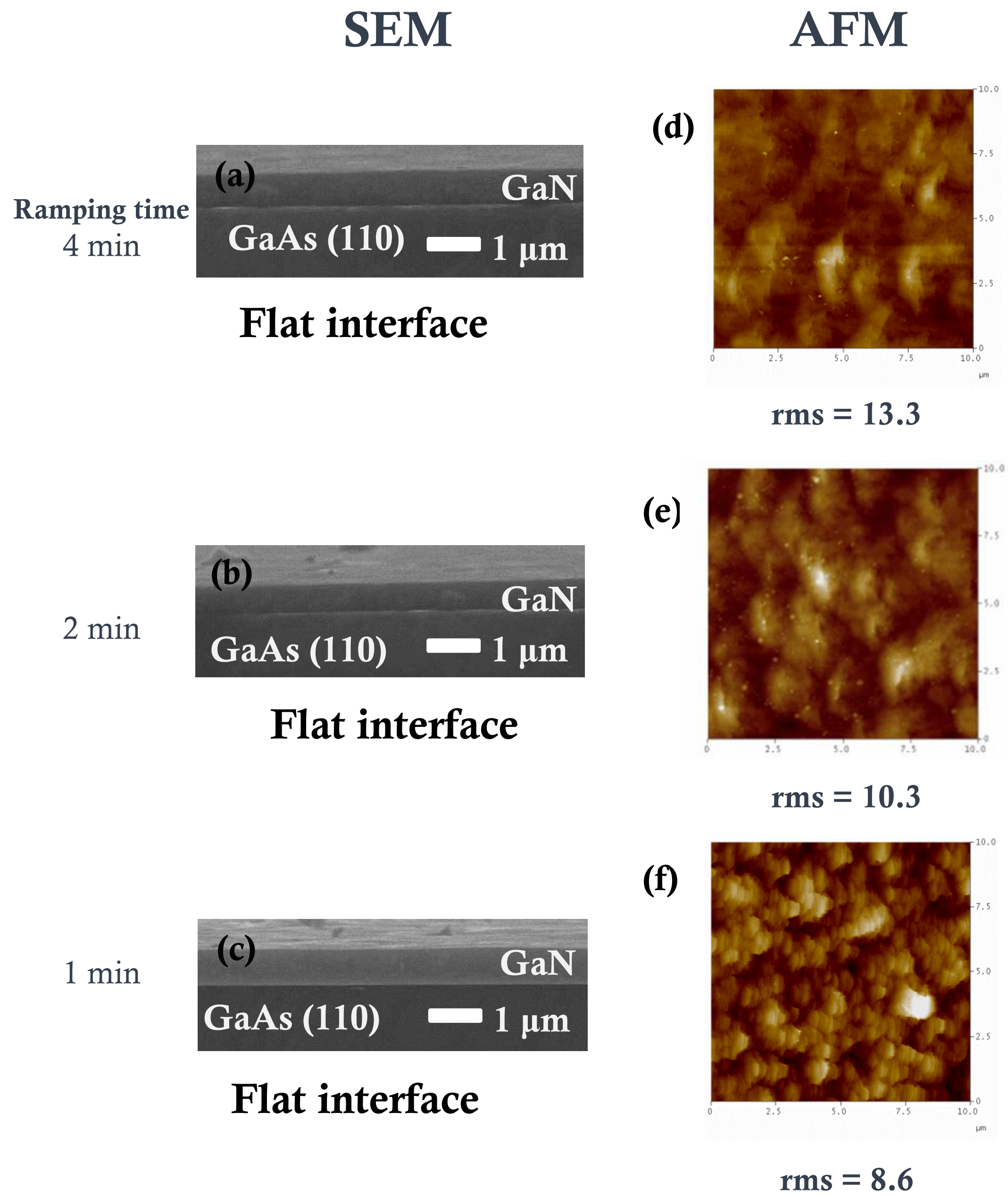


Figure 4.2 SEM images of GaN film grown on GaAs (110) with ramping time of (a) 4 min, (b) 2 min, (c) 1 min and AFM images with ramping time of (d) 4 min (e) 2 min (f) 1 min.

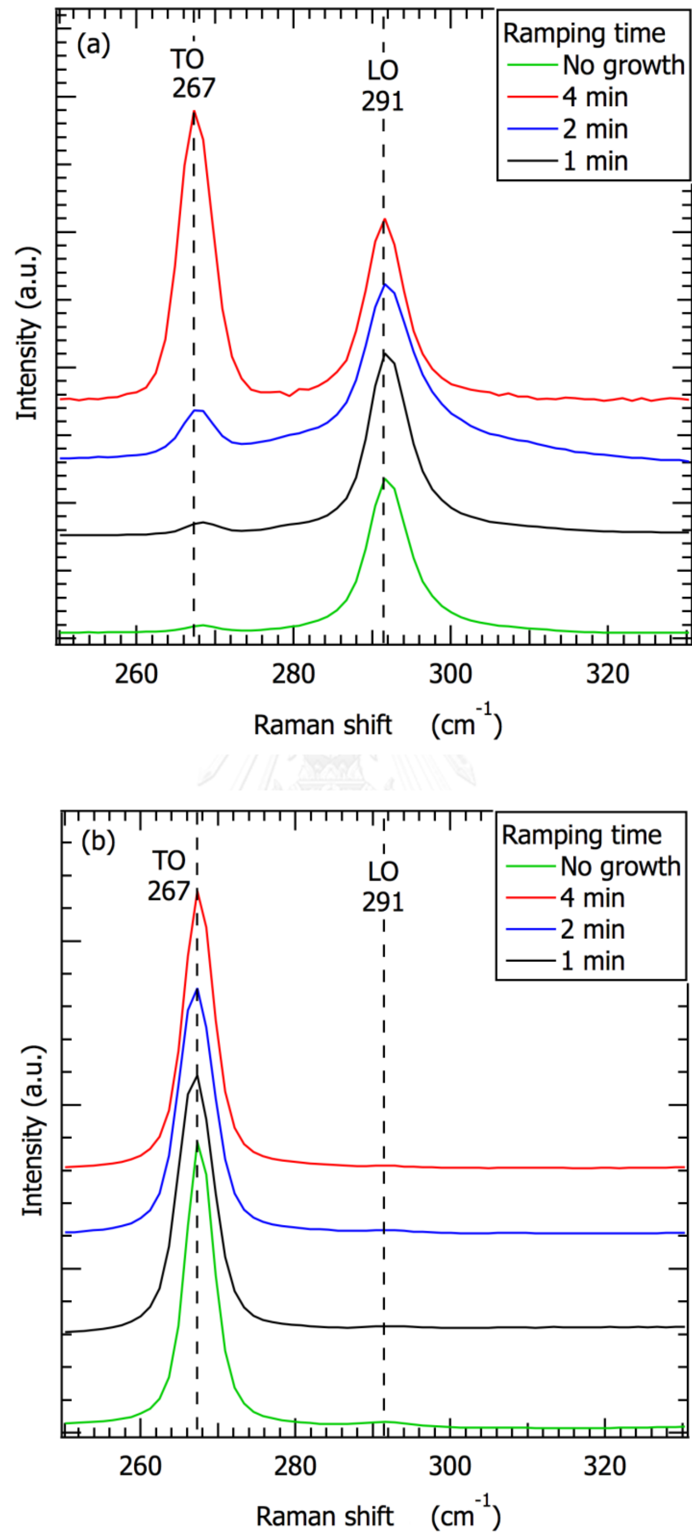


Figure 4.3 Raman spectra of GaAs (a) (001) – and (b) (110) – oriented substrates, which were grown by different ramping times.

