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Structural and morphological studies of GaN thin films grown on different oriented LiNbO₃ substrates by MOVPE

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Abstract. GaN epilayers were grown by metal-organic vapor phase epitaxy (MOVPE) on z - and x -cut lithium niobate substrates. Ex-situ characterizations of the epilayers by means of scanning electron microscope, atomic force microscope, X-ray diffraction and micro-Raman scattering measurements have revealed same growth features on both substrates. The observation of the morphology shows homogeneous and relatively smooth surface. The shape and density of GaN islands as well as the observed columnar growth mode are not dependent of the orientation of the LN substrates. The X-ray diffraction analysis of 450 nm thick GaN layers grown at 730 °C on z - and x -cuts showed that both GaN layers reveal the same crystallographic orientation, i.e. c -axis orientation normal to the substrate plane and in-plane orientation that coincides with the primary axis of LN substrates. The Raman scattering measurements confirm the growth of an oriented epitaxial GaN layer on LN substrate. Moreover, the deposited layer exhibit a quite good homogeneity, since the Raman spectra recorded for different positions in the layer do not reveal any significant variations in their relative intensities and frequency shifts.

1 Introduction

Bulk crystalline lithium niobate (LiNbO₃, also referred as LN) is a key component material in optoelectronic devices such as phase and amplitude modulators, high-speed optical switches, frequency converter in free propagation or integrated optics. The wide range of applications of LN is related to its large transparency range, high electro-optic, piezoelectric and non-linear optical coefficients, chemical and mechanical stability and the possibility of microstructuring its linear and non linear optical properties. Since LN is a material useful for optical processing, a new range of multifunctional devices could result from integration strategies such as electronic devices with LN optical devices integration. III-nitride GaN material can be one of the candidates to be integrated with LN since it has been established as the enabling material for green/UV light emitter/detector and high temperature, high power electronic applications due to its wide band-gap, high elec-

tron saturation velocity and high breakdown voltage. Recently, Doolittle et al. have demonstrated III-nitride transistor [1] structures epitaxially grown on (0001) oriented LN substrate. Since LN is ferroelectric, its use also allows polar III-nitride material to be grown with excellent polarity control [2]. The successful epitaxial growth of wide band gap GaN film on non-linear optical LN substrate could lead to the fabrication of integrated multifunctional electrical and optical devices that utilize both GaN and LN properties and this will make possible to develop optoelectronic devices in which sources, detectors and waveguides may be integrated on the LN substrate. Until now, only Hui et al. [3] have demonstrated the feasibility of making functional optical waveguide using GaN-AlGaIn heterostructure on sapphire. LN substrate can be an active part of the device instead of merely a structural template support. Furthermore, LN offers a much less in-plane lattice mismatch of 6.8% [4] compared to the value of 16% obtained for the growth of GaN on the most widely used sapphire substrate. Hence, the use of LN substrates may help to overcome the considerable drawbacks of the

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heteroepitaxial growth such as high dislocation density and build-in strain.

To date, only two teams have succeeded in the epitaxial growth of GaN films on (0001) oriented LN substrates using Molecular Beam Epitaxy (MBE) [4] and Pulsed Laser Deposition (PLD) [6] techniques. However, delamination of GaN epilayers has been observed for films grown directly on LN substrates due to the large discrepancy in the thermal expansion coefficients between GaN and LN. Furthermore, the diffusion of Li atoms into the GaN films and the formation of LiNb_3O_8 layer have been observed by Doolittle et al. [5] at the heterointerface between GaN and LN, leading to the degradation of the electrical properties and of the crystalline quality of the GaN layer.

In this study, we report the growth of GaN epilayers directly on LN substrates by metal-organic vapor phase epitaxy technique which offers advantages such as high available growth rates, large surface area and possibility of multi-wafer deposition, essential for mass production. Moreover, MOVPE is the most mature GaN epitaxial growth method and is up to now widely used in industrial applications of group-III nitrides. A conventional growth temperature of more than 1000 °C is generally used for the growth of GaN by MOVPE. However, the growth of GaN epilayers on LN substrates should ideally be performed at low temperatures in order to avoid the occurrence of delamination, the Li diffusion, and the interfacial reaction between GaN and LN.

