CHAPTER 3

STRUCTURAL AND ETCHING STUDIES
OF GaN THIN FILMS

A thorough and extensive characterization of an epilayer is very difficult because it requires a variety of tests using a number of sophisticated instruments. It is obvious that there are no ideal crystals in reality and all crystals grown by any technique contain some defects, impurities and inhomogenetics. Most of the physical properties are sensitive to the deviation from ideality therefore, generally the characterization of the grown crystals is a necessity. The assessment of crystalline perfection is essential to interpret the structure dependent properties. Post growth analysis of an epitaxial layer provides information on the process in order to improve the quality of the layers. Moreover characterization of the grown epilayers forms an integral part of the growth studies to perform by the crystal grower. The demand for layers of the highest quality is increasing and only systematic characterization enables the crystal grower to optimize the growth parameters in order to obtain better results.

An epitaxial layer characterized by a description of its chemical composition, its structure, its defects and the spatial distribution of these three features. It is very vital to know the degree of purity and perfection of epilayers to interpret structure dependent properties and in order to determine whether the material can be successfully employed in the experiments or device fabrication. GaN being a technologically important material has cited a large degree of characterization studies (Pearton et al 2002). Optimization of
GaN growth to reduce defect density is of paramount importance in achieving high quality GaN layers. In this chapter, the grown epilayers were subjected to the following characterization studies that provide a understanding the properties of gallium nitride.

(i) Determination of refractive index, extinction coefficient of GaN by spectroscopic ellipsometry.
(ii) Molecular structural analysis by Raman scattering studies
(iii) Etching studies by wet chemical etching.

A brief note on the principle and experimental procedure behind each of these techniques is also given in this chapter.

3.1 RAMAN SCATTERING

Raman scattering is a vibrational spectroscopic technique. When light is scattered from the surface of a sample, the scattered light is found to contain mainly wavelengths that were incident on the sample but also different wavelengths at very low intensities that represent an interaction of incident light with the material. The interaction of the incident light with optical phonons is called Raman scattering.

Raman spectroscopy can provide information on crystalline quality, impurity defects, stress and strain. GaN crystallizes in a hexagonal wurtzite structure, which belongs to \( C_{6v}\) space group with four atoms in the unit cell. The first order phonon Raman scattering is caused by phonons with \( k=0 \) (\( \Gamma \) point) because of a momentum conservation rule in the light scattering process. In the hexagonal structure, group theory predicts eight sets of phonon normal modes at the \( \Gamma \) point, \( \Gamma = 2A_1 + 2B_1 + 2E_1 + 2E_2 \). Among them, one set of \( A_1 \) and \( E_1 \) modes are acoustic, while the remaining six modes, \( A_1 + E_1 + 2B_1 + 2E_2 \) are optical modes. \( A_1 \) and \( E_1 \) modes are both Raman and
infrared (IR) active, while the two E\textsubscript{2} modes are only Raman active and the two B\textsubscript{1} modes are neither Raman nor IR active. A\textsubscript{1} and E\textsubscript{1} branches are polar with different energies for the longitudinal (LO) and transverse (TO) components (Fornari et al 2001a). Figure 3.1 shows the raman active modes of wurtzite GaN. The higher frequency E\textsubscript{2} mode is the strongest and is common in hexagonal GaN. Raman spectra of Cl-VPE grown GaN was measured using 488 nm excitation line of SPECTRA PHYSICS 2020-04S argon ion laser. Raman scattering of the sample taken in z(x, x, z) geometry is shown in the figure 3.2. The grown GaN layer shows two Raman modes E\textsubscript{2} (high) and A\textsubscript{1} (LO) at frequencies 569 and 737 cm\textsuperscript{-1} respectively along with sapphire substrate peak at 748 cm\textsuperscript{-1}.