Ramping time \ Substrate	GaAs (001)	GaAs (110)
No grown	41	0
1 min	42	0
2 min	6	0
4 min	1	0

Table 4.1 Intensity ratio of LO/TO phonon of GaAs substrates which grown using different ramping times of 1, 2, and 4 min.

investigate the imperfection of GaAs surface and reduced ramping time keep the ratio close to no growth sample. Next, we used the same method to investigate GaAs (110) crystal quality. Figure 4.3 (b) shows no change of TO/LO ratio for all ramping times. This according to SEM images of GaN/GaAs (110) and confirm that GaAs (110) substrate orientation can keep the crystal quality due to high temperature growth.

For GaN film, figure 4.4 shows Raman spectra of GaN film grown on GaAs (001) with different ramping times for 4, 2 and 1 min refer to red, green and blue lines, respectively. Hexagonal phase related phonons, A_1 (TO) and E_2 – high have been observed at 536 and 569 cm^{-1} and cubic phase related phonon, TO has been observed at 552 cm^{-1}. While the broaden peak represented merged phonons signal of hexagonal – A_1 (LO) at 735 cm^{-1} and cubic – TO at 737 cm^{-1}. Raman spectra shows cubic – TO phonon is dominated at 552 cm^{-1}, this interpreted that cubic TO phonons is sensitive to Raman scattering with excitation wavelength of 514 nm with back scattering condition. From the literature, GaN/GaAs (001) exhibited to cubic structure as a main crystal structure.

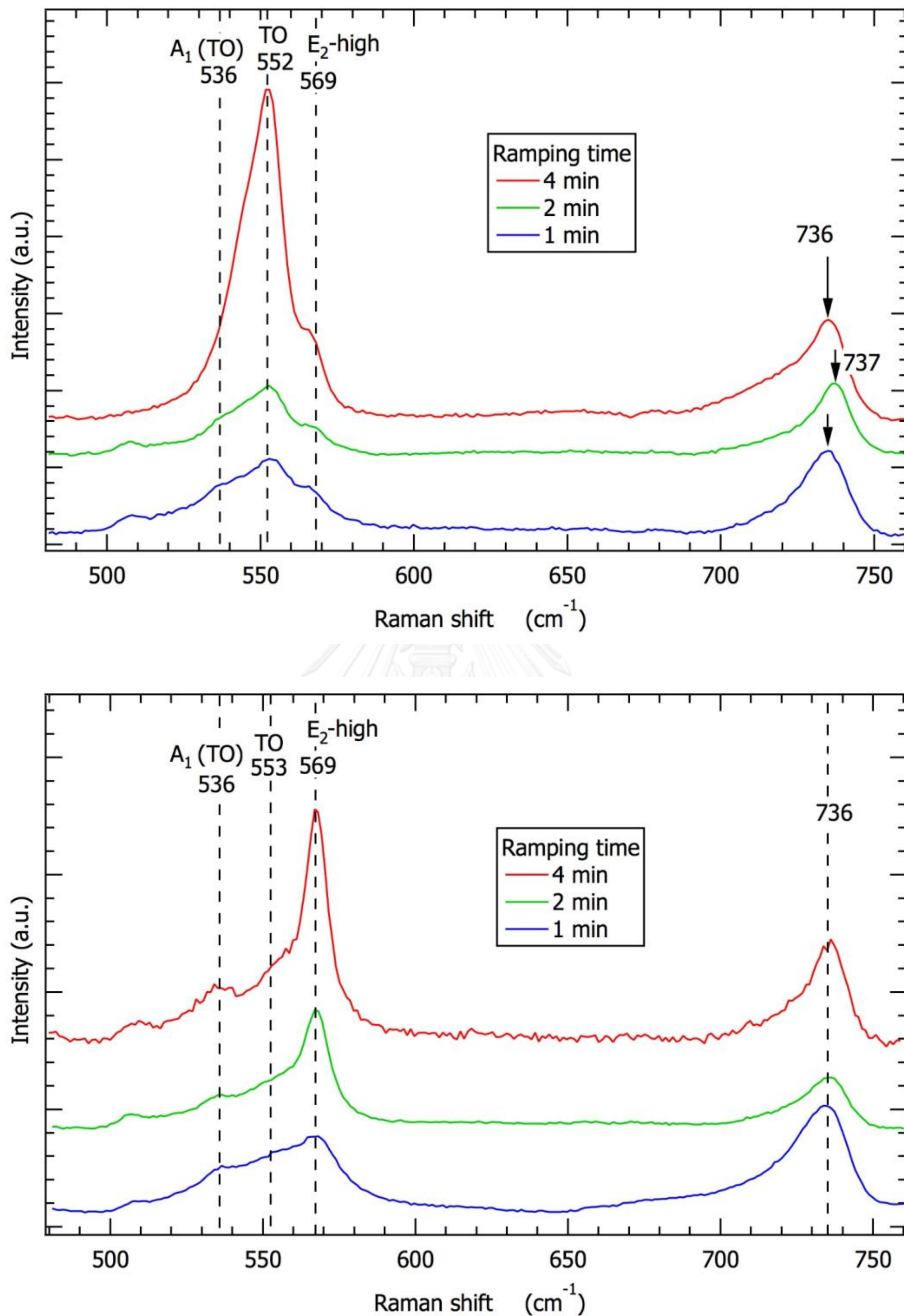


Figure 4.4 Raman spectra of GaN films on GaAs (a) (001)- and (b) (110)- oriented substrates, which grown using different ramping times.

Then, this Raman scattering results shows GaN films grown on GaAs (001) substrate surface exhibit to cubic as a main crystal structure and decrease with decreasing ramping time. For GaN films on GaAs (110) substrate orientations, hexagonal phase related phonon E_2-high at 569 cm^{-1} is dominate for all ramping time. However it decrease at the same way as ramping time. This shows that GaN film exhibit more cubic structure content with short ramping time.

In summary, surface morphologies and interface of GaN films on GaAs (001) and (110) oriented substrate have been observed by SEM and AFM. For GaAs (001), GaAs substrate was damaged due to thermal decomposition at high growth temperature of 900 ^oC. Cubic structure was observed as a main structure according to Raman spectra.
(b)
For GaN on GaAs (110), there are no damage on GaAs/GaAs interface. Hexagonal structure was observed as a main structure according to Raman spectra. Finally, decreasing ramping time trend to give a smooth interface, lower surface roughness and reduce hexagonal phase inclusion. Best optimum condition of growth parameter for ramping time is 2 min, with smooth surface and interface were used for the next section.

