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GaN layers with different polarities prepared by radio frequency molecular beam epitaxy and characterized by Raman scattering*

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GaN layers with different polarities have been prepared by radio-frequency molecular beam epitaxy (RF-MBE) and characterized by Raman scattering. Polarity control are realized by controlling Al/N flux ratio during high temperature AlN buffer growth. The Raman results illustrate that the N-polarity GaN films have frequency shifts at A_1(LO) mode because of their high carrier density; the forbidden A_1(TO) mode occurs for mixed-polarity GaN films due to the destroyed translation symmetry by inversion domain boundaries (IDBS); Raman spectra for Ga-polarity GaN films show that they have neither frequency shifts mode nor forbidden mode. These results indicate that Ga-polarity GaN films have a better quality, and they are in good agreement with the results obtained from the room temperature Hall mobility. The best values of Ga-polarity GaN films are 1042 cm^2/Vs with a carrier density of 1.0×10^{17} cm^{-3}.

Keywords: polarity, gallium nitride, Raman scattering
PACC: 6855, 6320K, 7280E, 7830

1. Introduction

GaN and related III-nitride materials have attracted much attention due to their applications in light emitting diodes[1,2] and high electron mobility transistors.[3] In the case of epitaxial GaN layers, the growth direction can be along either [0001] or [000$\bar{1}$] direction, resulting in Ga-polarity domains or N-polarity domains, respectively. Some literature has shown that a key characteristic of wurtzite GaN is its polarity[4] and polarity control can be achieved by the choice of different buffer layers, named Ga-polarity, N-polarity, and mixed-polarity GaN.[5,6] The mixed-polarity GaN, in which both Ga- and N- polarity domains exist, has also shown that the two domains are separated by inversion domain boundaries (IDBS).[7] The different polarities of GaN result in different lattice features and optical and electronic properties. On the other hand, Raman scattering technique, which is nondestructive, contactless, and flexible to samples, is very powerful tool for investigating the lattice features, and optical and electronic properties,[8,9] while few papers show that Raman scattering is applied to the study of GaN with different polarities. In the present work, we study Raman scattering on different polarities of GaN layers. The GaN layers are prepared by radio-frequency molecular beam epitaxy (rf-MBE) and different polarity GaN layers are prepared by controlling Al/N flux ratio during high temperature (HT) AlN buffer growth.

2. Experiments

GaN films with AlN buffer layers were grown on (0001) sapphire substrates in a Varian GEN II MBE system equipped with a SVTA Nitrogen plasma-assisted source (model 4.53). A 700V voltage was used to deflect active nitrogen ions. A photocurrent detector was equipped to detect the intensity of nitrogen plasma. Ga and Al were provided by standard effusion cell. The sapphire substrates were thermally cleaned at 850 °C for 30 min in the growth chamber and then nitridated at 200 °C for 30 min. Polarity control was achieved by controlling Al/N flux ratio. Three groups of AlN buffer layers (N-rich, intermediate and Al-rich) were prepared out. The growth con-

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ditions of GaN layers were controlled identically and the layer thickness was 1.5 μm. All the samples were unintentionally doped.

Raman measurements were carried out in a back scattering geometry at room temperature by using a polarized 514.5 nm line of Argon-ion laser in a LABRAM-HR system with a spectral resolution of about 1 cm^{-1}. Wet chemical etching was performed in 1.8 mol NaOH solution for 10 min. Atomic force microscopy (AFM) was used to characterize the surface morphologies of GaN films. The Hall mobility at room temperature was tested by the van der Pauw measurements.

3. Results and discussion

All of the GaN films grown in three regimes of AlN buffer layers show streaky 1×1 pattern during growth, which indicates the flat surface in a two-dimensional growth mode.[5] In the cooling process, surface reconstructions are judged by reflection high-energy electron diffraction (RHEED) and given in Table 1.

