Microstructural compositional, and optical characterization of GaN grown by metal organic vapor phase epitaxy on ZnO epilayers

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This article presents the results of microstructural, compositional, and optical characterization of GaN films grown on ZnO buffered *c*-sapphire substrates. Transmission electron microscopy showed epitaxy between the GaN and the ZnO, no degradation of the ZnO buffer layer, and no evidence of any interfacial compounds. Secondary ion mass spectroscopy revealed negligible Zn signal in the GaN layer away from the GaN/ZnO interface. After chemical removal of the ZnO, room temperature (RT) cathodoluminescence spectra had a single main peak centered at ∼368 nm (∼3.37 eV), which was indexed as near-band-edge (NBE) emission from the GaN layer. There was no evidence of the ZnO NBE peak, centered at ∼379 nm (∼3.28 eV), which had been observed in RT photoluminescence spectra prior to removal of the ZnO. © *2009 American Vacuum Society.*
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I. INTRODUCTION

The future development of GaN based light emitting diodes (LEDs) and laser diodes (LDs) is being hampered by constraints imposed by non-native *c*-sapphire (c-Al_2O_3) and 6*H*-SiC substrates.[1] In spite of a smaller lattice mismatch (∼1.8%), ZnO substrates have not been adopted because the NH_3 and H_2 carrier gases, used in conventional metal organic vapor phase epitaxy (MOVPE) growth of GaN, cause dissociation of ZnO at growth temperatures of about 650 °C.[2–4] Recently, the authors reported on a novel lower-temperature approach to grow GaN by MOVPE on ZnO template layers without dissociation of ZnO so as to give continuous wurtzite ZnO and GaN layers with a smooth, well-defined interface.[5] In addition, subsequent lift-off of the GaN from insulating c-Al_2O_3 substrates was demonstrated through preferential chemical etching of ZnO.[6] Such an approach opens up the possibility of wafer bonding GaN LEDs and LDs onto electrically and thermally conducting substrates. This would allow the fabrication of vertical devices with a smaller footprint, improved heat dissipation, and reduced current crowding. These would, in turn, boost wafer yield and device performance in terms of efficiency, lifetime, and brightness.

In our prior papers,[5,6] x-ray diffraction (XRD), scanning electron microscope (SEM), Auger electron spectroscopy, resonant Raman spectroscopy, resistivity, and photoluminescence (PL) studies of the GaN/ZnO structure were reported. In this article, we present complementary results of subsequent microstructural, compositional, and optical characterization, which answer some outstanding questions concerning the quality of the GaN and ZnO thin films.

II. EXPERIMENT

ZnO thin films were grown on c-Al_2O_3 substrates using pulsed laser deposition from a sintered ZnO target in molecular oxygen with a coherent KrF (248 nm) excimer laser, as described elsewhere.[7] GaN overlayers were grown using MOVPE with N_2 carrier gas and trimethylgallium and Dimethylhydrazine as group-III and group-V sources, respectively. This approach allowed growth of well-crystallized wurtzite GaN at a reduced substrate temperature (T_s).[8,9]

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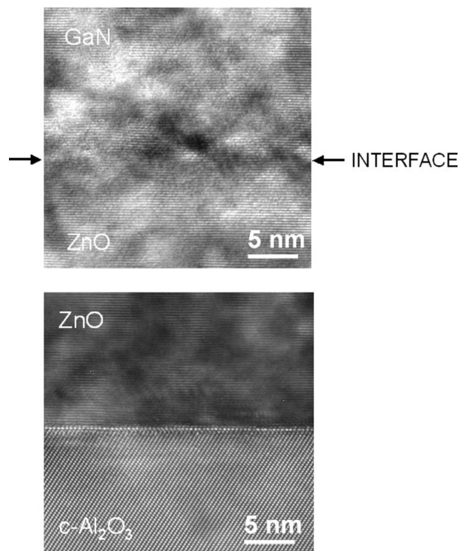

FIG. 1. HRTEM images of the interfaces in an ion-milled cross section of GaN/ZnO/c-Al_2O_3.

