Novel Method for Reclaim/Reuse of Bulk GaN Substrates using Sacrifical ZnO Release Layers

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ABSTRACT

Free-standing (0002)-oriented GaN substrates (ϕ = 2”) were coated with 200 nm of ZnO and used as templates for the growth of GaN thin films. SEM and AFM revealed that such GaN layers had a relatively homogenous surface morphology with an RMS roughness (5 μm x 5 μm) of less than 4nm. XRD studies revealed strained ZnO growth on the GaN substrate and the reproduction of the substrate rocking curve for the GaN overlayers after only a hundred nm of growth, thus indicating that the GaN films had superior crystallographic quality compared to those grown on sapphire or ZnO/sapphire substrates. Quarter-wafer areas of GaN were removed from the GaN substrate (by selective chemical etching away of the ZnO interlayer). The expensive GaN substrates were then reclaimed/reused (without the need for polishing) for a second cycle of ZnO and GaN growth, which gave similar XRD, SEM, CL and AFM results to the first cycle.

Keywords: GaN, substrate, ZnO, chemical lift-off, LED, reclaim

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INTRODUCTION

Currently, ~ 95% of GaN-based LEDs are grown heteroepitaxially on c-sapphire substrates because the ideal “native” GaN substrates are prohibitively expensive (~2 orders of magnitude more costly than sapphire) and are not available in the volumes required for LED mass production. Sapphire, however, has significant lattice and thermal-expansion mismatches with GaN and it is also both thermally and electrically insulating. The mismatches strain the GaN and lead to the generation of point defects and dislocations, which reduce light output. The high electrical resistivity of sapphire imposes a lateral LED configuration with top-contacts and a confined lateral current flow. This results in current crowding and localized thermal hot spots, which detrimentally impact the efficiency, lifetime and maximum brightness of the device. This is exacerbated by the thermally insulating nature of sapphire, which dramatically restricts heat dissipation, and thereby further limits efficiency, lifetime and brightness. In industry, this is currently combated by transferring the GaN-based epilayer to an alternative substrate with better electrical and thermal conductivity using a laser-lift-off (LLO) and wafer bonding process [1]. Unfortunately LLO is incompatible with GaN substrates, because they are not transparent to the short-wavelength lasers (typically 248 nm excimers), which are necessary for this process.

ZnO has the same crystal structure as GaN, very similar lattice parameters and comparable thermal expansion coefficients. Attempts to adopt bulk ZnO substrates for GaN growth have met with problems of ZnO back-etching by the process gases used in the GaN Metal Organic Chemical Vapor Deposition (MOCVD) manufacturing process, however.

Over the past few years, the authors have developed a novel Metal-Organic Vapor Phase Epitaxy (MOVPE) approach for the capping of ZnO-coated sapphire substrates with GaN without back-etching the ZnO [2, 3]. The authors also demonstrated that such ZnO thin film templates could then be used as sacrificial release layers by selectively dissolving the ZnO underlayer in an alternative process to LLO [2,4]. This could be done in a matter of hours in dilute acid or alkali (GaN is highly resistant to chemical etching in acids and alkalis other than HF) and lifted GaN layers showed no

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trace of Zn in High Resolution Electron Microscopy Energy Dispersive X-Ray microanalysis [5]. Similar transfer of a full LED structure was also demonstrated [1]. If bonded onto a thermally conductive substrate, such LEDs would have much better heat dissipation and a "vertical LED (VLED)" structure, with current flow through the substrate. Such VLEDs have much more homogeneous current distribution and can thus be driven with significantly higher currents. They would also avoid the complex and costly lithographic steps required to make the top contacts and have >30% smaller footprints (i.e significantly higher chip yield per wafer) [6].

In this study, the overall aim was to examine whether a similar process is also valid for the chemical lift-off of GaN from ZnO-coated bulk GaN substrates. The key advantage of this approach is that the expensive GaN substrate can be reclaimed and reused after preferentially dissolving the ZnO away in the transfer process.