![Raman active vibration modes of wurtzite GaN](image1.png)

**Figure 3.1** Raman active vibration modes of wurtzite GaN

![Raman scattering spectrum of GaN](image2.png)

**Figure 3.2** Raman scattering spectrum of GaN
3.2 ELLIPSMOETRY STUDIES

Ellipsometry is a technique, which measures the state of polarization of light reflected or transmitted from a material medium. A known polarization is reflected or transmitted from the sample and the output polarization is measured. The change in polarization is the ellipsometry measurement, commonly written as:

\[ \rho = \tan(\Psi)e^{i\Delta} \]  

(3.1)

where \( \Delta \) and \( \Psi \) are ellipsometry parameters (Yan et al 2000). For example, when plane polarized light is reflected from an optically smooth material, it becomes, in general, elliptically polarized. The nature of this elliptically polarized light carries information about the optical properties of the material. When change in the polarization state is measured as function of the wavelength \( \lambda \) (or energy /frequency) of the electromagnetic radiation, the measurement is said to be spectroscopic. The response of materials to electromagnetic radiation i.e., the extent to which it is reflected, transmitted or absorbed by the material also depends on the angle at which the electromagnetic wave is incident. The measurement of the state of polarization as a function of \( \lambda \) and incidence angle is called variable angle spectroscopic ellipsometry (VASE).

An ellipsometry study of Cl-VPE grown GaN is measured using Accurion Variable Angle Spectroscopic Ellipsometer. One of the early applications of single wavelength ellipsometry was the precise determination of the thickness of ultra thin surface layers. However, with the advent of spectroscopic measurements and fast computers, it is possible to build multilayer models of materials. Material properties of multilayers like surface & interface roughness, void fraction, individual layer thickness and compositions can also be extracted from ellipsometry. In this experiment the
incident angles is 57°, 60° and 63° and the energy is varied 1.3 to 4.1 eV (300 – 900 nm). The ellipsometric contrast micrograph in figure 3.3 shows the various region of interest taken for the measurements.

Figure 3.3 Ellipsometric contrast micrograph of GaN

Figure 3.4 Calculated $\Delta$ spectrum of GaN on sapphire at incidence angle a) 57° b) 60° and c) 63°
The measured data is fitted using the Lorentz oscillator model (Tompkins et al 2005). The best fit of $\Lambda$ and $\psi$ is pictured in the Figures 3.4 and 3.5. The Lorentz frequency, strength and damping parameters are allowed to vary and finally best fit of $\Lambda$ and $\psi$ shown in the Figures 3.4 and 3.5.

**Figure 3.5** Calculated $\psi$ spectrum of GaN on sapphire at incidence angle a) 57° b) 60° and c) 63°

The average thickness of the grown GaN calculated from the region of interest is 1720.6 nm. The calculated refractive index and extinction coefficient of the as grown GaN epilayer is 2.58, 0.654 at room temperature. These values are good agreement with the GaN films grown by plasma enhanced Molecular Beam Epitaxy (Lin et al 1993).
3.3 ETCHING STUDIES

Even though our grown sample shows very good quality, the occurrence of defects is inevitable like other methods because of the large lattice mismatch between GaN and sapphire and also their mismatch in thermal expansion coefficient. Wet etching is one of the convenient techniques to determine the density of defects propagating to the surface. In order to evaluate the type and density of dislocations occurred during the growth, the samples are studied by wet chemical etching in hot phosphoric acid (H₃PO₄) and molten potassium hydroxide (KOH). Etched samples are characterized with the use of scanning electron microscopy (SEM).