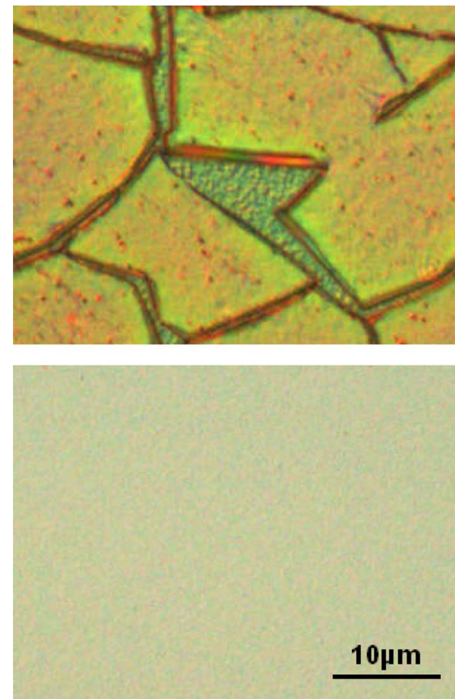

FIG. 2. (Color online) Conventional optical microscope images (same scale) of typical regions in a GaN/ZnO/c-Al_2O_3 samples before (above) and after (below) optimization of the GaN growth conditions.

High resolution transmission electron microscopy (HRTEM) was performed on mechanically ground then Ar-ion polished, cross-sectional samples in a 200 keV FEI Tecnai TF20 equipped with a field emission gun source. The variation in elemental concentration profiles along the growth direction was investigated using MCs^+ secondary ion microscopy (SIMS) in a Cameca IMS4F system. The primary (incident) ions were $133Cs^+$ with an impact energy of 5.5 keV. Positively charged secondary ions were detected.

The optical properties of the GaN/ZnO were studied using room temperature (RT) PL with a frequency-doubled argon-ion laser at 244 nm. The optical properties of the GaN were investigated (after chemical dissolution of the ZnO in dilute hydrochloric acid) using a homemade cathodoluminescence (CL) system in a SEM.[10] A 2 keV accelerating voltage was selected for the studies.

III. RESULTS AND DISCUSSION

Figure 1 shows HRTEM images of typical regions at the interfaces between the ZnO/c-Al_2O_3 and ZnO/GaN. The former shows highly ordered crystal structures in both ZnO and c-Al_2O_3, with a misfit region at the interface only a few atomic layers in thickness. In the latter image, there are continuous fringes across the ZnO/GaN interface, with no evidence of a misfit layer or any interfacial compounds. This confirms the epitaxial relationship revealed in XRD phi scans reported previously.[5]

Figure 2 shows conventional optical microscope images of typical regions in samples before and after optimization of the GaN growth procedure. Before optimization, there is cracking, peeling, and dark spots indicative of poor GaN quality and adhesion. After optimization, the surface is homogeneous and free from obvious pit, pinhole, particle, cracking, or defect problems, which were reported by other groups.[4] This difference is probably due to epitaxy of the GaN on ZnO plus the lack of back etching under the optimized GaN/ZnO growth conditions.

Figure 3 shows the SIMS depth profiles for Zn, Al, Ga, and N. The plot indicates a drop of about three orders of magnitude in the Zn concentration profile at the GaN/ZnO interface with negligible Zn signal in the GaN layer away from the GaN/ZnO interface (i.e., a Zn signal comparable with the background in the c-Al_2O_3 substrate) unlike other groups who reported significant Zn concentrations in the