Here, we report on the epitaxial growth of GaN thin films on (0001) oriented LN substrates, also referred as z -cut, by MOVPE with novel low temperature growth conditions. From a technological point of view, it should be also desirable to grow GaN on differently oriented LN substrates (e.g., x -cut) because it has a potential to produce GaN with other than c -axis orientation that results in a reduced piezoelectric field. In this study, two GaN epilayers were grown simultaneously on z - and x -cut LN substrates and the effects of substrate orientation on the morphological and structural properties of resulting GaN epilayers have been investigated.

2 Experimental details

The GaN epilayers were deposited by MOVPE on optical grade polished z - and x -cut LN single crystals polished on both sides. The growth was performed in a T-shaped horizontal reactor [11] in a pressure of 450 Torr. Pure nitrogen was employed as carrier and also bubbling gas. As mentioned above, discrepancy in the thermal expansion coefficients between GaN and LN is large enough to generate delamination of the GaN film, and the conventional growth temperature of 1000 °C by MOVPE of GaN on sapphire substrates is not applicable for LN substrates. Because of its low temperature of decomposition, the dimethylhydrazine (DMHy) precursor allows to lower the growth temperature down to 600 °C [12]. Then, the growth temperature was reduced to 730 °C and combination of ammonia and DMHy was used as the group V

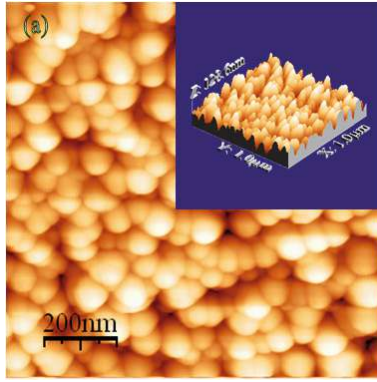
precursor. Trimethylgallium was employed as source material for gallium.

The surface quality and the growth rate were monitored in real time during the growth by in-situ reflectometry using semiconductor laser operating at a wavelength of 670 nm. Atomic force microscopy (AFM) operating in air and scanning electron microscopy (SEM) were used to study the surface morphology. The crystalline quality and orientation of the films were investigated by X-ray diffraction (XRD) using Philips X'Pert diffractometer. Raman spectroscopy was performed before and after growth of GaN to distinguish the GaN and LN peaks. The Raman spectra were recorded with a Dilor confocal micro-Raman spectrometer using the excitation laser wavelength of 514.5 nm with a low optical power of about $2 \times 10^5 \text{ W/cm}^2$ on the sample. The confocal aperture was fixed to analyze approximately $1 \mu\text{m}^3$ of sample volume. The backscattering $z(y, y)z$ and $z(y, x)z$ geometries were used to analyze the Raman spectra, and all measurements were carried out at 300 K.

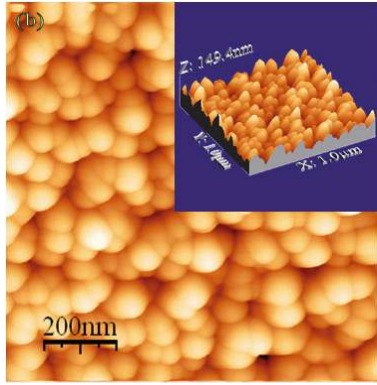
3 Results and discussion

Although precautions were taken, samples are dark in color mainly due to the well-known partial reduction of LN substrates which occur during the growth [13]. Figure 1 displays the $1 \mu\text{m}^2$ surface morphologies and topographies investigated by AFM on z -cut and x -cut oriented LN substrates. In both cases, homogeneous surfaces with dense islands are observed for as-grown GaN epilayers and a root mean square surface roughness (rms) of about 20 nm can be deduced for a $1 \mu\text{m}^2$ area. Since no high temperature thermal treatment has been used before growth to obtain atomically flat surface and to remove the surface damage from chemical mechanical polishing of the substrates, we can speculate that a part of the rms value results from the substrate surface roughness. The cross-section SEM image for GaN layers grown on x -cut (Fig. 2) and z -cut (not presented here) LN substrates shows densely packed columns extending along the growth direction. Thickness of the GaN film is estimated to be 450 nm for both substrates. This result is consistent with the value calculated from in-situ reflectometry measurements. The average diameter of nano-columns is roughly equal to about 50 nm. The AFM images as well as the columnar growth indicate that GaN seems to follow a three-dimensional growth mode according to heteroepitaxy of material with highly mismatched constants. Surprisingly, AFM and SEM images reveal the same island surface morphology, the same columnar growth as well as the same thickness i.e. the same growth rate, independently of the substrate orientation.