Chemical etching has completely different mechanism when compared to other etching process, it is not affected by an external potential. The reactive molecules from the etchant break the bonds at the semiconductor surface and form oxides that are subsequently dissolved in the etchant. Etching in general is a destructive procedure. Wet etching techniques are extensively used for defect evaluation due to its merits of low cost, simple experimental procedure, and no requirement of sample geometry (Zhuang and
Edgar 2005). The intense of etching of the defected area will be more when compared to the normal one so by selecting an appropriate set of etchants and conditions, the local etch rate at a defect can be made different from the defect-free regions, by that the defect is revealed (Bernardini et al 1997). Such defect-selective etching produces etch pits or hillocks on a semiconductor surface due to the inhomogeneous nature of defects (either in composition, physical structure, or both) compared with the crystal matrix. Usually hot acid, such as phosphoric acid (\(\text{H}_3\text{PO}_4\)) or sulfuric acid (\(\text{H}_2\text{SO}_4\)), and molten hydroxide, such as potassium hydroxide (KOH), have been used to examine the etch pits at the defect site of the GaN (0001) surface (Shintani et al 1976, Kim et al 1998). The main purpose of defect-selective etching is to reveal defects in the crystals including dislocations, precipitates, nanopipes, and inversion domains as well as their distributions. These defects, especially dislocations, are known to affect both the electrical and optical properties of the materials (Rosner et al 1997, Garni et al 1996).

Etching of the grown samples is carried out using \(\text{H}_3\text{PO}_4\) (85%) at four different etching temperature ranges from 383 – 463K. The acid container is placed on a precision digital hot plate and a temperature probe is immersed in the acid for temperature control. The acid solution is stirred for temperature uniformity and the temperature was controlled to an accuracy of \(\pm 1\)K. After the acid reached specified temperature, GaN samples are immersed in the acid for a time period of 5 minutes. While using molten KOH, it is heated in a ceramic crucible and the sample is immersed in it after reaching the specific temperature. In this case, the experiments are performed between 633 – 663K, lasting for 3 minutes. Etching is performed in a ceramic furnace. After finished the etching the samples are immediately taken out of the acid and quenched in cool water to stop further etching. Etching is a destructive process. The following Figures 3.7 and 3.8 shows the damage made by the etchant on the sample.
Figure 3.7 Surface image of GaN (a) before etching (b) after etching

Three kinds of etch pits have been observed. The first type is the largest regular hexagonal pits (S) with a large black core. The second type is intermediate hexagonal pits (M). The third type is the smallest one (E).

Figure 3.8 Three types of etch pits S (large), M (medium) and E (small) formed after (a) etching in molten KOH (b) etching in phosphoric acid
Liu et al (2008) have observed the similar three types of pits while etching the HVPE grown GaN layers using KOH. Hino et al (2000) have also observed these three types of pits in Si-doped GaN epitaxial layers grown on sapphire substrate by raised pressure metal-organic chemical vapor deposition (PR-MOCVD) using a HCl vapor phase etching technique and differentiated them with the TEM studies. With the comparison of their results the large pits S mostly corresponds to the screw dislocation, the intermediate pits M are more likely to be of mixed dislocations and the smallest pits are due to the edge dislocations. A dislocation is a crystallographic defect or irregularity, within a crystal structure. One can view the structure of the GaN with Burgers vector notation in Figure 3.9 to understand more about the origin of these threading dislocations (Sakai et al 1997).

![Figure 3.9](image)

**Figure 3.9 Direction and Burgers vector notation used for the hexagonal structure of GaN**

Usually the observed three dislocations are mainly dominates in the GaN epilayers - i) edge dislocations with a Burgers vector of $1/3 \langle 11 \overline{2} 0 \rangle$, ii) screw dislocations with Burgers vector of $[0001]$ and iii) mixed type dislocations with Burgers vector of $1/3 \langle 11 \overline{2} 3 \rangle$ (Mathis et al 2000)
Figure 3.10  (a) Edge dislocations in GaN with Burgers vectors of the type \( <\overline{1}120> \) and a vertical line direction (b) Perfect screw dislocations with \( b = \pm [0001] \) and line direction [0001] and (c) Mixed character dislocation with Burgers vectors of the type \( <\overline{1}1\overline{2}1> \)

Figure 3.11  SEM picture of Etch pit formed in etching of phosphoric acid at 403K