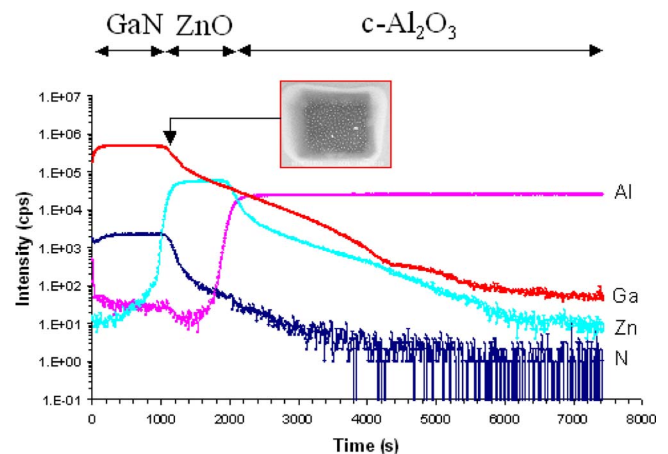

FIG. 3. (Color online) SIMS elemental concentration depth profiles for the Zn, Ga, N, and Al signals for the GaN/ZnO/c-Al_2O_3 (after the first 200 s, the etch rate was estimated to be about 0.226 nm/s). The inset SEM image shows the beam crater ($150 \times 150\ \mu m^2$) after etching of the GaN (i.e., at the GaN/ZnO interface) with residue particles at the base.

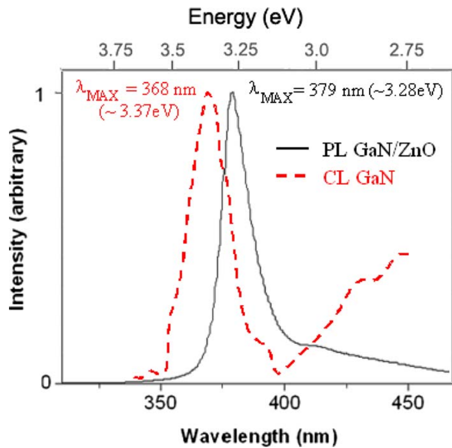

FIG. 4. (Color online) Normalized RT PL and CL spectra for GaN/ZnO and GaN, respectively.

GaN overlayers.[4,11] The ZnO layer also appears to act as a barrier for Al diffusing up from the c-Al_2O_3 substrate.[12] It should be noted that the tails in the concentration profiles for Zn, Ga, and N, which extend into the c-Al_2O_3 substrate, are probably artifacts due to residual particles of ZnO and GaN in the probe crater (visible in the inset SEM image of the analysis crater).

Figure 4 shows the normalized RT PL and CL spectra before and after chemical removal of the ZnO layer, respectively. The RT PL for the GaN/ZnO structure revealed a single peak at 379 nm (~3.28 eV), corresponding to wurtzite ZnO near-band-edge (NBE) emission. The full width at half maximum (FWHM) was about 13 nm (~95 eV). After chemical removal of the ZnO, RT CL spectra had a single main peak centered at ~368 nm (~3.37 eV) with a FWHM of about 20 nm (~62 eV). This peak was indexed as NBE emission from wurtzite GaN. There was no evidence of the ZnO peak, which had been observed prior to chemical etching of the ZnO. This suggests that the absence of NBE PL from the GaN prior to chemical lift-off was due to the presence of the ZnO underlayer. This may have been the result of preferential carrier recombination in ZnO (due to the smaller bandgap of ZnO) or through a masking of the GaN emission peak by the more intense PL from the ZnO layer.

IV. SUMMARY AND CONCLUSION

This article presents the results of microstructural, compositional, and optical characterisation of GaN films grown by MOVPE on ZnO buffered c-Al_2O_3 substrates. HRTEM revealed the epitaxy of the GaN on the ZnO with no evidence of any interfacial layer. SIMS indicated negligible Zn signal in the GaN layer away from the GaN/ZnO interface. After chemical removal of the ZnO, RT CL spectra had a peak centered at ~368 nm (~3.37 eV), which was indexed as NBE emission from wurtzite GaN. There was no evidence of the ZnO NBE emission peak centered at ~379 nm (~3.28 eV), which had been observed in RT PL studies prior to chemical etching of the ZnO.

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