Table 1. Surface reconstruction of GaN layers grown on HT AlN buffer layers with different Al/N ratios.

buffer layers	polarity	as growth during the cooling process
Al-rich	Ga	2×2
N-rich	N	3×3, 6×6
Intermediate	mixed	2×2, 6×6

For the case of the N-rich AlN buffer layers, 3×3 and 6×6 reconstructions are observed. A 2×2 reconstruction is seen for the case of Al-rich AlN buffer layers. Both 2×2 and 6×6 reconstructions are achieved under the intermediate Al/N ratio conditions. According to Refs.[4,6,9,10], we can conclude that Ga polarity GaN films are grown on Al-rich AlN surfaces, low Al/N ratio results in N-polarity GaN films, and intermediate Al/N ratio leads to mixed-polarity GaN films. The following wet chemical etching proves our judgments.

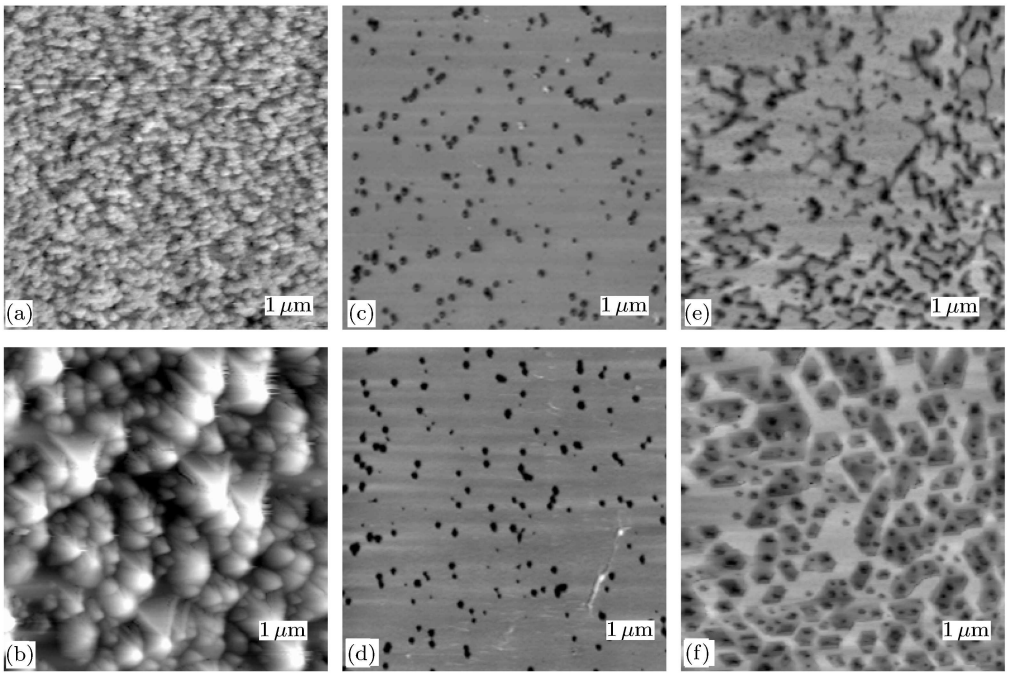


Fig.1. AFM images in a size of 5×5 μm^2 for (a) as grown N-polarity GaN, (b) N polarity GaN after etching for 10 min in a 1.8 M NaOH solution, (c) as grown Ga-polarity GaN, (d) after etching, (e) as grown mixed-polarity GaN, (f) after etching.

