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INFLUENCE OF HIGH NITROGEN FLUX ON CRYSTAL QUALITY OF MBE GROWN GaN LAYERS USING RAMAN SPECTROSCOPY: A THEORETICAL JUSTIFICATION

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Abstract

Crystal quality of plasma assisted MBE grown hexagonal GaN have been investigated at varying nitrogen and gallium fluxes using Raman spectroscopy. Theoretical calculations revealed the position of E_2(low) and E_2(high) in quality crystal of GaN to be 144 cm^{-1} and 568 cm^{-1} respectively. Crystal quality of the layers is discussed by comparing the experimentally measured Raman spectra with present calculations and other standard results. Room temperature Raman spectra of Ga-rich layers and stoichiometric GaN are similar as exhibiting excitation modes at 434 cm^{-1}, 568 cm^{-1} and 729 cm^{-1} identified as residual laser line, E_2^H and LO mode contribution (A_1(LO) and E_1(LO)) respectively. Similarity of Ga-rich and stoichiometric GaN layers is interpreted as the indication of comparable crystal quality of both GaN layers. In Raman spectrum associated with N-rich GaN samples all the spectral features are disappeared into a broad band in the range of 250–650 cm^{-1}. This typical observation, intensity distribution and missing of regular hexagonal modes, all are signatures of rough surface, bad crystal quality and high concentration of defects. More careful analysis of N-rich spectrum, based on atomic displacement scheme has revealed that these defects are actually Ga vacancies. Therefore, in order to obtain better crystal quality and smooth surface morphology, the optimal growth condition is stoichiometric or slight Ga-rich GaN.

Keywords: Crystal quality thin films, MBE growth, nitrogen flux, Raman spectroscopy, stoichiometry.

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INTRODUCTION

Gallium Nitride has proved to be very promising material for various electronic and optoelectronic devices [Gil 1998, Nakamura 1998]. Direct wide band-gap, high electron saturation velocity, and high breakdown strength are some of the features that make this material most suitable for light emitting diodes (LEDs), Blue Laser diodes, High power and high frequency applications [Strite and Marçoc 1992, Nakamura and fasol 1998, Orton and Foxon 1998, Kung and Razeghi 2000]. The growth of GaN is found to be sensitive against ratio of Ga/N fluxes. It has been shown that the crystal quality as revealed by surface morphology, changes drastically with respective III-V flux ratios [Tarsa *et al.* 1997]. Surface morphology and therefore crystal quality is found to be best near stoichiometric values and gets worsen at both extremes: rough surface morphology is reported at Ga/N ratios lower than stoichiometric values (N-rich regime) which indicate bad crystal quality, while Ga droplets are reported to exist at the GaN surface at Ga/N fluxes higher than stoichiometric values (Ga-rich regime). The results of surface morphology as obtained from atomic force microscopy (AFM) correlate well with reflection high energy electron diffraction (RHEED) [Tarsa *et al.* 1997, Haider *et al.* 2003], rough three dimensional growths in case of N-rich regime agrees well with spotty RHEED spectra but smooth two dimensional growth agrees with streaky RHEED spectra in case of slight Ga-rich regime. Transmission electron microscopy (TEM) has also shown similar results indicating high density of columnar defects. All these results indicate that crystalline quality is good in case of slightly Ga-rich condition and poor for N-rich.

The growth related features for the above mentioned modes of GaN have been performed through X-ray diffraction (XRD), RHEED, PL spectra, AFM and TEM. In order to investigate the lattice properties we address this critical issue of growth through Raman spectroscopy. We have calculated two of the standard hexagonal modes of GaN. Comparison of experimental results with theoretical calculations is employed in order to justify our results. Raman scattering spectroscopy is advantageous over the other techniques because it is non-destructive and requires no special sample preparation so that as-grown materials/layers can be characterized conveniently.

THEORETICAL CALCULATIONS

GaN has a hexagonal (wurtzite) structure and belongs to space group C^4_{6v}. The group theory analysis predicts $A_1 + 2B_1 + E_1 + 2E_2$ optical modes at the Γ point of Brillouin zone. Both B_1 modes are silent, whereas A_1, E_1 and E_2 modes are Raman active. Each of A_1 and E_1 are polar modes [Perlin *et al.* 1992, Bergman *et al.* 1999] and further splits up into their respective longitudinal (LO) and transverse optical (TO) modes denoted as A_1(LO), A_1(TO) and E_1(LO), E_1(TO). The two E_2 modes are non-polar and hereafter called as E_2^L and E_2^H (L and H stand for low and high frequency respectively). The measured phonon frequency ranges for hexagonal GaN are given in the Table 1 [Harima 2002]. A theoretical calculation based on the vibration of Ga and N atoms within the unit cell of hexagonal GaN is being presented. The dynamical matrix for non-polar mode of vibrations is given by Zhang *et al.* [1997] as follows:

$$\begin{pmatrix} -\omega^2 + \frac{k_{Ga}}{m_{Ga}} & \frac{k_{GaN}}{\sqrt{m_{Ga} m_N}} \\ \frac{k_{GaN}}{\sqrt{m_{Ga} m_N}} & -\omega^2 + \frac{k_N}{m_N} \end{pmatrix} \begin{pmatrix} e_{Ga} \\ e_N \end{pmatrix} = 0$$

Here m_{Ga} and m_N are the masses of gallium and nitrogen atoms and k's are the force constants: k_{Ga} and k_N represent the pure vibrations of Ga and N atoms, respectively whereas coupling interaction between the atoms is denoted by k_{GaN}. e_{Ga} and e_N are the respective eigenvectors of vibration for Ga and N atoms. The above given matrix can be written in terms of the following equations:

$$(-\omega^2 + \frac{k_{Ga}}{m_{Ga}})\, e_{Ga} + \frac{k_{GaN}}{\sqrt{m_{Ga} m_N}}\, e_N = 0 \qquad (1)$$

$$\frac{k_{GaN}}{\sqrt{m_{Ga} m_N}}\, e_{Ga} + (-\omega^2 + \frac{k_N}{m_N})\, e_N = 0 \qquad (2)$$

Table 1: Characteristics wavenumbers (phonon frequencies) for phonon modes of hexagonal GaN at room temperature.

Phonon Mode	Phonon Frequencies (cm^{-1})				
	Measured range*	Experimental			Theoretical
		Stoichiometric GaN	Ga-rich GaN	N- rich GaN	
E_2^L	142-145	-	-	-	144
A_1(TO)	530-534	-	-	-	-
E_1(TO)	558-563	-	-	-	-
E_2^H	567-572	567	567	564	568
A_1(LO)	734-739	729	729	-	734
E_1(LO)	734-745	-	-	-	-

* taken from Harima [2002].

The masses of gallium and nitrogen atoms are m_{Ga}= 1.158×10^{-25} Kg and m_N = 2.325×10^{-26} Kg. The force constants of gallium-gallium, nitrogen-nitrogen and gallium-nitrogen bonds are [Zhang *et al.* 1997]:

k_{Ga} = 1.89×10^2 N m^{-1}

k_N = 2.47×10^2 N m^{-1}

k_{GaN} = 1.54×10^2 N m^{-1}

Inserting these values of masses and force constants in eq.(1) and (2) we get

$$(-\omega^2 + 1.632\times10^{27})\, e_{Ga} + 2.968\times10^{27}\, e_N = 0 \qquad (3)$$

$$2.968\times10^{27}\, e_{Ga} + (-\omega^2 + 1.062\times10^{28})\, e_N = 0 \qquad (4)$$

In order to solve these two equations for ω, we re-arrange (3) to get

$$e_N = (3.37\times10^{-28}\omega^2 - 0.55)\, e_{Ga} \qquad (5)$$

Insertion of Eq. (5) into Eq. (4) will eliminate e_N to give

$$(3.37\times10^{-28}\omega^4 - 4.13\,\omega^2 + 2.872 \times 10^{-27})\, e_{Ga} = 0 \qquad (6)$$

Since $e_{Ga} \neq 0$, so one obtains

$$3.37\times10^{-28}\omega^4 - 4.13\,\omega^2 + 2.872 \times 10^{-27} = 0 \qquad (7)$$

This is quadratic equation in ω^2. Using quadratic formula the obtained solutions are:

$$\omega^2 = 1.15 \times 10^{28}\ sec^{-2} \quad \text{and} \quad \omega^2 = 7.42 \times 10^{26}\ sec^{-2}$$

Finally the frequencies of vibration are: $\omega = 1.07 \times 10^{14}$ Hz and 2.72×10^{13} Hz

Using the formula $\overline{\upsilon} = 2\pi c/\omega$, wavenumbers of vibration corresponding to the above frequencies are calculated as

$$\overline{\upsilon} = 568\ cm^{-1} \quad \text{and} \quad \overline{\upsilon} = 144\ cm^{-1}$$

These are the calculated wavenumbers for E_2 (high) and E_2 (low) respectively. Similarly, the calculated frequencies of A_1(LO) modes are found to be 734 cm^{-1} as shown in Table 1.

