

# Hydride vapor phase epitaxy growth of GaN on sapphire with ZnO buffer layers

S. Gu<sup>1,\*</sup>, R. Zhang<sup>1</sup>, Y. Shi<sup>1</sup>, Y. Zheng<sup>1</sup>, L. Zhang<sup>2</sup>, T.F. Kuech<sup>2</sup>

<sup>1</sup>Department of Physics, Nanjing University, Nanjing 210093, P.R. China

<sup>2</sup>Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706, USA

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**Abstract.** The initial stages and subsequent growth of GaN on sapphire using ZnO buffer layers is reported for the hydride vapor phase epitaxy technique. A high gas-phase supersaturation in the growth ambient was used to favor a rapid initial growth on the substrate. A subsequent growth step was employed under conditions that favor a high lateral growth rate in order to promote the coalescence of the initial islands and provide optimal material properties. The specific gas-phase mole fractions of the GaCl and NH<sub>3</sub> at the growth front control both the vertical and lateral growth rates. The use of a two-step growth process in the GaN growth leads to a controlled morphology and improved material properties for GaN materials when grown with a ZnO buffer layer. An optimized set of growth conditions, utilizing this two-step process, was found to also improve the growth directly on sapphire without a ZnO buffer layer.

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The initial nucleation and growth of GaN on sapphire substrates are the primary determinants of the subsequent material properties. In metal oxide vapor phase epitaxy (MOVPE), low-temperature GaN or AlN buffer layers are grown to provide a nucleation layer for the subsequent high-temperature GaN layer [1, 2]. The initial GaN island size, resulting from the nucleation, and surface roughness are the key factors in obtaining an improved quality of high-temperature GaN materials [3–5]. The growth temperature, buffer layer thickness, growth rate, V/III ratio, and temperature-ramping rate will determine the surface morphology of the final GaN buffer layer and hence influence the subsequent high-temperature GaN material quality [1–5]. These factors are intertwined with the specific reactor geometry, making the MOVPE buffer layer growth complicated and difficult to optimize. Several groups have reported that smoother buffer layers may result in better GaN epitaxial films [6–8], while other groups claim that an optimum nucleation layer results from a balance between surface roughness and internal defect structure [9–11].

In the case of the hydride vapor phase epitaxy (HVPE) process, the initial nucleation behavior can be improved by the inclusion of a ZnO buffer layer [12–15]. This buffer layer leads to the formation of a reactive diffusion couple with the underlying sapphire, leading to a thin epitaxial surface layer of ZnAl<sub>2</sub>O<sub>4</sub> with the concurrent evaporation of the unreacted ZnO film [16]. There have been few papers reporting the initial stages of GaN growth by HVPE, particularly when using ZnO-based buffer layers [17]. The mechanism of nucleation and subsequent growth by HVPE is not fully understood, making it difficult to optimize growth conditions in order to improve the material properties.

In this paper, we characterize the initial stages of GaN growth on these ZnO-based surfaces. Both rapid nucleation and coalescence led to improved material properties and surface morphology. The specific flow rates of the GaCl and NH<sub>3</sub> control the vertical and lateral growth rates. The use of a two-step growth process in the GaN growth has led to improved and controlled morphology and properties. The initial step utilizes growth conditions that promote rapid nucleation and a subsequent step under growth conditions that leads to a high lateral growth rate, resulting in rapid coalescence of the initial islands. While we have employed ZnO buffer layers for these studies, we show that the growth processes described here can be generalized to the case of direct growth on sapphire without a ZnO buffer layer.