4.2 Effect of excitation wavelength on Raman spectra of 473, 532 and 633 nm

In this section, Raman spectroscopy with different excitation wavelength of 473, 532 and 633 nm under back scattering condition was used as a tool to probe the phonon in different depth respect to penetration depth (in section 3.2). For GaN film, Figure 4.5 shows Raman spectra of GaN film grown on GaAs (001) with used ramping time of 4 min measured by using different excitation wavelength of 473, 532 and 633 nm refer to blue, green and red spectrum, respectively. Hexagonal phase related phonons, A_1 (TO), E_2-high and cubic phase related phonon TO have been observed at 533 and 568 and 552 cm^{-1}, respectively at the same Raman shift for all the excitation wavelengths. Broaden peak represented merged phonons signal of hexagonal – A_1 (LO) and cubic – TO around 735 - 738 cm^{-1}. Figure 4.5 (a) – (c) shows compared Raman spectra between excitation wavelengths of 473, 532 and 633 nm, which corresponded cubic – TO phonon is dominated at 552 cm^{-1} and less detection of hexagonal phase related phonons was observed for the longer excitation wavelengths, especially for 633 nm. For GaN film on GaAs (001) which used ramping time for 2 and 1 min, Raman spectra shows same result as the film which used ramping time 4 min, as figure 4.6 and 4.7, respectively. Compared Raman spectra between excitation wavelengths of 473, 532 and 633 nm, which corresponded cubic – TO phonon is dominated at 552 cm^{-1} and less detection of hexagonal phase related phonons was observed for the longer excitation wavelengths, especially for 633 nm, Also. Figure 4.8 shows Raman spectra between the ranges of 700 – 760 cm^{-1} for GaN film grown with different ramping times. Blue, green

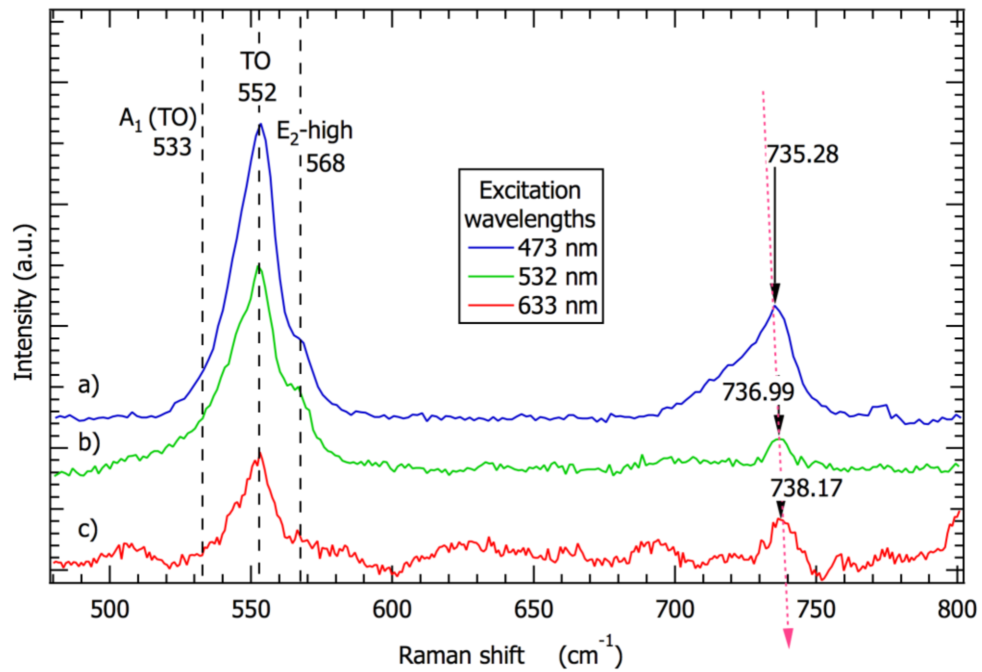


Figure 4.5 Raman spectra of GaN film grown on GaAs (001) with ramping time of 4 min for the excitation wavelengths of (a) 473 nm (b) 532 nm (c) 633 nm.

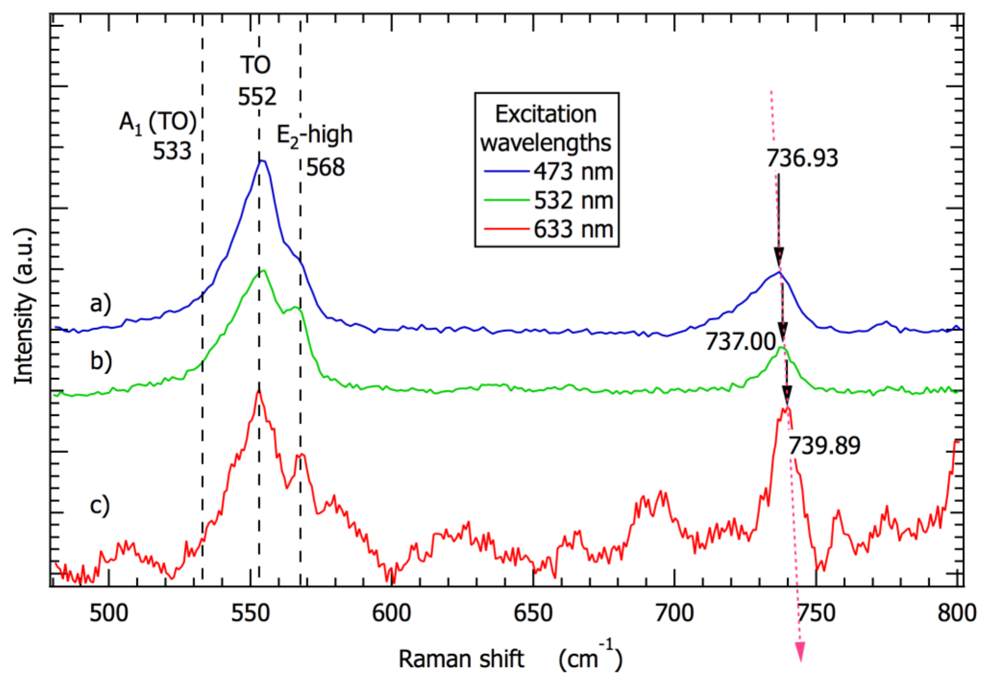


Figure 4.6 Raman spectra of GaN film grown on GaAs (001) with ramping time of 2 min for the excitation wavelengths of (a) 473 nm (b) 532 nm (c) 633 nm.