Figure 1 shows the AFM images of the surface morphologies of different GaN films after wet chemical etching. The surface morphologies of GaN films grown on the N-rich AlN buffer layers are changed evidently as shown in Figs.1(a) and 1(b). The root-mean-square (RMS) roughness is 3 nm before etching while

160 nm after etching, which is a typical characteristic of N-polarity GaN films.[11,12] Figures 1(c) and 1(d) show the AFM images of the GaN films grown on the Al-rich HT AlN buffer layers. The RMS roughness is 1.5 nm before etching while 1.3 nm after etching. There is no obvious change in the surface morphology after etching, that is, the surface is resistant to etching in NaOH solution, which is the characteristic of Ga-polarity.[11,12]

The etched morphologies of GaN films grown on the intermediate AlN buffer layers as shown in Fig.1(f) are different from those of N-polarity GaN films and Ga-polarity GaN films. The RMS roughness is 8 nm before etching, but it increases to 15 nm after etching and shows a fine porous structure after etching. The formation of this porous structure can be explained by the etching theory established by Rouviere *et al.*[11] N-polarity surfaces are chemically active in NaOH solutions while Ga-polarity surfaces are resistant to NaOH solutions. Thus domains of N-polarity are dissolved rapidly but Ga-polarity domains remain on the surfaces. Thus GaN films with fine porous structure are formed.

The room temperature (RT) Hall mobility measurements of the different polarities GaN have been carriered out. In Table 2 listed are the data of mobility and carrier concentration for all the undoped GaN films with different polarities. In the case of Ga-polarity GaN layers, the best mobility we have obtained is 1042 $\mathrm{cm}^2/(\mathrm{V{\cdot}s})$ with a carrier concentration of 1.0×10^{17} cm^{-3}. This indicates the high quality of our Ga-polarity samples.

Table 2. Electrical property of different polarity GaN films.

buffer layer	polarity	RT mobility/$(\mathrm{cm}^2/(\mathrm{V{\cdot}s}))$	carrier concentration/cm^{-3}
Al-rich	Ga	1042	1.0×10^{17}
N-rich	N	135	3.4×10^{17}
intermediate	mixed	25	2.8×10^{15}

The structure of the GaN grown on sapphire in wurtzite structure belongs to space group $C_{6\mathrm{v}}^4$. Group theory predicts eight sets of phonon normal modes at the Γ point:

$$\Gamma = 2A_1 + 2E_1 + 2B_1 + 2E_2. \quad (1)$$

Among them, it is well known that one A_1, one E_1 and two E_2 modes are Raman activated. The selection rule for Raman scattering by optical phonons is given by

$$I_{\mathrm{s}} \propto |\boldsymbol{e}_{\mathrm{i}} \cdot \boldsymbol{R} \cdot \boldsymbol{e}_{\mathrm{s}}|, \quad (2)$$

where $\boldsymbol{e}_{\mathrm{i}}$ and $\boldsymbol{e}_{\mathrm{s}}$ denote polarizations for the incident and scattered lights respectively. $\boldsymbol{R}$ is the Raman tensor that characterizes the phonon. The observation of allowed Raman scattering phonons depends on the geometry of the experiment, which is characterized by Porto's notation $\boldsymbol{k}_{\mathrm{i}}(\boldsymbol{e}_{\mathrm{i}}, \boldsymbol{e}_{\mathrm{s}})\boldsymbol{k}_{\mathrm{s}}$, where $\boldsymbol{k}_{\mathrm{i}}$ and $\boldsymbol{k}_{\mathrm{s}}$ are wavevectors of the incident and scattered lights respectively. The most reliable values of Raman-active phonon frequencies[13,14] are given in Table 3.

Table 3. Optically active phonon frequencies of wurtzite GaN.

symmetry	A_1 (TO)	A_1 (LO)	E_1 (TO)	E_1 (LO)	E_2 (low)	E_2 (high)
phonon frequency/cm^{-1}	533	735	561	743	144	569

In our studies, the Raman experiments have been carried out in a backscattering geometry with the incident light along the growth direction, which is a $\bar{z}(y, xy)z$ geometry. Therefore only E_2 and A_1(LO) modes are allowed by the selection rule. The typical Raman spectra in the backscattering geometry of different polarity GaN films are given in Fig.2.