MATERIALS AND METHODS

GaN samples were grown in hexagonal phase by Plasma assisted MBE under three different modes of growth, through adjustment of Ga and N flux ratios. Sample A was grown at stoichiometric condition, whereas Samples B and C were grown at Ga-rich and N-rich modes by selecting Ga/N flux ratios higher and lower than stoichiometric values respectively. The 500 nm thick hexagonal GaN layers were grown in each case, using MOCVD grown SiC as substrates. The growth temperature was maintained at 610 ºC. Ga flux was provided by conventional effusion cell, while active nitrogen resulted from radio frequency dissociation of nitrogen gas (N_2) using a plasma cell [Kuroda *et al.* 2003]. The grown surface was monitored in-situ by RHEED. The detailed growth procedure can be found elsewhere [Adelmann *et al.* 2002, Kuroda *et al.* 2003].

Raman experiments were performed at room temperature in backscattering geometry along c-axis of hexagonal GaN. A 325 nm laser line from a He-Cd cw laser was used as excitation source with power output ranging upto 5mW. The polarized incoming laser light was focused onto the sample surface through a microscope objective (40x). The scattered light was analyzed only for wavelength with a JY infinity-UV spectrometer and detected with a liquid nitrogen cooled charge coupled device. Since the excitation laser beam is Ultraviolet (325 nm), therefore, the scattering region is restricted to few tens of nanometers. Considering the penetration depth to be 10^{-6} cm, the incident laser penetrates through 40 monolayers (MLs) of GaN samples. So, in all cases the information carried out by the UV laser about the interior is reliable.

In order to describe Raman scattering we use conventional “Porto notation”. It consists of four symbols: two of the symbols are placed outside braces and two inside. The symbols outside the braces from left to right represent the direction of incident and scattered radiation while the symbols inside the braces from left to right represent the polarization direction of electric vector of incident and scattered radiations respectively [Damen *et al.* 1960, 1966]. For example the scattering geometry $Y(X,Y)\tilde{Z}$ describes that incident X- polarized radiation is directed along +Y direction and scattered radiation is Y-polarized and detected along –Z direction. Moreover only certain modes appear under certain geometry, these conditions are called Raman selection rules. Some of geometry dependent Raman selection rules are depicted in Table 2 [Harima 2002].

Table 2: Raman selection rules for characteristic phonon modes of hexagonal GaN.

Scattering Configuration	Allowed Mode
$X(Y,Y)\tilde{X}$	A_1(TO), E_2^H, E_2^L
$X(Z, Z)\tilde{X}$	A_1(TO)
$X(Z, Y)\tilde{X}$	E_1(TO)
$X(Y, Z)Y$	E_1(TO), E_1(LO)
$X(Y, Y)Z$	E_2^H, E_2^L
$Z(Y, X)\tilde{Z}$	E_2^H, E_2^L
$Z(Y, Y)\tilde{Z}$ (present work)	A_1(LO), E_2^H, E_2^L

RESULTS AND DISCUSSION

Fig. 1 displays the Raman spectra curves A, B and C associated with GaN under stoichiometric condition, Ga-rich and N-rich regimes of growth respectively. Curve A shows three excitations at 434 cm^{-1}, 567 cm^{-1} and 729 cm^{-1}. Curve B is quite similar to that of curve A, i.e. having three excitations at nearly the same set of wavenumbers. The similarity of the two spectra hints to the crystal quality of associated layers. Curve C (N-rich) is very different: a band of excitations between 250 cm^{-1} and 650 cm^{-1} centered at 434 cm^{-1} is evident.