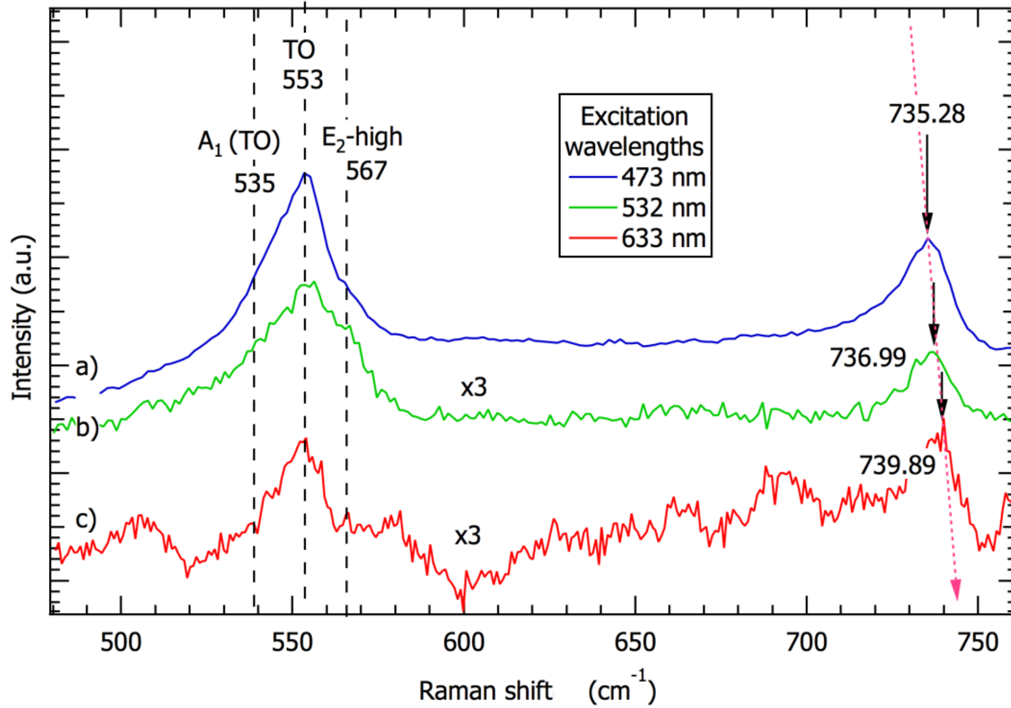
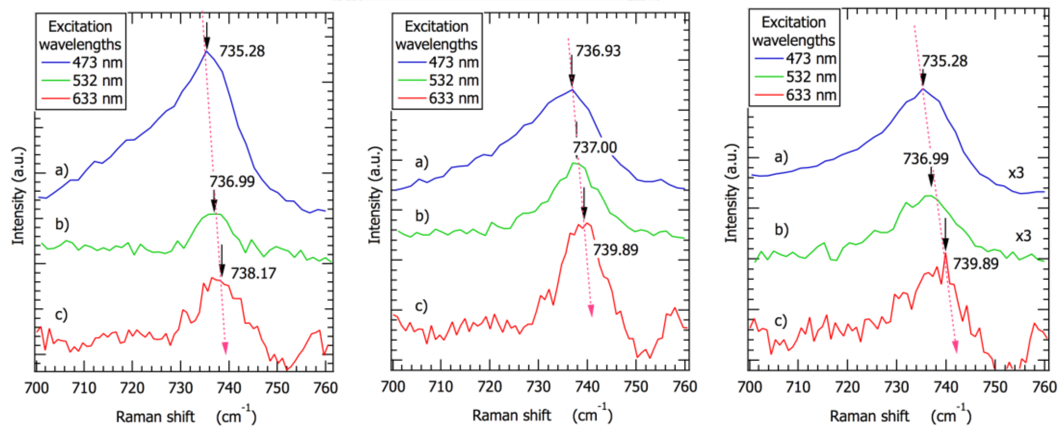


Figure 4.7 Raman spectra of GaN film grown on GaAs (001) with ramping time of 1 min for excitation wavelengths of (a) 473 nm (b) 532 nm (c) 633 nm.



Ramping time 4 min 2 min 1 min

Figure 4.8 Raman spectra of GaN films grown on GaAs (001) with different ramping times of 4, 2 and 1 min, at the range between 700-760 cm^{-1} for the excitation wavelengths of (a) 473 nm (b) 532 nm (c) 633 nm.

and red lines represents as excitation wavelengths of 473, 532 and 633 nm, respectively. The peak covered in the range with corresponded to hexagonal phase related – A_1 (LO) at 735 cm^{-1} and cubic phase related – TO at 738-739 cm^{-1}. Raman feature observed this peak at 735 cm^{-1} significantly shifted to 739 cm^{-1} and sharper with changing the excitation wavelength from 473 nm to 633 nm, indicating a less sensitive of hexagonal phase related phonon – A_1 (LO) to Raman scattering for longer excitation wavelengths.

For GaN films on GaAs (110) substrate, Raman spectra have been shown as figure 4.9 - 4.12. Figure 4.9 shows corresponded phonons with excitation wavelength of 473, 532 and 633 nm represented as blue, green and red spectrum, respectively. Hexagonal phase related phonons, A_1 (TO), E_2-high and cubic phase related phonon TO have been observed at 533 and 568 and 552 cm^{-1}, respectively at the same Raman shift for all the excitation wavelengths. Broaden peak represented merged phonons signal of hexagonal – A_1 (LO) and cubic – TO around 735 - 739 cm^{-1}. For GaN film with grown by using ramping time for 4 min, Raman spectra shows hexagonal phase related phonon namely E_2 - high was dominated with using GaAs (110) surface. For GaN film grown with used ramping time of 2 min, as figure 4.10, Raman spectra shows hexagonal phase related phonon E_2 – high is dominated for all excitation wavelength. There is less detection of hexagonal phase related phonons was observed for longer excitation wavelengths, especially for 633 nm. Finally, figure 4.11 shows Raman spectra of GaN film grown on GaAs (110) with ramping time for 1 min. Hexagonal phase related phonon

