RAMAN SPECTROSCOPY OF GaN/Al$_x$Ga$_{1-x}$N/AlN/Si STRUCTURES

Nguyen Linh Chi, Pham Van Hai and Luc Huy Hoang

Faculty of Physics, Hanoi National University of Education

Abstract. In this work, the Raman and IR active vibrational modes of GaN structure were calculated using correlation method. All the experimental Raman peaks were assigned in the Raman spectra of GaN/Al$_x$Ga$_{1-x}$N/AlN/Si structures, which were prepared using metalorganic chemical vapor deposition (MOCVD) technique. The effect of Al$_x$Ga$_{1-x}$N buffer layer with various of x values (0.011; 0.02; 0.037; 0.053; 0.49; 1) on the structure properties of GaN was studied by mean of Raman spectroscopy. The stabilization of the position and the change of full width at half maximum (FWHM) of E$_2$ mode in the Raman spectra of GaN/Al$_x$Ga$_{1-x}$N/AlN/Si structures confirmed the high crystalline quality of the GaN layer.

Keywords: Raman spectroscopy, GaN, AlGaN buffer layer.

1. Introduction

Gallium nitride (GaN) belongs to a binary III/V direct band gap semiconductor. With its direct and wide band gap of 3.39 eV at room temperature, high thermal stability, high breakdown field voltage (high breakdown field of approximately 5×10^6 V/cm) [1] and high saturation drift velocity, GaN is considered a promising material for optoelectronic application in the blue and UV wavelengths, as well as in high power and high temperature electronics [1]. GaN is usually grown on sapphire or SiC substrates and Si. Compared with SiC substrates and sapphires substrate which are also expensive, Si substrates have the advantage of signification lower cost, and the availability of a large size substrate. However, due to the different of lattice constants (17%) and thermal coefficients (46%) between Si and GaN, it is difficult to grow single crystalline GaN directly on Si substrates [2]. One of the ways to solve this problem is to use buffer layers. The AlN and GaN doped Al are used as intermediate layers between these two layers. Because AlN can supports a high- quality GaN layer due to the good wettability of GaN, which produces two dimensionals (2D) growth [3], thereby preventing a meltback etching reaction of Si with Ga [4]. In addition, it reduces the lattice and thermal mismatch between GaN and Si. The crystalline quality of GaN epitaxy,

therefore, is influenced on the properties of buffer layers. Moreover, Raman spectroscopy is considered as a powerful nondestructive method to determine the crystalline quality of epitaxial layers. In this paper, the structural properties of epitaxial GaN growth on Si substrate with two buffer layers Al$_x$Ga$_{1-x}$N/AlN were studied using Raman spectroscopy.

2. Content

2.1. Experiments

The epitaxial GaN was grown on Si substrate via MOCVD process, in which the Al$_x$Ga$_x$N (x : 0.011; 0.02; 0.037; 0.053; 0.49) and AlN buffer layers were used to reduce the lattice mismatch between the GaN and the Si wafer (Figure 1).

GaN 800nm
$Al_{024}Ga_{0.76}N$ 300nm
AlN 200nm
Si

Figure 1. MOCVD-grown GaN template

The growth parameters of A1 to A6 samples are listed in Table 1.

Table 1. **The growth parameters of A1 to A6 samples, T$_{sub}$: The subtrate temperature**

Sample	Ga flux (10^{-7}torr)	Al flux (10^{-8}torr)	T$_{sub}$	N$_2$ flow rate	Al/Ga ratio	Thickness (nm)
A$_1$	0.98	0.2	700 °C	0.5 SCCM	0.02	320
A$_2$	5.9	0.64	740 °C	0.3 SCCM	0.011	380
A$_3$	1.2	0.44	740 °C	0.9 SCCM	0.037	210
A$_4$	2.2	1.16	740 °C	0.3 SCCM	0.053	430
A$_5$	0.23	1.16	740 °C	0.3 SCCM	0.49	430
A$_6$	0	4.09	740 °C	0.3 SCCM	1	400

LabRam HR Evolution Raman spectrometer was used to observe Raman spectrum of GaN/Al$_x$Ga$_{1-x}$N/AlN/Si structures at room temperature. All spectra were excited with laser light of wavelength $\lambda = 532nm$ and a power of 2.5 mW. The 100$\times$ objective lens was used to focus laser light and collect scattered light from surface of sample. Raman scattering measurements were performed with a 10s integration time and three accumulations for each spectrum. The 521 cm^{-1} peak of Silicon wafer was used as a standard for Raman spectrometer frequency calibration.