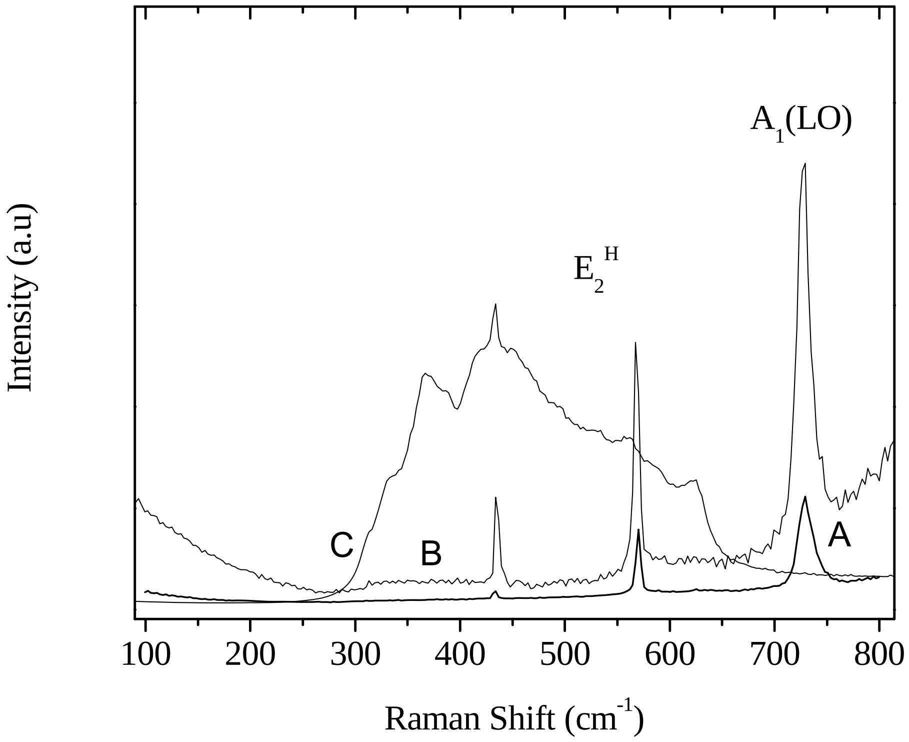

Fig. 1: Raman spectra curves A, B and C associated with stoichiometric GaN, Ga-rich GaN and N-rich GaN respectively. All samples are of hexagonal phase.

Based on the scattering geometry $Z(Y, Y)\tilde{Z}$, the allowed modes are E_2 and AB_1(LO), hence the excitations at 567cm^{-1} and 729 cm^{-1} are easily identified as E_2(high) and A_1(LO) respectively (see Tables 1 and 2). The value of E_2^H in stoichiometric GaN is agreed well with the theoretical value, E_2^L could not be observed because of low intensity. The frequency positions of both E_2^H and A_1(LO) modes are characteristic ones of GaN lattice as obvious in Table 1. The frequencies of these modes in Ga-rich GaN are on lower side which may be attributed to the strain effect. However, the excitation at 434 cm^{-1} is observed in all samples irrespective of the material and/or substrates it is identified as a plasma line of He-Cd laser, perhaps could not be fully stopped by the silica prism mono-chromator placed before the excitation laser beam.

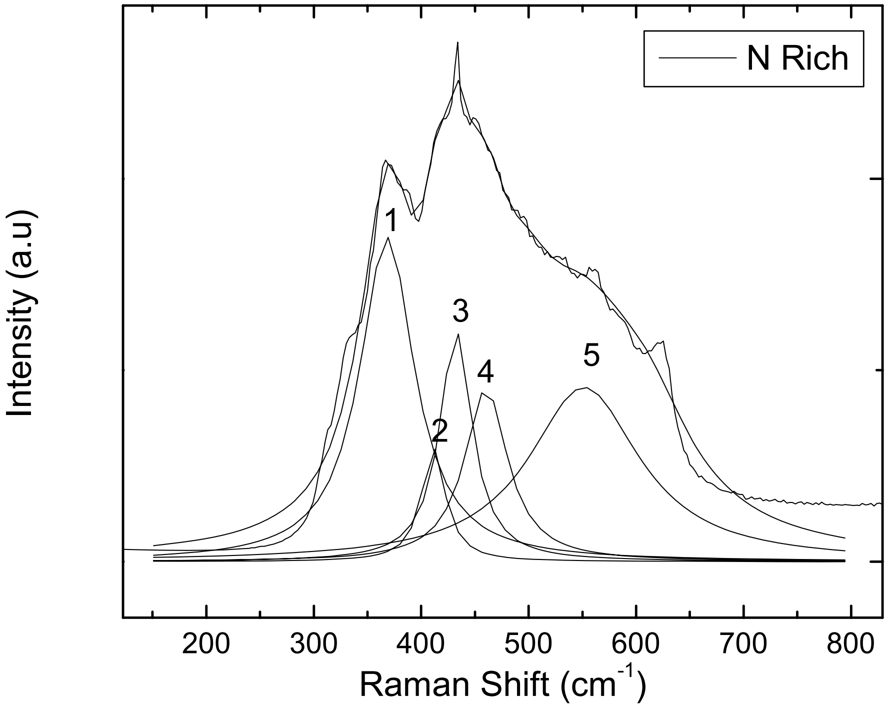

Fig. 2: Lorentzian fit to Raman spectra curve of N-rich GaN (Curve C). The Lorentzian fit reveals five component peaks 1, 2, 3, 4 and 5.