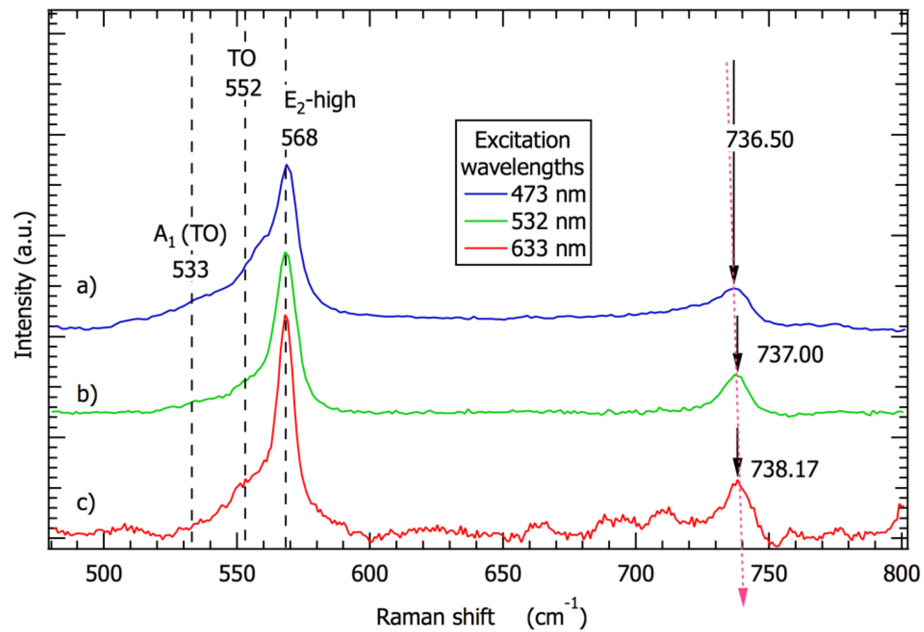


Figure 4.9 Raman spectra of GaN film grown on GaAs (110) with ramping time of 4 min for the excitation wavelengths of (a) 473 nm (b) 532 nm (c) 633 nm.

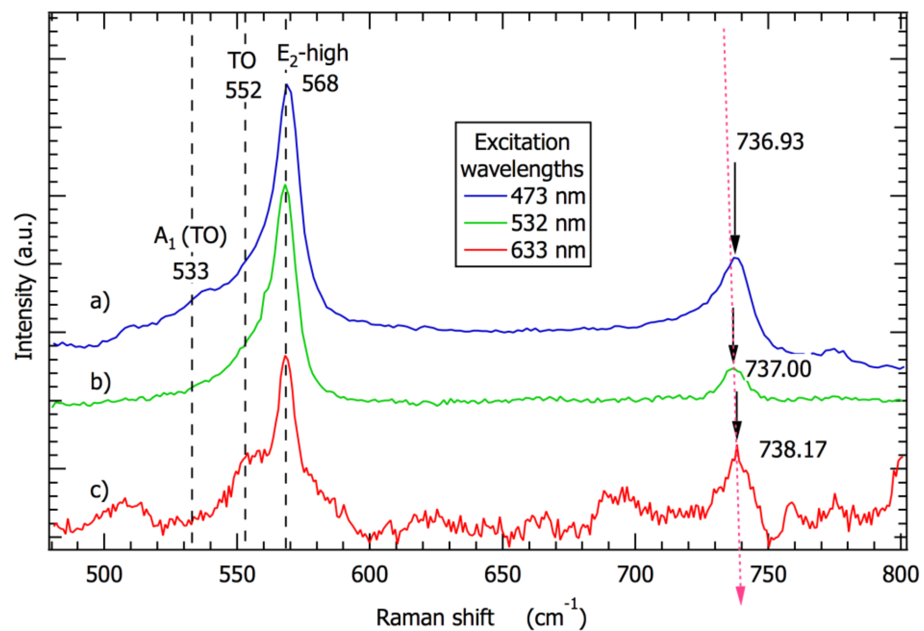


Figure 4.10 Raman spectra of GaN film grown on GaAs (110) with ramping time of 2 min for the excitation wavelengths of (a) 473 nm (b) 532 nm (c) 633 nm.

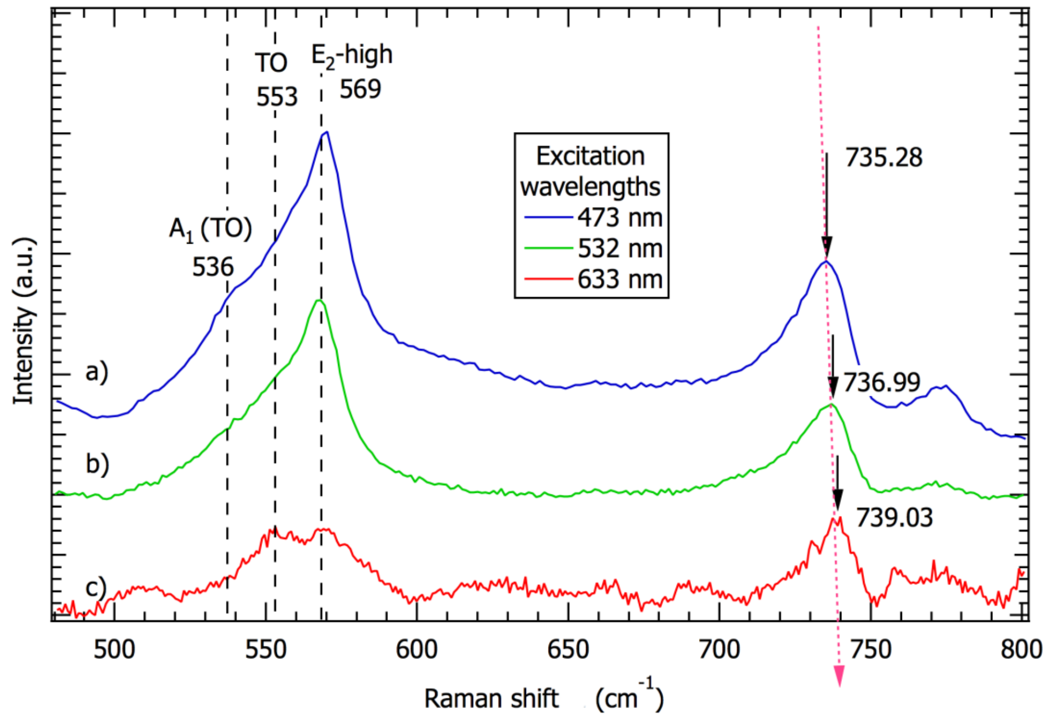
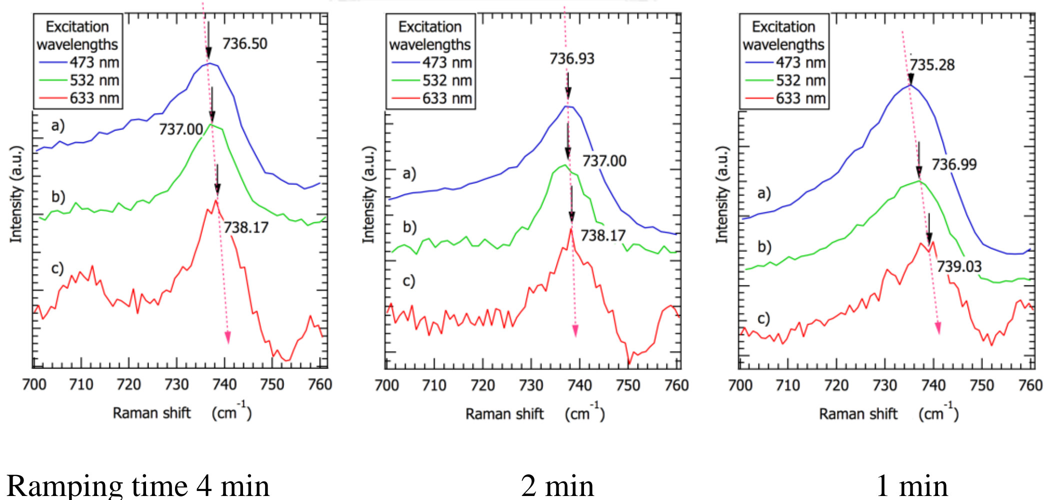


Figure 4.11 Raman spectra of GaN film grown on GaAs (110) with ramping time of 1 min for the excitation wavelengths of (a) 473 nm (b) 532 nm (c) 633 nm.