In order to understand the film/substrate epitaxial relationship and to accurately describe growth feature, XRD measurements were performed. At first, using pole figures for (11.4) reflection for GaN, we have found that the primary orientation of both GaN films is with the c -axis [(00.1) direction] being perpendicular to the substrate. Figure 3 shows diffraction curves for GaN layers deposited



(a)



(b)

Fig. 1. (Color online) AFM images and topographies (inset) of GaN epilayers grown on (a) *x*-cut and (b) *z*-cut LN substrates.

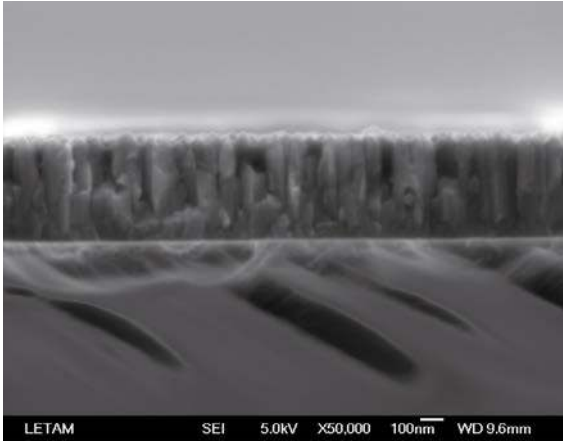


Fig. 2. Cross-section SEM image of a 450 nm thick GaN epilayer deposited on *x*-cut LN substrate.

on *z*-cut and *x*-cut LN substrates. In each spectrum, only the peaks corresponding to the *c*-axis oriented GaN epilayer and the LN substrate are present. Scans show the (00.4) reflection peak of GaN layers that is shifted with respect to that for free-standing GaN represented by an arrow in Figure 3. This shift corresponds to a compressive residual strain of 0.37% and 0.20% for sample grown on *z*-cut and *x*-cut LN substrates, respectively. Here, strain

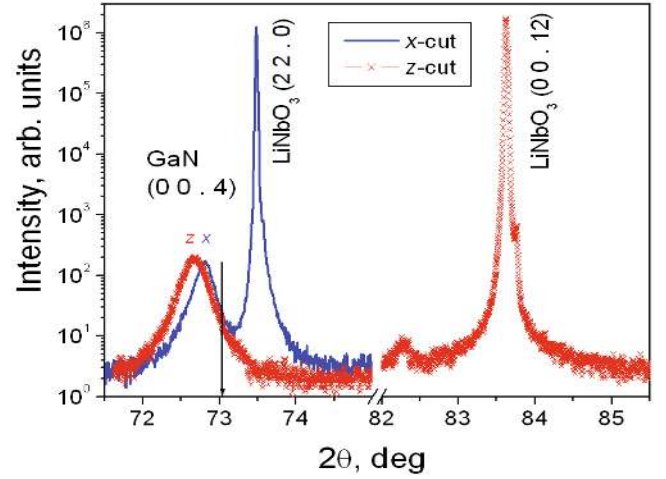


Fig. 3. (Color online) XRD 2θ - θ scans for GaN layers grown on *z*- and *x*-cut LiNbO₃ substrates. Scans show the (00.4) reflection peaks of GaN layers. Peak at $2\theta = 73.5^\circ$ corresponds to (22.0) reflection of the *x*-cut LN substrate. Peak at $2\theta = 83.6^\circ$ corresponds to the (00.12) reflection of the *z*-cut LN substrate.

