

Growth of GaN by metal organic vapor phase epitaxy on ZnO-buffered c-sapphire substrates

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Abstract

The materials quality and availability of large-area bulk GaN substrates is currently considered a key problem for the continuing development of improved GaN-based devices. Since industrial fabrication of bulk GaN substrates with suitable materials quality has proven very difficult, the opto-GaN industry is currently based on heteroepitaxy using either c-sapphire or 6H SiC substrates. ZnO is promising as a substrate material for GaN because it has the same wurtzite structure and a relatively small lattice mismatch (~1.8%).

In this study, we have successfully grown GaN by MOVPE on ZnO-buffered c-sapphire. The growth conditions required to both prevent ZnO degradation and grow monocrystal thin film of GaN have been obtained. SEM, HRXRD and micro-Raman characterizations underlined the presence of the two layers GaN and ZnO with high structural quality.

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1. Introduction

ZnO is considered a promising candidate as a substrate for GaN. There are two main reasons for this: firstly, it has the same wurtzite structure and a relatively small lattice mismatch (~1.8%) with GaN compared with conventional

substrates such as sapphire, AlN and 6H-SiC. Secondly, it has a small difference in thermal expansion coefficient relative to GaN [1]. Two main approaches can be used to grow GaN on ZnO. The first one consists of growing on a bulk ZnO substrate [1] and the second, studied here, consists of using a ZnO thin film template. These ZnO templates were seen to promote high structural quality of GaN after only 140 nm of growth, whereas deposition directly on c-Al₂O₃ would have required a couple of micrometers of GaN to obtain an equivalent quality. This improvement of GaN material quality when grown on ZnO was primarily linked to the high crystallographic quality

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and low surface roughness of the ZnO template layers used in this study. This, in turn, was attributed to the capacity of ZnO for more compliant adaptation to mismatched substrates compared with GaN [2]. Furthermore, thin ZnO templates can be used as a sacrificial layer since ZnO is easily etched by most dilute acids or alkalis. As a result, freestanding films of GaN can be obtained by chemical lift-off and then wafer bonded onto any other substrate of choice.

In this paper, we present study of GaN grown by MOVPE on ZnO buffered c-Al₂O₃ via structural and optical characterization.

2. Experimental procedure

Two hundred and twenty-five nanometer thick layers of ZnO were grown on 2 in diameter c-Al₂O₃ substrates. The growth was performed using pulsed laser deposition (PLD) with a Coherent KrF excimer laser (248 nm), as described elsewhere [3]. For the thin GaN layer on the ZnO, the growth was performed by MOVPE at relatively low substrate temperature using N₂ as carrier gas and dimethylhydrazine as a precursor of atomic nitrogen [8]. The GaN/ZnO layers were characterized by:

- Field emission gun scanning electron microscopy (FEG–SEM) in an FEI Nova Nanolab 200 Dualbeam system to study an ion-milled cross section of the GaN/ZnO.
- High-resolution X-ray diffraction (HRXRD) in triple axis configuration using an MRD PRO system from Panalytical. The optics comprised a 4-bounce Ge(220) monochromator in the incident beam path and a 3-bounce Ge monochromator in the diffracted beam path.
- Dilor confocal micro-Raman spectrometer using an excitation laser wavelength of 514.5 nm with a relatively low optical power of about 2×10^5 W/cm². The confocal aperture was fixed so as to analyze approximately 1 μm³ of sample. The measurements were conducted in a backscattering geometry, in which the incident as well as the scattered light were almost orthogonal to the c-plane of ZnO. All measurements were carried out at 300 K. Table 1 summarizes the Raman-active modes for GaN in a backscattering $z(y,-)z$ geometry [9].
- Transmission measurements were carried out at room temperature with a Perkin-Elmer LAMBDA 950 spectrophotometer.

Table 1
GaN Raman-active modes in the $z(-,-)z$ geometries

Geometry	Allowed Raman modes	Raman shift (cm ⁻¹)
$z(y,y)z$	E ₂ , A ₁ (LO)	568, 734
$z(y,x)z$	E ₂	568

3. Results and discussions

Few publications have reported use of the MOVPE to grow GaN/ZnO because of challenging issues related to the growth process: in bulk ZnO, sub-surface polishing damage propagates to the surface at substrate temperatures over about 650 °C, which leads to degradation of the ZnO surface morphology [4]. Secondly, back-etching of ZnO under the NH₃ and/or H₂ environments, typically used in the MOVPE growth chamber, either damages the bulk surface or removes ZnO thin film template layers during the growth temperature ramp up [1,5,6]. Therefore, liberated Zn and O are unintentionally incorporated into the GaN epilayer to the detriment of the optical and electrical quality. Next, intermediate alloys of ZnO and GaN can form at the interface with no controlled composition [7]. Finally, cracks are often observed to appear, which almost inevitably lead to a delamination of the GaN layer [1]. We have developed our GaN growth conditions so as to overcome all of these issues. A 140 nm GaN layer was grown on top of the ZnO buffer layer without evaporating the ZnO.