Ramping time 4 min 2 min 1 min

Figure 4.12 Raman spectra of GaN films grown on GaAs (110) with different ramping times of 4, 2 and 1 min, at the range between 700-760 cm^{-1} with excitation wavelengths of (a) 473 nm (b) 532 nm (c) 633 nm.

of E_2 – high still dominated and it obviously shown that less detection for the excitation wavelength of 633 nm. Additional, figure 4.12 shows Raman spectra between the ranges of 700 to 760 cm^{-1}. For GaN film on GaAs (110) with all of ramping times, the broaden peak which included by hexagonal phase related phonon A_1 (LO) and cubic phase related phonon TO still observed around 735 to 740 cm^{-1}. With changing the excitation wavelength from 478 nm to 633 nm, hexagonal phase related phonon A_1 (LO) is less sensitive to Raman scattering for longer excitation wavelengths. These results shows that cubic phase dominant spectra for longer wavelength especially 633 nm while 473 and 532 nm induces both of hexagonal and cubic phases related phonons.

In summary, the GaN films on GaAs (001) and (001) substrate orientations were investigated by Raman scattering with different excitation wavelengths for 473, 532 and 633 nm. Lower Raman signal related to hexagonal phase was observed for the longer excitation wavelengths. Hexagonal phase dominant spectra observed by excitation wavelengths of 473 and 532 nm, while cubic phase dominant spectra observed by excitation wavelength of 633 nm. A use of excitation wavelength potentially to induce both hexagonal and cubic phase related phonons in GaN film with polytype structures.

4.3 GaN/GaAs (110) films with different thickness

In this session, GaN grown on GaAs (110) with using 2 min of ramping time and increased growth time due to GaN films with different thickness were discussed. Structural properties were investigated by Raman scattering with excitation wavelengths of 532 and 633 nm and X-Ray diffraction.

4.3.1 Raman scattering results

Crystal structure of GaN/GaAs(110) which are have different thickness of 0.8, 2.7, 3.9 and 8.4 µm have been investigated by Raman scattering, which excitation wavelengths of 532 and 633 nm, as shown in figure 4.13 and figure 4.14, respectively.

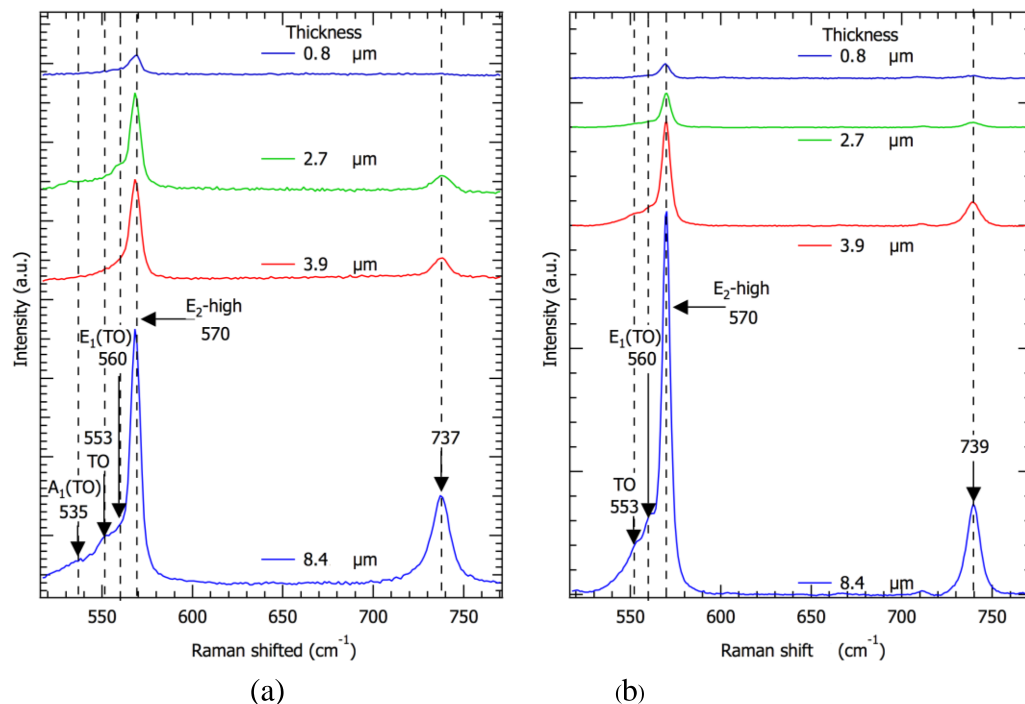


Figure 4.13 Raman spectra of GaN films on GaAs (110) with different thickness of 0.8, 2.7, 3.9 and 8.4 µm using excitation wavelengths of (a) 532 nm (b) 633 nm.

Hexagonal phase related phonons of A_1 (TO), E_1 (TO), E_2 – high, A_1 (LO) have been observed at 535, 560, 570 and 737 cm^{-1}, respectively. Cubic phase related TO phonon still observed at 553 cm^{-1}. These phonons observed at the same wave number for all thickness. The relative intensity of Raman spectra shows higher signal when film thickness increase. These result interpreted that GaN/GaAs (110) films which larger thickness are dominated to h-GaN with less cubic phase structure inclusion. Additional, phonon modes at 735 - 739 cm^{-1} are found to independent from layer thickness with changing excitation wavelength from 532 nm to 633 nm.