The E_2 (high) and A_1(LO) modes can be observed clearly in all the samples, and they are well consistent with those reported in Refs.[13,14]. Peaks at 750 cm^{-1} and 418 cm^{-1} are for $E_{1\mathrm{g}}$ and for $A_{1\mathrm{g}}$ modes of the sapphire substrates separately. The E_2 (high) mode is seen at 569 cm^{-1} for all the samples. This value is in good agreement with the standard stress-free value, which shows the good crystal quality of our samples.[13] While, the A_1(LO) modes are different for the three polarities GaN films.

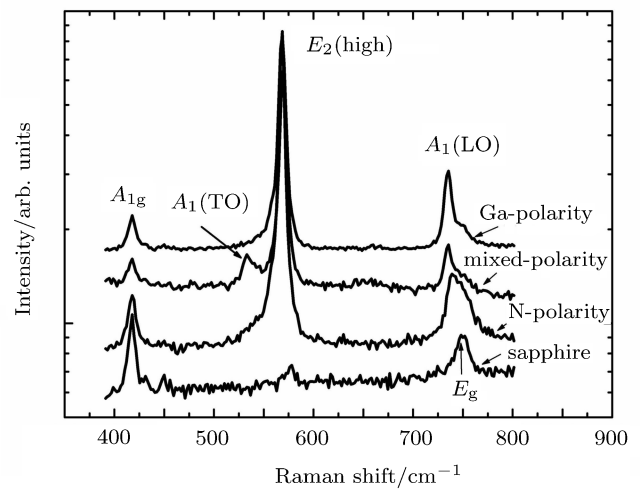


Fig.2. Raman spectra in the backscattering geometry for different polarity GaN layers and sapphire substrates.

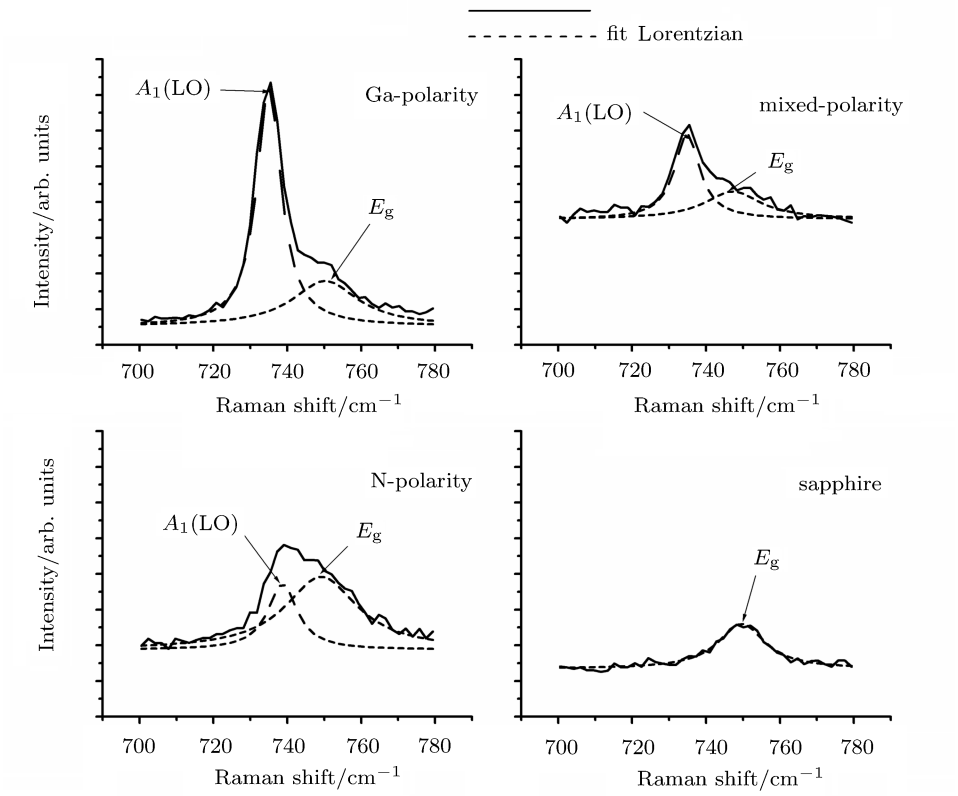


Fig.3. Fit Lorentzian of A_1(LO) mode for GaN and Eg mode for sapphire.