Optical microscopy (not shown here) revealed a homogeneous surface free of obvious pit, pinhole, particle, cracking or defect problems.

The FEG–SEM photo in Fig. 1 shows the presence of three distinct layers: Al₂O₃ substrate, ZnO buffer layer and GaN epilayer. A Pt strip was deposited on the top of the structure to facilitate charge dissipation. The thickness of the ZnO layer was similar before and after GaN growth, which was taken as evidence of successful avoidance of back etching of the ZnO. The interface c-Al₂O₃/ZnO exhibits a gradient of contrast on the ZnO side which could be related to a rearrangement of atoms between ZnO and c-Al₂O₃. However, the interface between the ZnO/GaN is well-defined straight line.

Fig. 2 shows the XRD space map around the (0002) peak before and after GaN growth. Two intense peaks were observed after the GaN growth: one on the left side related to the ZnO layer, and one on the right side corresponding to the GaN layer. The high intensity of the GaN peak indicates that the films were well crystallized.

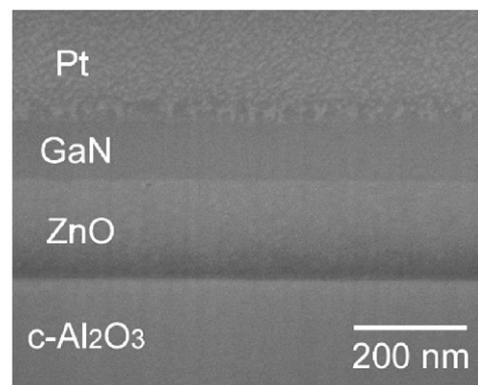


Fig. 1. FEG–SEM image of GaN/ZnO/c-Al₂O₃ structure.

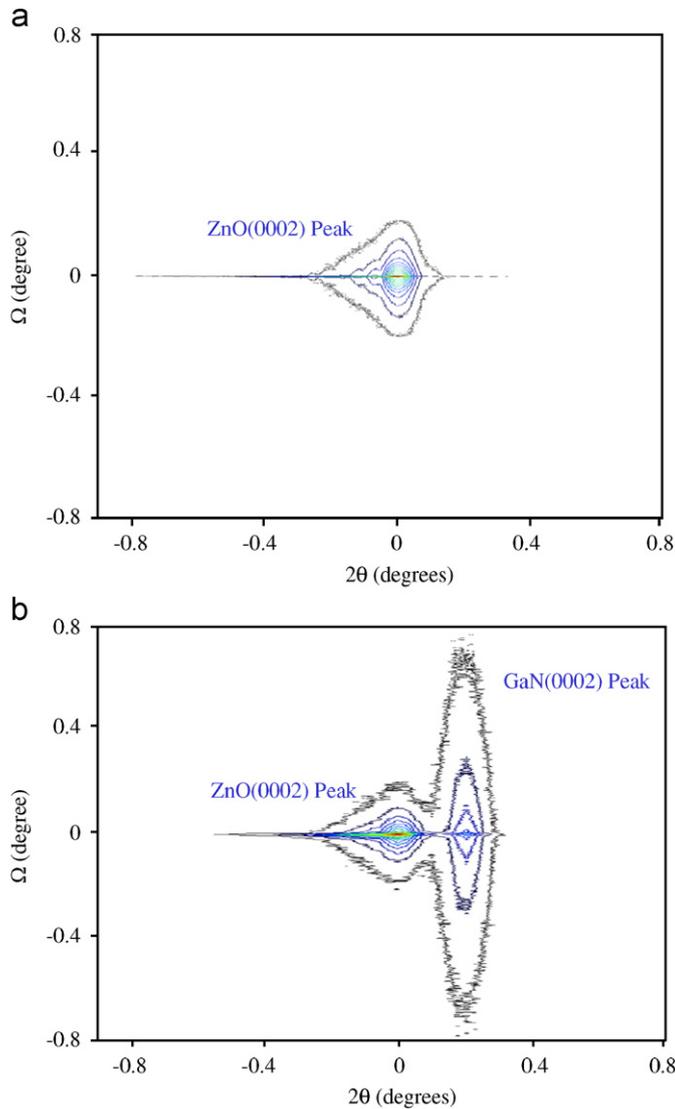


Fig. 2. HRXD space maps (a) before and (b) after growth of GaN.