2.2. Results and discussions
2.2.1. Group theory analysis

GaN is crystallized in a wurtzite structures, which belongs to space group C_{6v}^4 $(P6_3mc)$ and that there are two GaN units in a Bravais cell. Therefore, there are two equivalent Gallium atoms and two equivalent Nitride atoms in the Bravais unit cell. From Ref. [12], we find that this is space group number which has the site symmetries 2 C_{3v} (2); C_2 (6); C_1 (12). Table 2 lists the site symmetry of each atom.

Table 2. The site symmetry of each atom

Atom	Z_B	Wyckoff index	Point group
Ga	2	B	C_{3v}
N	2	B	C_{3v}

The characteristic table of C_{3v} point group is shown in Table 3

Table 3. Characteristic table of C_{3v} point group

C_{3v} species	Translation	t^γ	Degrees of vibrational freedom $f^\gamma = n.t^\gamma$
A_1	T_z	1	2
E	T_x, T_y	2	4

Where $t^\gamma =$ the number of translations in a site specied and $f^\gamma =$ degrees of vibrational freedom present in each site species γ for an equivalent set of atoms, ions, or molecules.

Table 4 shows the correlation for the lattice vibrations of the Ga/N atoms in GaN wurzite crystal between the site group C_{3v} and the factor group C_{6v}.

Table 4. The correlation for the lattice vibrations of the Ga (N) atoms in GaN wurzite crystal between the site group C_{3v} and the factor group C_{6v}

f^γ	t^γ	C_{3v}	Correlative	C_{6v}	C_ζ	a_γ $a_\zeta = a_{A_1} + a_E$		
2	$1\,(T_z)$	A_1		A_1	1	1	1	0
				B_1	1	1	1	0
4	$2(T_x, T_y)$	E		E_1	2	2	0	1
				E_2	2	2	0	1

Therefore, the species of the factor group that contains lattice vibration involving the Ga/ N atom can be written as the following irreducible representation Γ :

$$\Gamma = \left(A_1 + B_1 + E_1 + E_2 \right) \tag{3.1}$$

Thus, the total irreducible representation of the GaN crystal, Γ^{cryst} can be constructed as follows:

$$\Gamma^{cryst} = 2A_1 + 2B_1 + 2E_1 + 2E_2 \tag{3.2}$$

The acoustical modes are readily identifiable in factor groups, since they have the same character as the translation. Table 5 shows this identification.

Table 5. The translation of C_{6v} species

C_{6v} **species**	**Translation species**
A_1	T_z
E_1	T_x, T_y

Therefore, the irreducible representation of the acoustical vibrations:

$$\Gamma^{acoust} = A_1 + E_1 \tag{3.3}$$

The acoustical vibrations are included in the irreducible representation, $\Gamma^{GaNcryst}$, given above. Of the 3N degrees of vibrational freedom, three of these vibrations are acoustical modes. When we consider only those vibrations at the center of the Brillouin zone, $k \cong 0$, the three acoustical vibrations have nearly zero frequency. Since vibrations with zero frequency are of no physical interest here, these acoustical vibrations can be subtracted from the irreducible representation as suggested in equation:

$$\Gamma^{cryst}_{vibr} = \Gamma^{cryst} - T^{acoust} = A_1 + 2B_1 + E_1 + 2E_2 \tag{3.4}$$

Among them, A$_1$ and E$_1$ modes are both Raman and infrared (IR) active, while 2 E$_2$ modes are only Raman active, and 2 B$_1$ modes are silent modes. Here, the polar A$_1$ and E$_1$ modes are split into longitudinal optical (LO) and transverse optical (TO) phonons by the macroscopic electric field. Thus, six optical modes, A$_1$ (LO), A$_1$ (TO), E$_1$ (LO), E$_1$ (TO), E$_2$ (high), E$_2$ (low) can be observed for the first order Raman scattering.

