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Use of ZnO thin films as sacrificial templates for metal organic vapor phase epitaxy and chemical lift-off of GaN

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Continued development of GaN-based light emitting diodes is being hampered by constraints imposed by current non-native substrates. ZnO is a promising alternative substrate but it decomposes under the conditions used in conventional GaN metal organic vapor phase epitaxy (MOVPE). In this work, GaN was grown on ZnO/c-Al_2O_3 using low temperature/pressure MOVPE with N_2 as a carrier and dimethylhydrazine as a N source. Characterization confirmed the epitaxial growth of GaN. The GaN was lifted-off the c-Al_2O_3 by chemically etching away the ZnO underlayer. This approach opens up the way for bonding of the GaN onto a support of choice. *© 2007 American Institute of Physics*. [DOI: 10.1063/1.2770655]

The need for blue and ultraviolet (UV) solid-state emitters has propelled the investigation of wide band gap semiconducting materials in recent years. Commercial applications typically include light emitting diodes (LEDs) for signage and lighting plus lasers for data storage. Most of the recent materials development for these applications has centred around GaN-based alloys.

Continuing development of GaN based devices is being hampered because good quality native substrates are not widely available at acceptable cost levels.[1] Indeed, the vast majority of GaN based LEDs are currently grown on c-plane sapphire (c-Al_2O_3) substrates. c-Al_2O_3 presents significant mismatches in lattice parameter (16.1%) and thermal expansion coefficient, however, which promote strain, dislocations and poor structural quality in the GaN. Such LEDs also have poor heat dissipation due to the thermally insulating nature of c-Al_2O_3, which reduces device lifetime and prevents performance near the efficiency "sweet spot" at higher drive currents. In addition, the electrical insulating nature of c-Al_2O_3 creates a need for lateral devices with extra lithography steps and the use of a proprietary top contact approach. These, in turn, entail further issues such as increased device size, current crowding, and dynamic resistance.

An alternative and promising substrate for GaN epitaxy is ZnO. Besides having the same wurtzite structure and a small lattice mismatch (1.8%), GaN and ZnO also have the same (HH) stacking sequence. Hence, stacking mismatch boundaries and inversion domain boundaries should be less likely to occur in GaN grown on ZnO. Furthermore, c-axis GaN/ZnO shows a much reduced mismatch in thermal expansion coefficient compared with GaN/c-Al_2O_3. Moreover, thermal strain has been shown to be compressive for GaN/ZnO, whereas it is tensile for GaN/c-Al_2O_3. This means that there should be reduced likelihood of cracking in GaN grown on ZnO. Another attractive characteristic of ZnO is its amenability to chemical etching in most acids and bases. Since GaN is resistant to most of these same etchants, ZnO could be removed selectively so as to lift-off the GaN based device from the substrate.

Several groups have already worked on the growth of GaN on both bulk ZnO substrates and thin film ZnO templates using a wide variety of deposition techniques. Although there has been some success using molecular beam epitaxy (MBE)[2–4] and pulsed laser deposition (PLD)[5,6] results have been less encouraging using the dominant indus-

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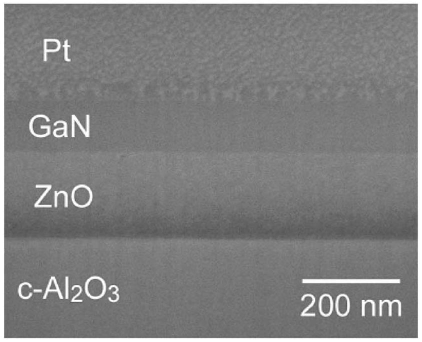

FIG. 1. SEM image of an ion-milled cross-section of Pt/GaN/ZnO/c-Al_2O_3.

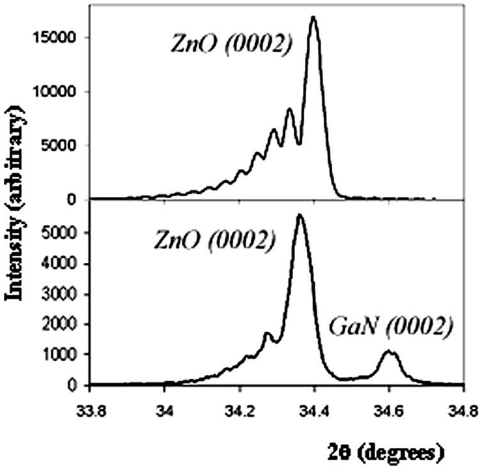

FIG. 2. $2\theta/\omega$ XRD scans of the wurtzite (0002) peak before and after GaN layer growth (upper and lower scans, respectively).