Fig. 3 shows the Raman spectra before and after growth of GaN. A peak characteristic of the ZnO wurtzite phase is observed at 436 cm^{-1} . The presence of this peak, after the growth of GaN, demonstrates the transparency of the GaN epilayer. E_2 and $A_1(\text{LO})$ GaN phonon peaks with the correct symmetry (Table 1) were clearly identified in the GaN/ZnO/ Al_2O_3 spectra. These results indicate the presence of well-crystallized ZnO/GaN and confirmed those obtained by SEM and HRXRD. Moreover, Raman spectra recorded at different positions in the layer (not shown here) do not reveal any significant variations in their relative intensities and frequency shifts. This suggests that the deposited layers have relatively good homogeneity.

The transmission measurements were also performed before and after GaN growth. Fig. 4 shows the transmission spectra. Both spectra exhibit a very sharp and well-defined transmission wavelength edge at 387 nm, near the ZnO band gap energy at 3.3 eV. The transmission spectrum

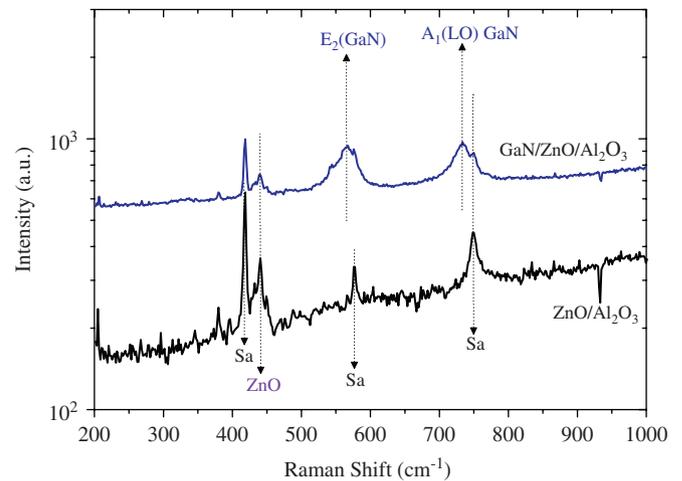


Fig. 3. Raman microscopy of GaN/ZnO/ $c\text{-Al}_2\text{O}_3$.

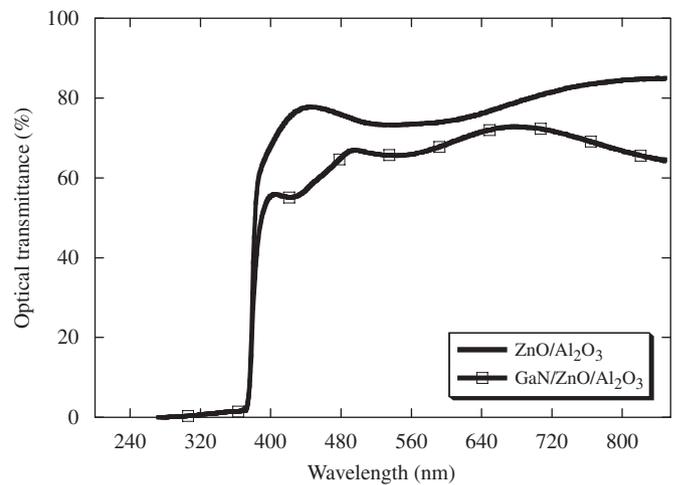


Fig. 4. Transmission of ZnO/ $c\text{-Al}_2\text{O}_3$ and GaN/ZnO/ $c\text{-Al}_2\text{O}_3$.

after GaN growth confirms the presence of the ZnO layer underneath the GaN epilayer.

The transmission wavelength edge of the GaN epilayer (around 360 nm) cannot be seen in the transmission spectra. This is probably because of the lower band gap value of the ZnO underlayer since incident light with a wavelength between the ZnO and GaN band edge values would be absorbed by the ZnO.

4. Conclusion

In this paper, we presented growth of high-quality GaN after only 140 nm of MOVPE through use of a ZnO buffer layer. A growth process based on N_2 as a carrier gas and dimethylhydrazine as a precursor of atomic N was developed so as to avoid ZnO buffer degradation and GaN epilayer delamination. Thus, growth of GaN on ZnO-buffered $c\text{-Al}_2\text{O}_3$ could be an attractive alternative to produce good GaN device structures. Moreover, this approach provides the extra benefit of an elegant and

economical wet etching method to produce freestanding GaN through use of ZnO as sacrificial layer.

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