is expressed in terms of *d*-spacing mismatch in (00.1) direction and is calculated with respect to a free-standing GaN. Note that the close proximity of the (00.4) peak for GaN and (22.0) peak for *x*-cut LiNbO₃ substrate indicate only that the out-of-plane lattice parameters of these two materials are almost commensurate, which does not necessarily mean that the in-plane lattice of both materials matches. The full width at half maximum (FWHM) deduced from reciprocal space map measured for (00.2) reflection is 0.7° . Since the lattice mismatch between LN and GaN in the (00.1) plane is 6.8%, a relatively high mosaicity for the GaN is not surprising. However, the mismatch between sapphire and GaN is much higher, 16%, and the FWHM is typically lower than 0.1° . Thus, the residual strain in GaN layers cannot be straightforwardly explained by the remains of the lattice mismatch between the layers and the substrates. Indeed, residual strains in heteroepitaxial layers are influenced by both the lattice mismatch strain and the thermal mismatch strain, which is due to a difference in thermal expansion coefficients. Pseudomorphic layers have strains entirely due to lattice mismatch whereas the strains in thick layers are dominated by the thermal mismatch. The difference (given by $(\alpha_{\text{GaN}} - \alpha_{\text{LN}})\Delta T$) of in-plane thermal expansion coefficients between GaN ($\alpha_a = 5.59 \times 10^{-6} \text{ K}^{-1}$) and *z*-cut LN ($\alpha_a = 16 \times 10^{-6} \text{ K}^{-1}$ [13]) are considerably higher than that between GaN and sapphire ($\alpha_a = 7.5 \times 10^{-6} \text{ K}^{-1}$), leading to a higher thermal compressive strain. Therefore, the larger thermal expansion coefficients for LN could give rise to higher density of dislocation during cooling down from the growth temperature (730°C) to the room temperature, even though the lattice mismatch is smaller compared to that of sapphire substrate. Thus, the GaN (00.2) reflection is broadened by screw and mixed dislocations. These dislocations distort the (00.1) plane and result in the tilt. Then, the FWHM values derived from the XRD

Table 1. GaN Raman-active modes in the $z(-, -)\underline{z}$ geometries [15].

Scattering configuration	Allowed Raman modes
$z(y, y)\underline{z}$	$E_2, A_1(\text{LO})$
$z(y, x)\underline{z}$	E_2

data are closely related with the dislocations inside the GaN film. Structural quality of the grown GaN layers can be assessed with the help of the reciprocal space map measured for (00.2) reflection. We have recently reported [14] the presence of a weak peak, which appears in RSM above the LiNbO_3 (11.0) reflection. As the same peak was observed in LiNbO_3 substrate after simulation of the growth regime in MOVPE reactor without actual deposition of GaN, we can assume that this peak originates from the substrate and is probably related to the interface reconstruction due to the loss of oxygen during the growth. This observation indicates that the two lattices, c -axis oriented GaN and x - or z -cut LN, are significantly decoupled due to the transitional interface layer of reduced oxide substrate. Thus, the large FWHM value as well as the presence of residual compressive strain in both cases can be related with a strong structural change of the oxide substrate, leading to a decrease of the crystalline quality of GaN films. Previous studies have shown that an LiNb_3O_8 layer is formed at the heterointerface in GaN epilayers directly grown on LN substrates [5,6]. However, additional peaks, which could be attributed to the formation of transitional interface layers of LiNb_3O_8 , are not observed in Figure 3. In opposite to MBE or PLD growth techniques, we can assume that the MOVPE growth conditions avoid the Li-rich phase formation. Furthermore, previous works [1] report that the top-most layer of the z -cut LN substrate consists of oxygen atoms and that the GaN grown layer is c -axis oriented with a lattice mismatch of 6.8% (z -cut substrate has c -axis normal to the surface plane, while the x -cut substrate has c -axis in the plane and the lattice parameters of the two materials are $a = 5.148 \text{ \AA}$, $c = 13.863 \text{ \AA}$ for LN [13] and $a = 3.189 \text{ \AA}$, $c = 5.185 \text{ \AA}$ for GaN) and a 30° rotation with respect to the LN lattice. Here, the fact that both GaN layers grown on z - and x -cuts reveal the same thermal compressive strain indicates that the initial step of GaN formation on LN results in a strong structural change of the oxide substrate, such as a significant reduction of its oxygen content. The mechanisms that promote thermal compressive strain in both cases are not clear and require additional investigation.