trial GaN growth tools: hydride vapor phase epitaxy[7–9] and metal organic vapor phase epitaxy (MOVPE).[10–14] The studies identify three main obstacles. Firstly, VPE of GaN is typically done at substrate temperatures (T_s) over 1000 °C, and the surface morphology of bulk ZnO substrates has been observed to degrade at such elevated T_s. This is thought to be due to the propagation of subsurface polishing damage to the substrate surface.[15] Secondly, hydrogen (H_2) is often employed as a carrier gas in MOVPE and ZnO is unstable at elevated T_s in H_2 ambient. Finally, the ammonia (NH_3), which is commonly used as source of atomic nitrogen, attacks ZnO at T_s over about 650 °C. Indeed, in the case of ZnO thin film templates, it was generally observed that the ZnO layer was etched back during the initial stages of GaN growth. In this work, we report, firstly, on MOVPE growth of GaN on a ZnO buffer layer. We then demonstrate chemical lift-off of the GaN layer.

High quality ZnO layers were grown directly on 2 in. diameter c-Al_2O_3 substrates by PLD as described elsewhere.[12] A GaN layer was then grown on top of the ZnO using an innovative T-shape low pressure (LP) MOVPE reactor[16] and a procedure allowing the growth of high quality GaN at reduced T_s.[17] This approach was based on using N_2 as a carrier gas, trimethylgallium (TMG) as a source of Ga, and dimethylhydrazine (DMHy) as a source of N.

Cross-sectional samples were prepared for imaging by electron beam deposition of a protective Pt strip ($6\times 2\ \mu m^2$) on the GaN/ZnO/c-Al_2O_3 surface followed by milling through the layer stack with a focused beam of Ga ions in a FEI Nova Nanolab 200 Dualbeam system. Figure 1 shows a field emission gun scanning electron microscope (FEG-SEM) image of the cross-section. The sample shows continuous GaN and ZnO layers with a smooth interface and surface. Film thickness was estimated to be about 215 nm for the ZnO layer and 135 nm for the GaN layer.

Optical microscopy revealed a homogeneous surface free of obvious cracking, pit, pinhole, particle, or defect problems. Atomic force microscopy (AFM) was conducted in tapping mode using a Park Scientific Instruments autoprobe system. Before the growth of GaN, the ZnO layer showed a root mean square (rms) roughness of about 0.7 nm (over an area of $5\ \times 5\ \mu m^2$). After GaN growth, the rms roughness of the surface was about 2 nm (over an area of $5\times 5\ \mu m^2$) and the surface morphology had a finer structure. Auger electron spectroscopy (AES) was conducted on the top surface of the GaN using a nano-probe PHI680 system. Several regions were examined with a beam incidence angle of 30° and various voltage/current combinations. No evidence of Zn or Al was observed. Resonant Raman spectroscopy was performed at room temperature using a Jobin Yvon Horiba HR800 UV system with 3.81 eV excitation. Characteristic ZnO and GaN LO peaks were clearly distinguished, indicating the presence of well-crystallised wurtzite ZnO and GaN layers. The peak positions for the GaN layer were close to those for a relaxed wurtzite GaN. This suggests that the GaN had little strain. High resolution x-ray diffraction (HRXRD) studies were conducted with both a Panalytical X-Pert MRD PRO system and a Seifert PTS system. Both systems used a Cu $K\alpha_1$ source. In the incident beam path, both were equipped with four-bounce Ge (220) monochromators and multilayer mirrors. Both systems were also equipped with Ge (220) monochromators in the diffracted beam path (three-bounce and two-bounce, respectively).

Figure 2 shows $2\theta/\omega$ HRXRD scans around the ZnO (0002) peak position before and after the growth of GaN. The ZnO c lattice parameter was measured at 5.209 ± 0.001 Å using the (0002), (0004), and (0006) peaks. This is comparable with that for relaxed wurtzite ZnO (5.207 Å). We can also see pronounced Pendellösung fringes. These confirm a low surface roughness and indicate the coherence length of the (000l) crystalline planes to be about 225 nm, which is close to the thickness of 215 nm estimated from the SEM cross-section image. After the growth of GaN, a second peak emerged at a slightly higher 2θ. This peak corresponds to a lattice parameter of 5.182 ± 0.001 Å and was indexed as the (0002) peak of wurtzite GaN (theoretical $c=5.186$ Å). After GaN growth, the ZnO c lattice parameter increased slightly to 5.215 ± 0.001 Å. This shift can be attributed to stress induced in the ZnO layer by the GaN overlayer and is consistent with the higher compliance proposed for the ZnO layer.[14] We can also still see Pendellösung fringes in the GaN/ZnO scan.