4.3.2 X-ray diffraction results

To confirm section 4.3.1, hexagonal content in GaN film grown on GaAs (110) with different thickness have been investigated by X-ray diffraction. GaN films specimens which are 0.8, 2.7, 3.9 and 8.4 μm of thickness have been investigated by X-ray diffraction with 2θ/ω mode between the range of 40° to 120°, represented as green, blue, red and purple spectrums, respectively. This range covered the range of GaAs (220) to GaAs (440) planes. Figure 4.15 shows X-ray diffraction profile corresponded to GaAs (220), GaN (220), GaN ($10\bar{1}3$) and GaAs (440) planes at 45.3°, 57.98°, 63.48 ° and 100.78 °, respectively. Diffraction profile of 0.8 μm GaN film shows that the peak which reflected from GaN (220) plane has been clearly observed. There is no signal of hexagonal phase related plane in the film with thickness of 0.8 μm while it has been found in the film that has thickness more than 0.8 μm. The signal of hexagonal phase

related plane has been detected on GaN/GaAs (110) film which have thickness more than 0.8 μm. It corresponded to both of GaN (220) and GaN ($10\bar{1}3$) planes. This showed There are mixed structure in GaN film grown on GaAs (110) with the thickness more than 0.8 μm. GaN ($10\bar{1}3$) plane corresponed to semi-polar h-GaN crystal[34]. The intensity of GaN ($10\bar{1}3$) reflection is significanly increased with layer thickness. These showed semi-polar hexagonal GaN ($10\bar{1}3$) plane is parallel to GaN (220) and GaAs (220) planes

To explain the mechanism of GaN ($10\bar{1}3$) construction, we have considered the unit cell of cubic GaN in the direction of diagonal plane <$1\bar{1}0$> incline with <001> and < 110> for 90°, as Figure 4.16. Non – polar GaN (110) surface shows that this surface

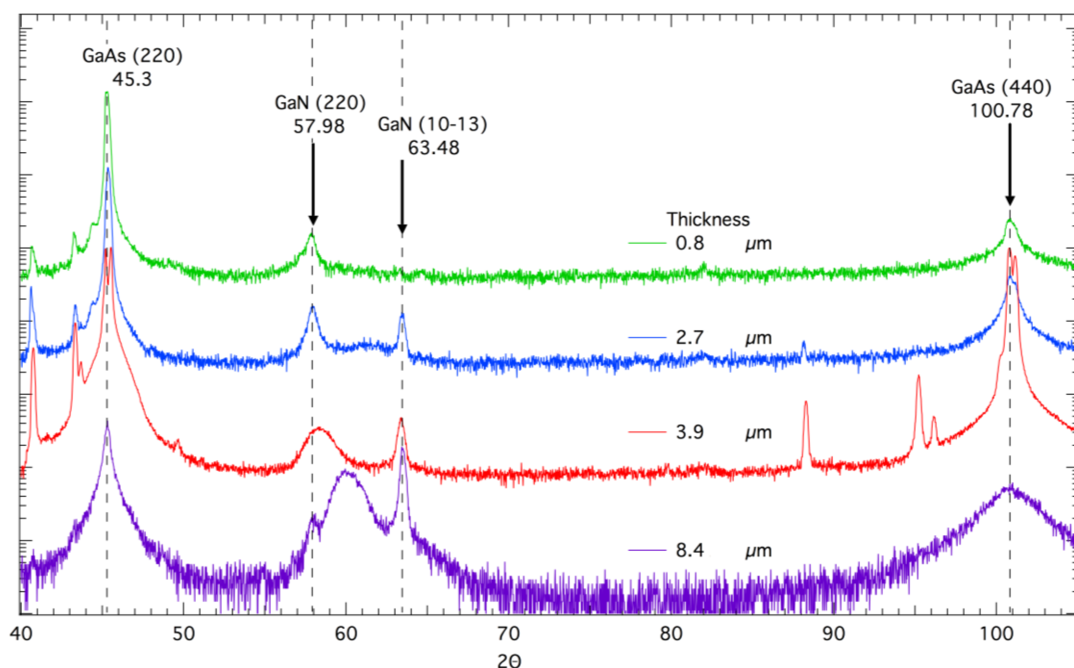


Figure 4.14 Compared Diffraction profiles of GaN on GaAs (110) with different thickness of 0.8, 2.7, 3.9 and 8.4 μm.

have both of As and Ga atom, then hexagonal phase should constructed and placed on both elements. The calculation shows that lattice constant **a** is 4.503 Å in cubic system coresponded to d – spacing of Ga atoms in bottom of hexagonal system give 0.06 % of lattice mismatch. This shows lattice matched between c – GaN (110) and h – GaN ($10\bar{1}3$) and next N atoms incline to (0001) plane for 30°. Strain in GaN film is posible to bended this plane for more 2° to hexagonal plane of ($10\bar{1}3$) which inclined to 32° to (0001) plane. Figure 4.17 shows schematic h – GaN (0001) incline to GaAs (110) substrate surface for 58° or in the other word, h – GaN ($10\bar{1}3$) plane is parallel to GaAs (110) substrate surface [35]. This result interpreted that GaN film grown on GaAs (110) substrate exhibit to c – GaN at first and it construct to h – GaN when grown thicker. These results shows semi-polar h – GaN ($10\bar{1}3$) can be grown by using GaAs (110) as substrate.

In summary, the GaN films grown on GaAs (110) substrate have been investigated by Raman scattering and XRD. Raman scattering showed higher hexagonal phase for thicker films. Different excitation wavelengths independent from the film thickness. This confirm that exciation wavelength is induced different types of phonons. For XRD, hexagonal signal have been detected on GaN/GaAs (110) which have thickness more than 0.8 μm, this coresponded to ($10\bar{1}3$) plane of semi – polar h – Gan crystal. h – GaN (0001) plane incline to GaAs (110) substrate surface for 58° or in the other word, h – GaN ($10\bar{1}3$) plane is parallel to GaAs (110) substrate surface. This result shown that semi – polar h – GaN ($10\bar{1}3$) can be grown by using GaAs (110) as substrate.

The growth mechanism explained by lattice mismatch between c – GaN (110) and h – GaN $(10\bar{1}3)$ ~ 0.06 %, this implied that lattice match involve to construct hexagonal structure due to $(10\bar{1}3)$ plane.