It is seen from Fig.3 that for the Ga- and mixed-polarity GaN films, the values of Raman shifts for both the E_2 (high) (569 cm^{-1}) and A_1 (LO) (735 cm^{-1}) modes are consistent with the values given in Table 3. While for N-polarity GaN films, the A_1(LO) mode is seen at 739 cm^{-1}, with a 4 cm^{-1} shift for the Ga-polarity sample. The frequency shift can be explained by a LO-phonon-plasmon coupled (LOPC) mode. In polar semiconductors, the collective excitation of free carriers can couple with LO phonons to

form the LOPC mode. Convenient empirical formula to deduce carrier density n (cm^{-3}) from the LOPC mode peak frequency $\Delta\omega(\mathrm{cm}^{-1})$ has been proposed as[15]

$$n = 1.1 \times 10^{17} \Delta\omega^{0.764}\,. \tag{3}$$

For the N-polarity GaN films, the free carrier density deduced from formula (3) is about 3.2×10^{17} cm^{-3}, which is very close to the value measured by RT Hall experiments (as shown in Table 1). It is seen from Table 1 that the free carrier density of N-polarity GaN films is larger than those of Ga-polarity and Mixed-polarity GaN films. As the carrier density increases, the LOPC mode peak broadens and shifts towards high frequencies. For Ga and Mixed polarity GaN films, there are no obvious shifts because of their low carrier densities.

On the other hand, the A_1(TO) mode at 533 cm^{-1} is observed for Mixed-polarity GaN films, which should be forbidden in the backscattering geometry. The most possible reason for contributing to this forbidden A_1(TO) mode is that a large number of inversion domain boundaries (IDBS) exist in the mixed-polarity GaN films. As seen in Fig.4, at an inversion domain boundary in wurtzite GaN structure, Ga and N atoms are interchanged alone the $[10\bar{1}0]$ direction. Ga–Ga and N–N bonds are substituted for Ga–N bonds. The translation symmetry is destroyed partly, which results in the occurrence of the forbidden A_1(TO) mode.

Therefore, our results suggest that Raman research can show the crystalline quality of GaN with different polarities and confirm the polarity of GaN.

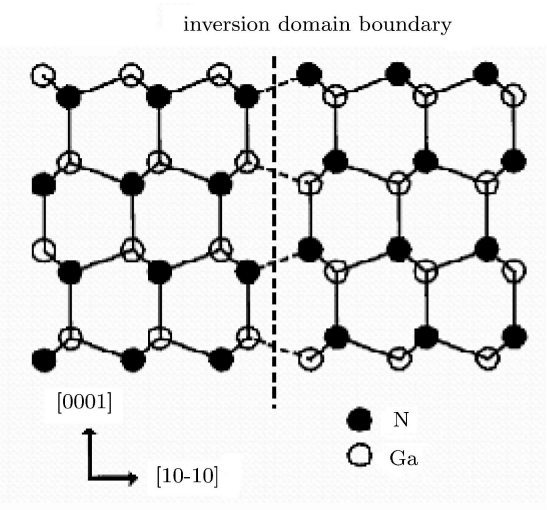


Fig.4. Image of inversion domain boundary.

4. Conclusion

Raman spectra in a backscattering geometry have been applied to different polarity GaN layers. Polarity control is achieved by controlling Al/N flux ratio during high temperature AlN buffer growth. Ga-polarity GaN layers show a good quality. N-polarity GaN films show frequency shifts at A_1(LO) mode because of its high carrier density coupling with LO phonon. The forbidden A_1(TO) mode occurs for mixed-polarity GaN films due to the destroyed translation symmetry by inversion domain boundaries (IDBS).

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