In order to confirm the growth of an oriented epitaxial GaN layer on LN substrate, Raman spectra were measured in GaN in $z(y, y)\underline{z}$ and $z(y, x)\underline{z}$ geometries for GaN grown on z -cut LN substrate. Table 1 summarizes the Raman-active modes for GaN in the backscattering $z(y, -)\underline{z}$ geometries [15]. Figure 4a clearly shows the spectrum obtained for the $z(y, y)\underline{z}$ geometry. Both E_2 and $A_1(\text{LO})$ main peaks of GaN are present. As expected, Figure 4b reveals that the $A_1(\text{LO})$ peak vanishes in crossed polarization ($z(y, x)\underline{z}$). Indeed according to the Raman selection rules, the $A_1(\text{LO})$ mode can be observed

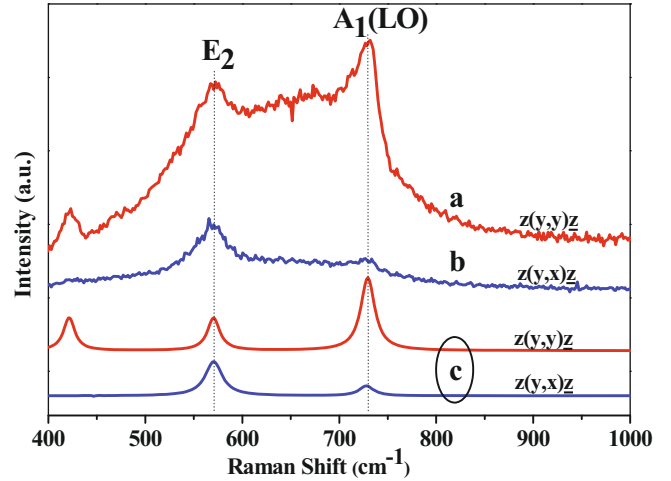


Fig. 4. (Color online) Raman spectra of GaN growth on z -cut LiNbO_3 substrate in the $z(y, -)\underline{z}$ geometries: (a) and (b) as-recorded spectra and (c) Raman spectra corrected from the substrate related broad feature.

only when the incident and scattered light have parallel polarization ($z(y, y)\underline{z}$ geometry) while the E_2 mode is observed in both parallel and crossed polarization geometries ($z(y, y)\underline{z}$ and $z(y, x)\underline{z}$). These results indicate the presence of well-crystallized GaN and confirm those obtained by the high resolution X-ray diffraction measurements presented above. Moreover, the deposited layer exhibits a quite good homogeneity, since the Raman spectra recorded at different places in the layer do not reveal any significant variations in their relative intensities and frequency shifts. The broad feature observed in Figure 4a and centered around 650 cm^{-1} is clearly not related to the GaN layer since this feature appears also in the spectrum recorded at the surface of the LN substrate. It could be attributed to the interface reconstruction due to the loss of oxygen. Figure 4c shows both Raman spectra corrected from this interface-related broad feature. The E_2 mode frequency is mainly affected by the strain and does not depend on the free carrier concentration, due to its nonpolar character, and it shifts toward higher frequencies when increasing compressive strain and toward lower frequencies when increasing tensile strain, with the strain-free frequency at 566.2 cm^{-1} [16]. The measured E_2 mode frequency for GaN films on z -cut oriented LN substrates was 571.3 cm^{-1} indicating a residual compressive strain in the GaN layer. The magnitude of the strain was obtained from the E_2 Raman mode shift by using the equations detailed in [16]. For the GaN elastic constants given in [15], the compressive strain was found to be 0.23%. This value is in agreement with the value calculated from high-resolution X-ray diffraction measurements.

4 Conclusion

We have investigated the influence of substrate orientation on the crystalline quality and surface morphology of

GaN films. Morphologies, structural properties and crystallographic orientations of GaN films are similar to each other and do not depend on the orientation of the LN substrate. This phenomenon originates probably from the lack of oxygen atoms at the top-most LN surface, leading to a transitional interface layer of reduced oxide substrate. This interface reconstruction may give rise to the compressive strain observed from XRD and Raman measurements, and the degradation of the structural quality (high rms and FWHM values) of the layers. To overcome this problem, the use of stoichiometric LN substrates, instead of congruent one, is more suitable and will be studied in future work. The next step of the work will concern the growth at the micron scale of GaN ribbons using selective area growth technique with silica patterns.

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