## 1 Experimental details

ZnO buffer layers were initially deposited on a sapphire surface by RF diode sputtering [16]. GaN was then grown on these ZnO-coated sapphire wafers in a vertical HVPE reactor. The details of the HVPE reactor and growth procedures have been described previously [16]. After loading into the reactor, the ZnO-coated wafer was preheated to the growth temperature of 1100 °C for 10 min under a flowing N<sub>2</sub> environment and then introduced to the flowing growth stream containing the GaCl and NH<sub>3</sub> to initiate growth. For the ZnO buffer layer thickness of 20 nm used in our studies, no residual ZnO was present in the final structure [16]. The flow rate or the

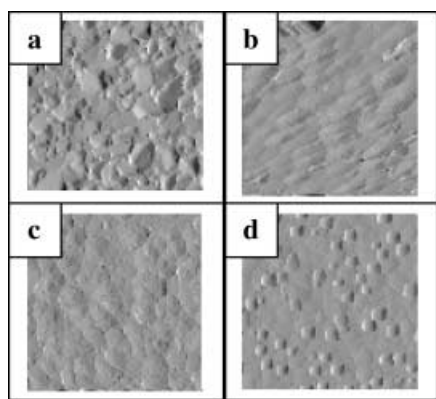
\*Corresponding author. (E-mail: slgu@jlonline.com)

mole fraction of HCl to the Ga source controlled the growth rate over a range of 0.5–4  $\mu\text{m}/\text{min}$  in this work. All the reported mole fractions or partial pressures in this work are based on the total average gas phase and there are local spatial variations due to the reactor geometry. Atomic force microscopy (AFM), photoluminescence (PL), X-ray diffraction (XRD), and capacitance–voltage (CV) measurements have been employed to determine the surface morphology, carrier concentration, and optical and structural properties of the GaN materials.

## 2 Results and discussion

For HVPE GaN heteroepitaxy, as well as in other growth techniques, a high supersaturation in the growth ambient favors rapid nucleation on the substrate. A high lateral growth rate on the surface promotes coalescence of the initial islands. Both growth modes are important for obtaining materials with acceptable material properties, indicative of a reduced impurity and defect concentration along with a smooth surface. The growth conditions that can promote a high lateral versus vertical growth rates, such as the mole fraction of the GaCl and  $\text{NH}_3$ , are quite different. A high HCl flow to the Ga source zone leads to a high GaCl partial pressure that promotes a high vertical growth. A low GaCl partial pressure can enhance the surface-diffusion length of the adsorbed Ga adatoms, promoting a high lateral growth rate. A previous report indicated that a high N activity at the growth surface hinders Ga adatom surface diffusion [18]. A high  $\text{NH}_3$  partial pressure at the growth front would diminish the lateral transport, reducing the lateral expansion of the growing islands and hence promote the nucleation of additional GaN growth islands, as well as the vertical growth of existing islands. The high  $\text{NH}_3$  partial pressure also increases the local supersaturation, leading to enhanced nucleation.

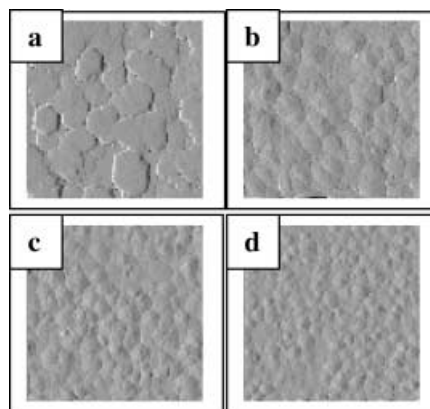
Figure 1 shows AFM micrographs of the initial growth layers, which are about 200-nm thick, grown at different V/III ratios under the same nominal growth rate as determined from the constant HCl flow rate. The surface-feature size does not appreciably change with  $\text{NH}_3$  mole fraction over the range accessed in our growth system. The lateral growth rate, reflected in the initial surface features, has a weak dependence on the  $\text{NH}_3$  mole fraction in HVPE for mole