The etch pit density of the GaN in phosphoric acid at 383K is found to be \( 5 \times 10^7 \) cm\(^{-2} \). The Figure 3.11 shows a etch pit formed while etching in phosphoric acid at 403K. One can also say here the hexagonal pits reflect the crystal symmetry of GaN. In this case the calculated etch pit
density is $8 \times 10^7 \text{ cm}^2$. The etch pit of 4.5µm formed while etching at 423K in H$_3$PO$_4$ is shown in the Figure 3.12. Occurrence of a clear hexagon (black) can be visualized inside the hexagonal pit. Clear steps can be seen in the Figures 3.11 and 3.12 stating that the etching occurred in the removal of layer by layer which in turn also hints that the layer by layer growth has been taken place.

![Etch pit of 4.5µm formed while etching at 423K in H$_3$PO$_4$](image)

**Figure 3.12  Etch pit of 4.5µm formed while etching at 423K in H$_3$PO$_4$**

It has been said in general that the EPD is lower than the dislocation density evaluated by TEM (Kozawa et al 1996, Ono et al 1998). EPD for the samples etched at 423K and 443K are $2 \times 10^8 \text{ cm}^{-2}$ and $5 \times 10^8 \text{ cm}^{-2}$ respectively. While increasing the etching temperature there is increase in the pit size due to coalescence of neighboring pits. The joining of the pits can be clearly seen in the Figure 3.13.
Figure 3.13  SEM image of GaN etched in phosphoric acid at 443K

In molten KOH etching, the temperature is varied at the increase of 283K from 633K to 663K. The etch pit formed are to be larger when compared to phosphoric acid etching.

Figure 3.14  (a) Etch pits formed in KOH etching at 633K (b) Immense etching in KOH at 663K

The EDP calculated at 633K is $8 \times 10^7$ cm$^{-2}$. Shiojima (2000) reported the observations of mixed dislocations in Si doped GaN grown by MOCVD on KOH etching through the studies of TEM and AFM. As the temperature is increased the EDP also found to be increased. The EDP at 643K and 673K are $2 \times 10^8$ cm$^{-2}$ and $6 \times 10^8$ cm$^{-2}$. The etching of KOH at 663K
is found to be vigorous as shown in the figure 3.14 (b). Compared to phosphoric acid the average EDP is more in the case of molten KOH.

Li et al (2001) have shown that the polarity of the GaN will play the main role in KOH etching, independent of the deposition method and the growth condition. Xu et al (2002) studied the phosphoric acid etching on HVPE and MOCVD grown GaN layers and summarized that the optimal etch condition depends on the film deposition technique and film quality, and it is recommended that several etch conditions should be used when evaluating new GaN samples. Reduction of the dislocation density has been observed by the growth of buffer or interlayers (Xue et al (2010, Sanchez et al (2001)). The etch pit density observed in our grown films are comparable to the other results (Hino et al (2000), Shiojima (2000) Xu et al (2002)).

3.4 CONCLUSION

The properties of the grown GaN samples are investigated using Raman and ellipsometry studies. The results of Raman studies show the high crystalline growth of GaN epilayers. The $\Delta$ and $\psi$ parameters in ellipsometry are fitted using the Lorentz oscillator model. And the refractive index, thickness and extinction co-efficient are calculated. GaN grown on sapphire by Cl-VPE is investigated by wet etching in hot phosphoric acid ($H_3PO_4$) and molten potassium hydroxide (KOH). Both $H_3PO_4$ and molten KOH chemical etching are performed GaN samples to investigate the nature of the etch pits. Hexagonally shaped etch pits are formed on the etched sample surfaces. Etched samples are characterized by plan view and cross section SEM. Results showed that both phosphoric acid and molten potassium hydroxide are good wet etchants for GaN and the pits created by molten KOH etching were numerous when compared to the pits created by phosphoric acid. Three types of etch pits are observed on GaN in using both etchants. The result shows acid etching is an effective method for evaluating the type and density of dislocations in GaN.