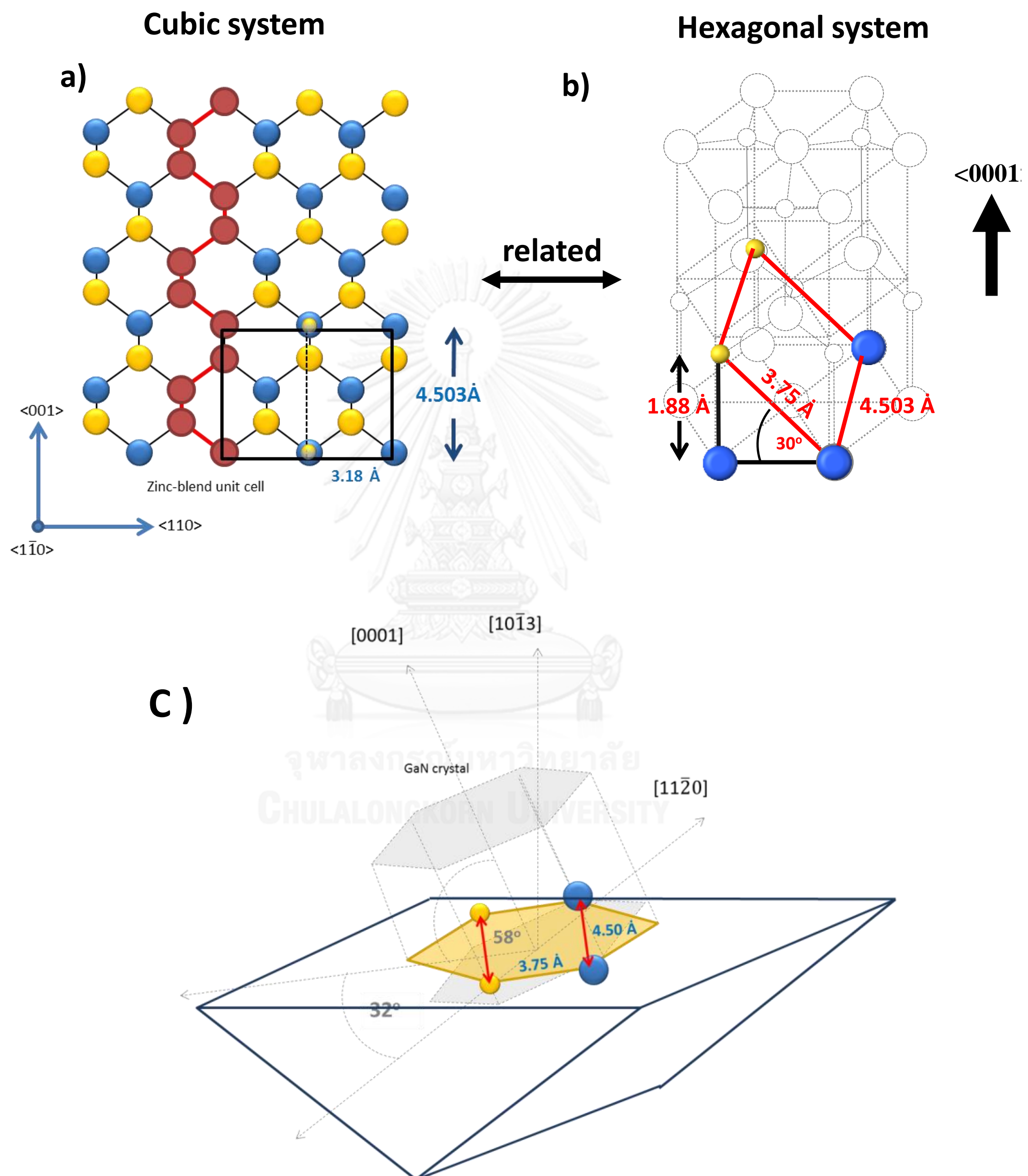


Figure 4.15 Crystallographic relationship showing h – GaN $(10\bar{1}3)$ constructed on c – GaN (110), (a) cubic structure unit cell (b) Ga and N atoms which related to phase transformation (c) schematic h – GaN (0001) incline to GaAs (110) substrate surface

CHAPTER V
CONCLUSION

In the thesis, the author described a study of crystal structures of the GaN film grown on GaAs (110) substrate orientation by MOVPE using different growth conditions. By varying the growth condition, it is expected to get an optimum condition for the growth of high quality cubic GaN film.

As a result, growth morphology including interface and surface of the GaN grown films were investigated by SEM, AFM. Crystal structure and its transformation were investigated by Raman scattering and X-ray diffraction. Based on our results, the conclusion can be divided in 4 parts as follows:

1. We found that the ramping times less than 4 min is trend to exhibit to higher Cubic structure. Use of ramping time for 2 min gives smoother interface and surface for the GaN film on GaAs (001) substrate.
2. The use of GaAs (110) substrate surface demonstrated smooth surface and interface for the GaN films grown all ramping time. This suggests that the higher step density GaAs (110) surface, which is expected to give a high nucleation, can protect the GaAs substrate surface from the thermal decomposition at high growth temperature as high as 900°C. However, the use of GaAs (110) trends to give the GaN films with both the cubic and hexagonal structures.

3. To investigate the main crystal structure in the GaN grown films, Raman spectroscopy was performed to compared with the results from XRD measurements. Raman scattering results showed a mixed structures of cubic and hexagonal structures in the GaN films grown on both the GaAs (001) and (110) substrate orientations. By varying the excitation wavelengths, it is found that the lower hexagonal related phonons are sensitively to observe for the longer excitation wavelengths, especially for 633 nm. For GaN on GaAs (001), GaAs substrate was damaged due to thermal decomposition at high growth temperature of 900°C. Cubic structure was observed as a main structure. On the other hand, for GaN on GaAs (110), No damage on GaN/GaAs interface was observed for all ramping times. However, the hexagonal structure was observed as a main structure. Decreasing ramping time trends to give a smooth interface and lower surface roughness and trend to reduce hexagonal phase generation.
4. XRD results show that the GaN film with layer thickness showed a single crystal of cubic structure. With increasing layer thickness, however, hexagonal signal have been detected on GaN/GaAs (110) which have thickness. This signal is found to correspond to the $(10\bar{1}3)$ plane of h-GaN, indicating a formation of semi-polar h-GaN crystal. Since, the h-GaN (0001) plane inclined to the GaAs (110) surface for 58° or in the other word, the h – GaN $(10\bar{1}3)$ plane is parallel to the GaAs (110) surface. Moreover, lattice mismatch between c-GaN (110) and h-GaN $(10\bar{1}3)$ is as small as 0.06% ,this implies that lattice match significantly involve a construction of hexagonal structure due to a generation of the $(10\bar{1}3)$ plane. These results showed that a semi-polar h-GaN $(10\bar{1}3)$ can

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be grown by using the GaAs (110) as a substrate. With shorter ramping time and thin layer, the cubic GaN crystal is expected to have more stability.

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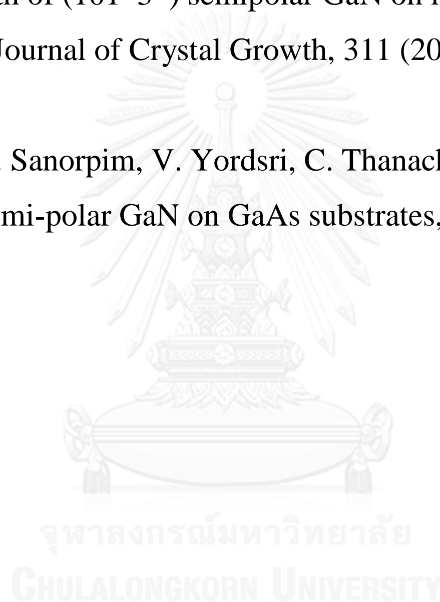

APPENDIX

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VITA

Pitshaya Praigaew has graduated from Chulalongkorn University, Major in Physics, since 2010. He has continued his study in 2012. He also as a fashion photographer.

He has participated four conferences, as follows:

1.International Union of Materials Research Society (IUMRS) 2012, 26-31 Aug 2012, Korea.

2. 9th Mathematics and Physical Sciences 2014, 8-10 Jan 2014, Malaysia.

3.Siam Physics Congress 2015 (SPC2015), 20-22 May 2015, Krabi, Thailand.

4.Siam Physics Congress 2016 (SPC2016), 8-10 June 2016, Ubonratchatani, Thailand.

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