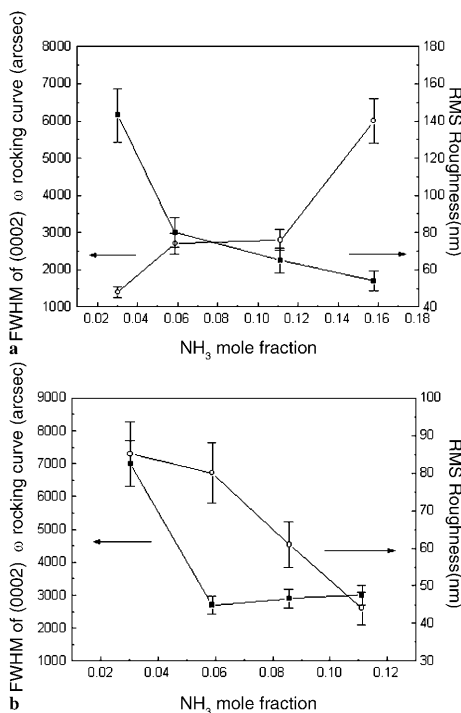
**Fig. 1a–d.** AFM micrographs of the initial GaN layers ( $10 \times 10 \mu\text{m}^2$ , 50-nm height scale). HCl mole fraction:  $7.5 \times 10^{-4}$ ;  $\text{NH}_3$  mole fraction **a** 0.03, **b** 0.06, **c** 0.11, **d** 0.16

fractions greater than 0.03 as shown in Fig. 1a, where non-(0001) surface facets and features are becoming apparent. Figure 2 presents AFM micrographs of the initial layers, which are about 200 nm thick, grown at different growth rates but the same V/III ratio. For these samples, both the HCl, and hence the GaCl, mole fraction and the  $\text{NH}_3$  mole fraction are changed in order to have a fixed V/III ratio. At the low growth rates, a larger lateral growth, as deduced from the change in average feature size in the AFM micrographs, was seen, supporting the suggestion that the lateral growth behavior is controlled by the surface-diffusion process.

The growth uniformity and surface roughness are greatly improved at high  $\text{NH}_3$  mole fractions with a fixed HCl mole fraction or V/III ratio, as shown in Fig. 3. Figure 3 presents



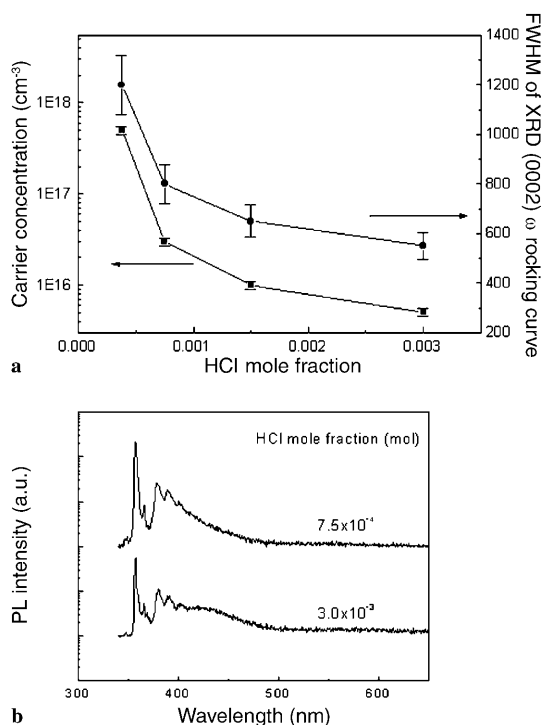
**Fig. 2a–d.** AFM micrographs of the initial GaN layers ( $10 \times 10 \mu\text{m}^2$ , 50-nm height scale). V/III ratio: 62.5; HCl mole fraction **a**  $5.0 \times 10^{-4}$ , **b**  $1.0 \times 10^{-4}$ , **c**  $1.5 \times 10^{-3}$ , **d**  $2.0 \times 10^{-4}$



**Fig. 3a,b.** The surface roughness and the FWHM of the (0002) XRD  $\omega$  rocking curve at different  $\text{NH}_3$  mole fractions at fixed HCl mole fraction (**a**) and fixed V/III ratio (**b**)

the averaged surface roughness (obtained from the AFM micrographs in Figs. 1 and 2) and the full width at half maximum (FWHM) of a (0002) X-ray diffraction (XRD)  $\omega$  rocking curve at different  $\text{NH}_3$  mole fractions. The FWHM of the (0002)  $\omega$  rocking curve increases at a high  $\text{NH}_3$  partial pressure, as shown in Fig. 3a. A high N activity would serve to depress the Ga adatom surface diffusion rate, leading to smaller growth islands and a greater spread in surface tilt among the islands, reflected in the increased FWHM of the (002) reflection.