2.2.2. Vibrational mode assignment
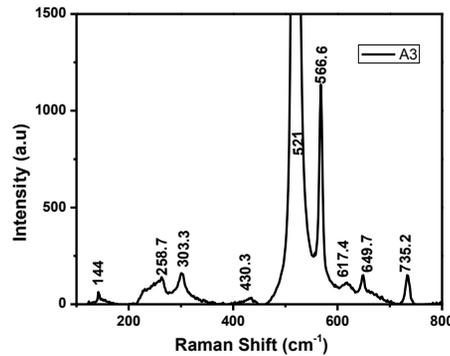
Fig 2 shows the Raman spectrum of A3 sample.

Figure 2. Raman spectra of GaN /Al$_x$Ga$_{1-x}$N/ AlN / Si epitaxy with x = 0.037

It can be seen from Figure 2 that there is a number of Raman peaks appearing at 144, 258.7, 303, 430.3, 521, 566.6, 617.4, 649.7 and 735.2 cm^{-1}. The peaks at 566.6 and 735.2 cm^{-1} correspond to GaN E_2 high and A_1 (LO), respectively [5]. The GaN E_2 (low) mode is observed at 144 cm^{-1}. The band at 649.7 cm^{-1} can be assigned to the E_2^2 from the AlN layer as well as Al$_x$Ga$_{1-x}$N intermediate layers [5]. The strongest peak in each spectrum at about 520.3 cm^{-1} is from the Si substrate. The band at the 610- 625 cm^{-1} range of the spectra is attributed to phonon originating from the AlGaN [6]. The mode is observed at 303 cm^{-1}, which has been assigned by many groups as disorder activated Raman Scattering mode [7]. The peak at 617.4 cm^{-1} corresponds to boron doping of the silicon wafer [9]. The origin of the week peak at 430.3 cm^{-1} is less obvious, but might be attributed to the overtones of transverse acoustic phonons at the symmetry points [10, 11].

Table 6 shows the wavenumbers and symmetries of Raman active modes of A3 sample. It can be seen that, the vibration frequencies of the observed modes are in good agreement with that reported in references [5, 6].

Table 6. The parameters of Raman modes of A3 samples

	Symmetry	Wavenumber (cm^{-1})	Reference (cm^{-1})
	E_2^L	144	144 [5]
GaN	E_2^H	566.6	567 [5]
	$A_1(LO)$	735.2	734 [5]
AlN	E_2^2	649.7	648.8 [6]
Si		617.4	618 [9]
AlGaN	E_2	620.3	620 [6]

Figure 3 shows the atomic displacement scheme of optical phonon E$_1$, E$_2$ (L, H), A$_1$ and B$_1$ (L,H) modes of the GaN wurtzite structure.
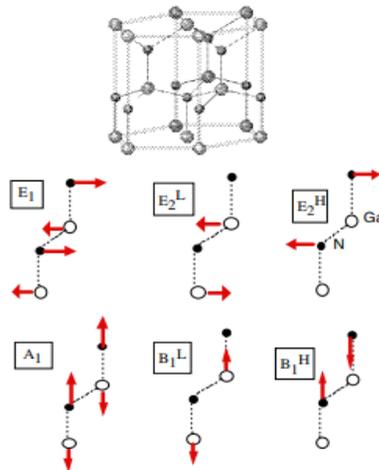

Figure 3. Atomic displacement scheme of optical phonon modes of the GaN wurtzite structure [8]

As can be seen in Figure 3, there are two types of the E_2 and B_1 modes that are distinguished by superscripts L and H. The (E_2^L) mode at 144 cm^{-1} is typically assigned for symmetry stretching [8]. The (A_1 (LO)) at 735 cm^{-1} and (E_2^2) at 566.6 cm^{-1} are identified as symmetric stretching and symmetrical bending, respectively [8].

2.2.3. The effects of Al_xGa_1-xN on the crystalline quality of GaN

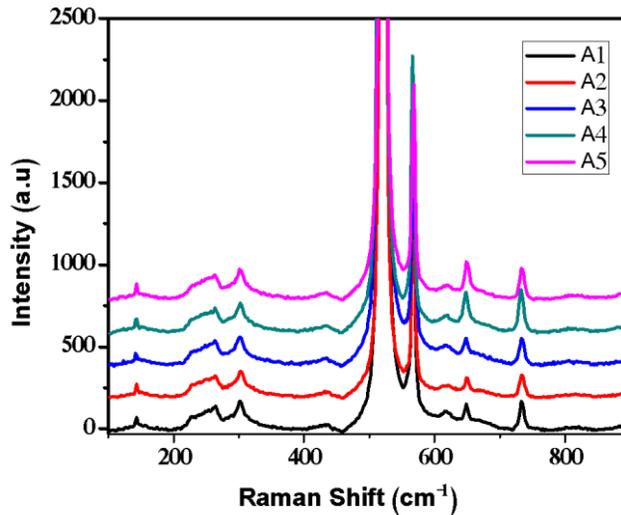Figure 4 shows the Raman spectra of A1- A5 samples.