The associated spectrum of N-rich (curve C) is of special interest where all the spectral features, as observed in curves A and B, disappear into a broad band ranging 250 to 650 cm^{-1}. Lorentzian fit of the broad band clearly yields five component peaks 1, 2, 3, 4 and 5 at wavenumbers 369 cm^{-1}, 412 cm^{-1}, 434 cm^{-1}, 456 cm^{-1} and 564 cm^{-1} respectively (see Fig. 2). Peak 3 at wavenumber 434 cm^{-1} is attributed to the residual laser line as discussed earlier. Looking at the frequency position and Raman selection rules, peak 5 at 564 cm^{-1} is assigned to the E_2^H phonon mode. Other peaks represent defect activated modes to be originated from crystal disorder. However, the A_1(LO) peak is missing in the spectra of N-rich layers. This feature may be related with atomic displacement scheme [Cardona 1982] for optical phonon modes, given in Fig. 3. It is evident from Fig. 3 that both LO modes especially A_1 modes is generated due to the vibration of both N and Ga atoms, while the mode E_2 (high) involves the vibration of N atoms only. Since in the N-rich layers, the presence of Ga-vacancies is more likely; therefore, the LO modes cannot be generated therein, hence the missing of such modes are justified. This argument is in agreement with the investigations of Tarsa *et al.* [1997], which reported the presence of Ga vacancies in N-rich GaN, through analysis of PL spectra. The crystal disorder, especially Ga vacancies give rise to DARS and have been found to exist in the form of columnar defects, originated due to relative mobility of Ga and N adatoms during growth [Tosja *et al.* 1998]. The mobility of Ga atoms under Ga-rich regime is sufficient to incorporate N adatoms efficiently within GaN layers, whereas huge surface barrier exists at the surface on the N-rich GaN due to N accumulation on the surface. Under this situation, Ga adatoms would have very low mobility into the surface in case of N-rich GaN and, therefore, would not be able to become incorporated within GaN layers causing Ga vacancies. Moreover, under same measuring conditions, the intensities of the excitations in curve C are higher as compared with those found in curves A and B. This observation is attributed to surface roughness of the film where most of the GaN lattice-related Raman active frequencies are scattered while the residual laser line does not undergo scattering. We are of the opinion that the disappearance of Raman active modes in N-rich layers is probably, related to the surface roughness [Tarsa *et al.* 1997]. Accordingly, one can conclude that the GaN layers grown under Ga-rich condition have comparable crystalline quality with stoichiometric GaN layers and that grown under N-rich condition, are of poor crystalline quality.

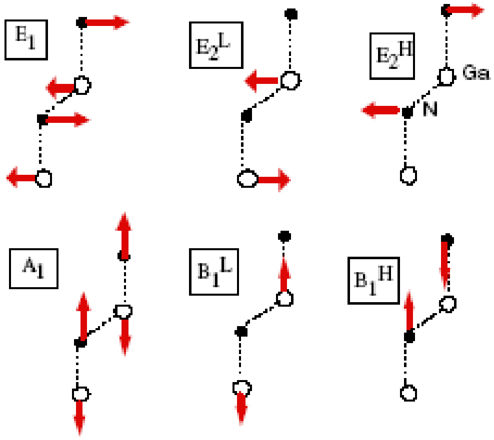

Fig. 3: Typical vibration of Ga and N atoms for phonon modes in hexagonal GaN: atomic displacement scheme.

CONCLUSIONS

The Raman spectroscopy of the GaN layers has led us to the following results:

(i) The standard Raman modes observed in stoichiometric GaN are 567 cm^{-1} and 729 cm^{-1}, identified as E_2^H and A_1(LO) of hexagonal GaN. The observed values of E_2^H and A_1(LO) agree well with the theoretically calculated value however E_2^L could not be observed probably due to very low intensity. The excitation at 434 cm^{-1} is attributed to the plasma line/residual laser line of the source.

(ii) Raman modes observed in Ga-rich GaN and stoichiometric GaN layers are very similar. The similarity is interpreted as a signature of comparable crystal quality of both the layers.

(iii) The Raman spectra of N-rich GaN layers are concentrated in the range 250 cm^{-1} - 650 cm^{-1}. This observation is related with high density of defects within the layers and defects are shown to be consisting mainly of Ga vacancies.

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