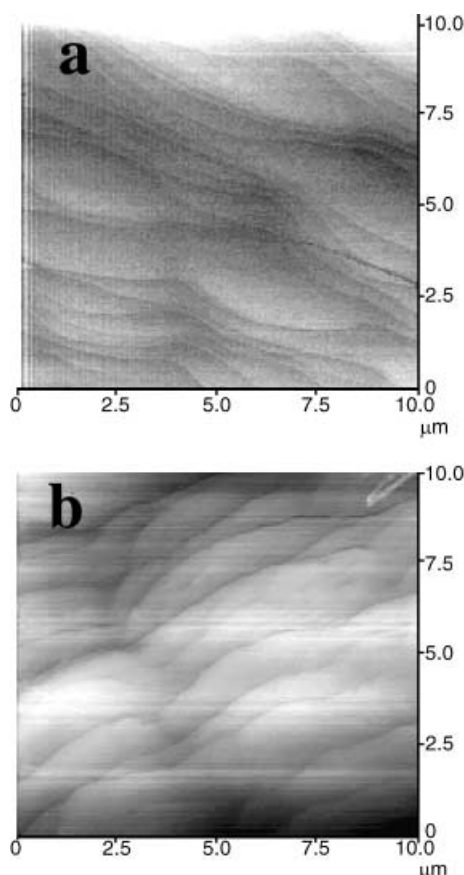
High growth rates and high  $\text{NH}_3$  flow rates are favorable to obtaining a rapid initial growth leading to a smooth surface. An improvement in the overall material properties, as measured by the (0002) XRD line width, requires a low  $\text{NH}_3$  mole fraction and a reduced growth rate. These conflicting requirements at different stages of growth complicate the overall growth process. The conditions for the growth initiation and the subsequent growth are therefore different. This growth study suggests that a two-step growth technique can optimize these two growth processes of nucleation and coalescence and lead to improved material properties. The growth conditions for the initial step are chosen to lead to high vertical growth rates for the initial nucleation phase. Growth conditions leading to a large lateral growth rate for subsequent coalescence and growth improve the surface morphology and structural material properties. We have combined these two conditions to produce improved GaN materials. The surface-carrier concentration, FWHM of the XRD (0002)  $\omega$  rocking curve, and low-temperature photoluminescence of GaN materials, which were grown by this two-step process, are shown in Fig. 4. In the initial step, HCl and  $\text{NH}_3$ , at the appropri-



**Fig. 4a,b.** Surface-carrier concentration and the FWHM of the XRD (0002)  $\omega$  rocking curve of GaN materials versus HCl mole fraction (a) and low-temperature PL spectra (b) at a fixed V/III ratio of 66 for the first step grown by the two-step process. The mole fraction of the HCl and  $\text{NH}_3$  are kept at  $5.6 \times 10^{-4}$  and  $4.8 \times 10^{-2}$ , respectively, for the second step

ate mole fraction, were simultaneously introduced to initiate growth at a fixed V/III ratio of 66 and a resulting growth rate of  $0.25\text{--}2 \mu\text{m}/\text{min}$ , corresponding to a HCl mole fraction ranging from  $3.8 \times 10^{-4}$  to  $3.0 \times 10^{-3}$ . The growth thickness was held to  $0.6 \mu\text{m}$  for the first step. The growth conditions for the second step had a typical HCl and  $\text{NH}_3$  mole fraction of  $7.5 \times 10^{-4}$  and  $4.8 \times 10^{-2}$ , respectively, resulting in a growth rate of  $0.5 \mu\text{m}/\text{min}$  and a thickness of  $5 \mu\text{m}$  for 10-min growth. The subsequent GaN structural and optical properties improve with an increased growth rate of the nucleation layer.