Figure 4. Raman scattering spectra of GaN /Al_xGa_1-xN/ AlN / Si epitaxy (x = 0.011; 0.02; 0.037; 0.053; 0.49)

Table 7. Wavenumbers and linewidths of E_2 mode in Raman spectra of A1 to A5 samples

Samples	E_2 (high) peak		Thickness (nm)
	Position (cm^{-1})	FWHM (cm^{-1})	
A3 (x = 0.037)	567.75	8.02	210
A1 (x = 0.02)	567.21	7.34	320
A2 (x = 0.011)	567.58	6.44	380
A4 (x = 0.053)	567.57	5.43	430
A5 (x = 0.49)	567.80	5.40	430

It is clearly seen from Figure 4 that, there is no strange observed peaks in the Raman spectra of A1, A2, A4 and A5 samples in comparisons to that of A3 sample, which was discussed above.

In order to find the effect of buffer layers and the thickness of GaN layer on the structure properties of GaN epitaxy, the linewidths and frequencies of E_2 Raman active mode of Raman spectra in Figure 4 were carefully analyzed. The results are listed in Table 7 and Figure 5.

It is indicated from Table 7 that the frequency of E_2 mode remains unchanged for all samples. It is evident that the frequency of the E_2 (high) mode is not affected by both x values in $Al_xGa_{1-x}N$ buffer layer and the thickness of GaN layer. However, it is interesting to see in the Figure 5 that the linewidths of the E_2 mode decreases from 8.02 to 5.4 cm^{-1} with the increasing of the thickness of GaN layer from 210 to 430 nm. As mentioned above, the E_2 (high) mode feature is strongly related to structure disorders of GaN, therefore, the narrower of E_2 modes indicates the higher crystalline quality of GaN epitaxy.
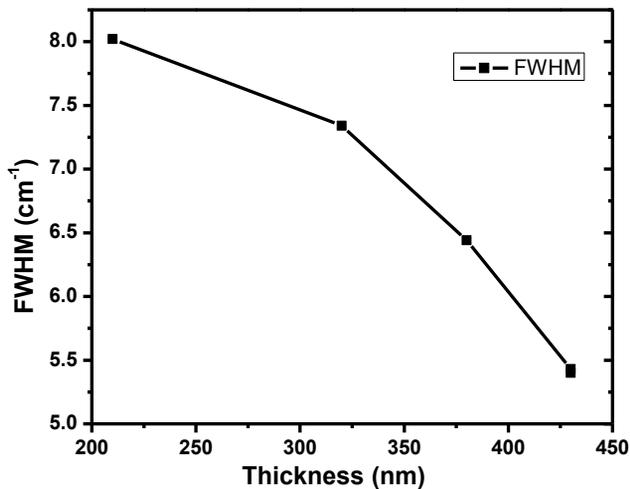

Figure 5. The dependence of the linewidth of E_2 mode on the thickness of GaN epitaxy

3. Conclusions

The phonon characteristics of epitaxial GaN growth by MOVCD method are studied by means of Raman scattering spectroscopy. Group theoretical analysis shows that there are 6 vibration mode $A_1+2B_1+E_1+2E_2$ of GaN wurtzite structures, in which, A_1 and E_1 modes are both Raman and infrared (IR) active, 2 E_2 modes (E_2^H, E_2^L) are only Raman active, and the 2 B_1 modes are silent modes. The observed 1 A_1 and 2 E_2 phonon modes of GaN epitaxy in Raman spectra of GaN /$Al_xGa_{1-x}N$/ AlN / Si structures were identified. The frequency stabilization and the narrow linewidth of E_2 mode of GaN confirmed the high crystalline quality of the epitaxial GaN. Moreover, the crystalline quality of GaN epitaxy is improved when its thickness is increase.

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