The ω rocking curve (no monochromator in diffracted beam path) showed both the ZnO and GaN (0002) peaks. For the ZnO, the full width half maximum (FWHM) was 220 arc sec. For the GaN, the FWHM was comparable but difficult to estimate numerically because the base of the peak was obscured by the skirt of the, more intense, ZnO peak. It should be noted that the pertinence of these FWHM figures is limited, in this case, because of intrinsic peak broadening due to the low film thickness. Phi scans performed on the (1102) peak film after GaN deposition (Fig. 3) show that the

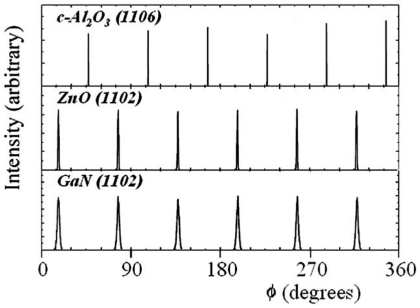

FIG. 3. XRD ϕ scans for the GaN/ZnO/c-Al_2O_3 film.

GaN grew epitaxially on the ZnO and that there is a 30° twist with respect to the c-Al_2O_3 substrate. The slightly broader peaks for GaN compared to ZnO indicate increased crystallographic dispersion in the GaN.

Photoluminescence (PL) was performed at 1.6 K with an Ar laser. Figure 4 shows the PL spectra before and after GaN growth. The spectrum for the ZnO layer shows typical ZnO donor bound exciton (DBE) emission with a wavelength maximum (λ_{max}) of 3.356 eV and a FWHM of 5 meV. Negligible green signal is observed, inferring a low defect density in the sample. After GaN deposition, the ZnO DBE emission is still dominant but the peak is an order of magnitude less intense; the λ_{max} has shifted to 3.353 eV and the peak has broadened to a FWHM of 9 meV. Again, very low green signal is detected. Interestingly, no clear GaN peak is visible. This may be related to the lower band gap of the ZnO combined with the relatively low thickness of the GaN layer because excited carriers transfer to the ZnO layer before radiative recombination. Film resistivity was measured using a four point measurement system equipped with a Keithley 2400 source meter. Values of $0.02 \pm 0.01\ \Omega$ and $0.7 \pm 0.2\ \Omega$ cm were recorded before and after GaN growth, respectively.

Lift-off was performed by immersing a GaN/ZnO/c-Al_2O_3 sample in dilute HCl after mechanical delimitation of submillimetric mesas with a diamond scribe. Figure 5 shows a time sequence of the chemical lift-off process. After several minutes, the ZnO dissolved completely and the GaN mesas floated to the surface of the etchant.

This letter presented the MOVPE growth of GaN thin films on ZnO-buffered c-Al_2O_3 substrates. The evaporation of ZnO during GaN growth reported in prior literature was combated through use of LP-MOVPE with N_2 as a carrier gas, TMG as a source of Ga, and DMHy as a source of N. Using this approach, high quality GaN growth could be conducted at reduced T_s. SEM, AFM, and optical microscopies confirmed continuous ZnO and GaN layers with a smooth interface, low surface roughness and no obvious cracking, pit, particle, pinhole, or defect problems. AES showed no evidence of Zn or Al at the film surface. HRXRD, resonant Raman spectroscopy and PL studies confirmed epitaxial growth of wurtzite GaN layers which were well-crystallised after only 135 nm of growth.

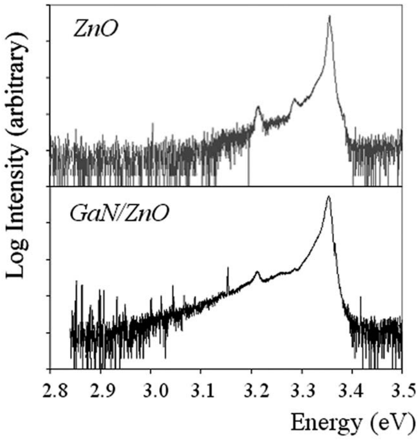

FIG. 4. 1.6 K PL spectra of the ZnO/c-Al_2O_3 and GaN/ZnO/c-Al_2O_3.

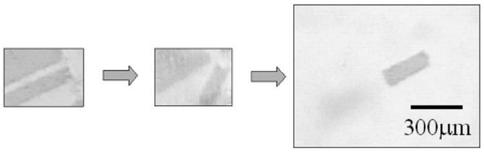

FIG. 5. Time sequence optical microscope images of the chemical lift-off.

The letter also demonstrated chemical lift-off of the GaN layer from the c-Al_2O_3 substrate. This was achieved via immersion in dilute HCl. Optical microscopy revealed the GaN separating from the substrate and floating to the surface of the acid. Such an approach represents a straightforward, wet-etching method to obtain freestanding GaN, which could then be wafer bonded onto substrates with advantages such as superior electrical and thermal conductivity.

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