By optimizing this two-step technique, including the V/III ratio and the growth rate for both steps, GaN has been successfully grown on sapphire with a ZnO buffer layer and the relevant material properties were optimized. We have also successfully applied the two-step process to improve GaN material growth directly on sapphire without a ZnO buffer layer. The AFM micrographs of the GaN grown on sapphire with and without ZnO buffer layers grown with a two-step technique are shown in Fig. 5. Both samples are  $\sim 30 \mu\text{m}$  thick. The terrace structures resulting from the step-flow growth process, at the larger layer thickness, are similar in both samples. Cracks on the material surface are visible; however, few surface pits, which are often characteristic of the HVPE growth, are observed under optical microscopy. The FWHM of the XRD (0002)  $\omega$  rocking curve for 30- $\mu\text{m}$ -thick GaN is about 350 arcsec, with a carrier concentration of below  $10^{16} \text{cm}^{-3}$  obtained from a CV measurement from both



**Fig. 5a,b.** AFM micrographs of GaN grown on sapphire grown by the two-step process a with and b without ZnO buffer layers

samples. Low-temperature (20 K) PL spectra from the above samples possess a strong optical emission related to bound-donor or free excitons and their phonon replicas, as shown in Fig. 6. The donor-acceptor pair (DAP) and its phonon replica centered at 380 nm and higher are often attributed to impurities in the materials [13] and are weaker for sample b when compared to sample a. A weak yellow luminescence, which can be observed centered at 550 nm for sample a, previously related to defect complexes [19], is very weak in the spectrum b, perhaps indicating a reduced concentration of such complexes. The surface cracks existing in the GaN have been found to be related to the growth conditions and sapphire-surface pretreatment and have been eliminated by optimizing the growth conditions and surface pretreatment. Thicker GaN can be grown under such conditions, leading to a 30–40  $\mu\text{m}$  with a smooth surface morphology and a low FWHM of the (0002) XRD  $\omega$  rocking curve of 270 arcsec. Figure 7 is the

typical low-temperature PL of the samples grown under such optimized growth conditions and surface pretreatment. The intensity of the DAP and its phonon replicas is significantly decreased.

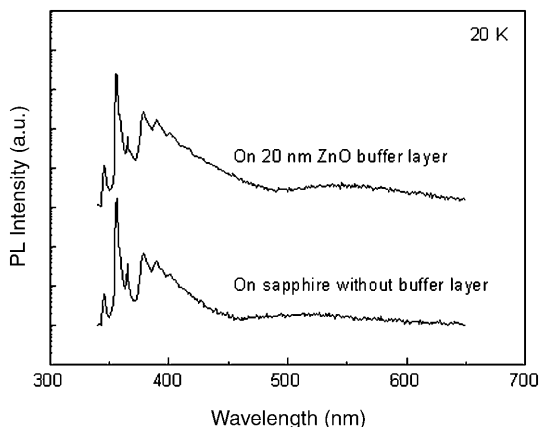
### 3 Summary

The use of a two-step growth process in the GaN growth on ZnO-based sapphire surfaces has led to improved and controlled morphology and properties. The initial choice of growth conditions promotes rapid initial growth and a subsequent change in growth ambient was chosen to allow a high lateral growth rate. GaN materials with a narrow X-ray line width have been successfully grown on sapphire substrates with and without ZnO buffer layers using this two-step process.

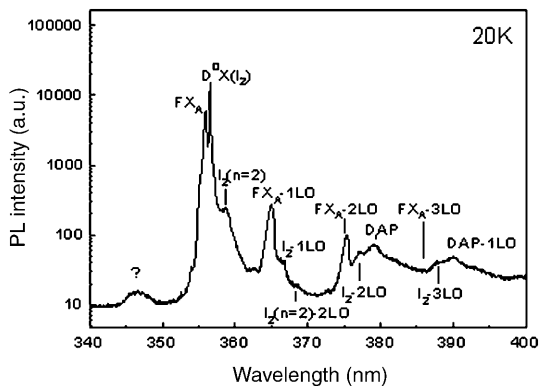
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**Fig. 6.** Low-temperature photoluminescence spectra obtained from the samples shown in Fig. 5 possess strong optical emissions related to bound-donor or free excitons and their phonon replicas



**Fig. 7.** Low-temperature photoluminescence on the typical samples obtained under optimized growth conditions utilizing a two-step growth process. The sample thickness was 30–40  $\mu\text{m}$