EXPERIMENT

ZnO thin films were grown on two-inch-diameter, bulk, (0002)-oriented GaN substrates using pulsed laser deposition (PLD) from a 99.99% pure, sintered, ZnO target in molecular oxygen with a coherent KrF (λ = 248 nm) excimer laser, as described elsewhere [8]. Free-standing (300µm thick) Commercial Hydrogen Vapor Phase Epitaxy (HVPE) GaN substrates were purchased from Lumilog. The specified threading dislocation density was $< 5 \times 10^6$ / cm^2 (typical threading dislocation density in state-of-the-art GaN films grown by heteroepitaxy on sapphire is ~ 10^7 or 10^8 / cm^2). GaN overlayers were grown using MOVPE. The dissociation of ZnO observed during conventional MOVPE growth of GaN was combated through the use of a low pressure/temperature MOVPE approach, with N_2 as a carrier gas and dimethylhydrazine added to the ammonia (nitrogen precursor) in order to enhance the concentration of atomic nitrogen. This methodology allowed growth of well-crystallized wurtzite GaN at a relatively reduced substrate temperature [2, 3]. GaN films were transferred onto optically-flat Corning microscope slides (soda-lime glass) via a process of chemical lift-off and direct fusion bonding, using an approach described previously [1, 4, 5]. Sample morphology was examined at the optical scale using a Leitz-Wetzlar microscope (with digital image acquisition) and, in the sub-optical range, using a Philips S800 field emission gun-Scanning Electron Microscope (FEG-SEM). The crystal structure of the samples was investigated using high resolution X-Ray Diffraction (XRD) performed in a Panalytical MRD Pro system using Cu Kα radiation. Surface topography and roughness were investigated by tapping mode Atomic Force Microscopy (AFM) in a Veeco 3100 Dimension system. Room temperature Cathodoluminescene (CL) measurements were performed in a Zeiss supra^{TM} 55VP SEM with a parabolic collector mirror and an iHR320 spectrometer (focal length of 320 mm and a 1200 groove/mm grating) which give a spectral resolution of 0.06 nm.

3. RESULTS & DISCUSSION

SEM studies (Fig. 1) confirmed that GaN layers were grown successfully on the ZnO/GaN substrates.

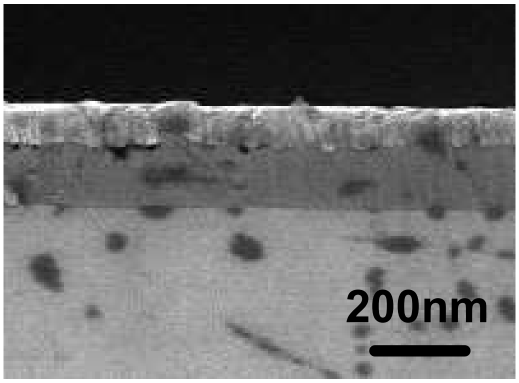

Figure 1: SEM image of a fracture cross-section of a GaN layer grown on a ZnO-coated GaN substrate.

The SEM image shows continuous GaN and ZnO layers. ZnO thickness was about 200 nm and GaN thickness was about 100 nm. The dark spots in the image are most probably a contamination of the electron microscope specimen.

Figure 2 shows XRD 2θ/ω and ω scans around the (0002) peak for the GaN substrate.

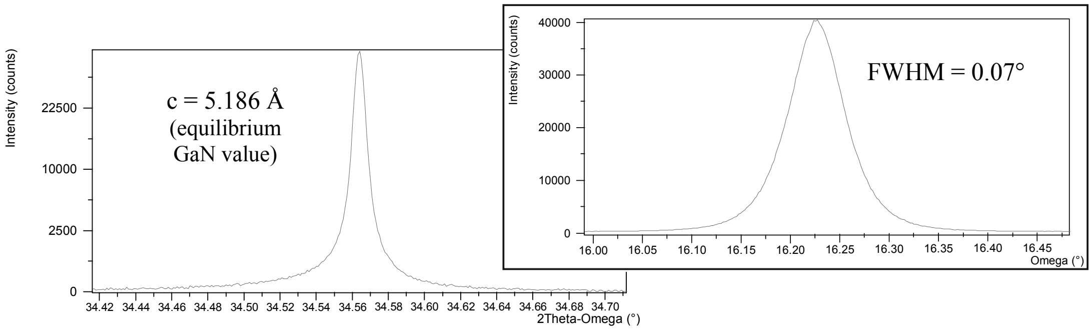

Figure 2: XRD 2θ/ω and ω scans around the (0002) peak for the GaN substrate.

The peaks are symmetric and have typical positions and Full Wave Half Maxima (FWHM) expected for equilibrium wurtzite (0002) GaN substrates. Figure 3 shows XRD 2θ/ω and ω scans around the (0002) peak for the ZnO-coated GaN substrate.

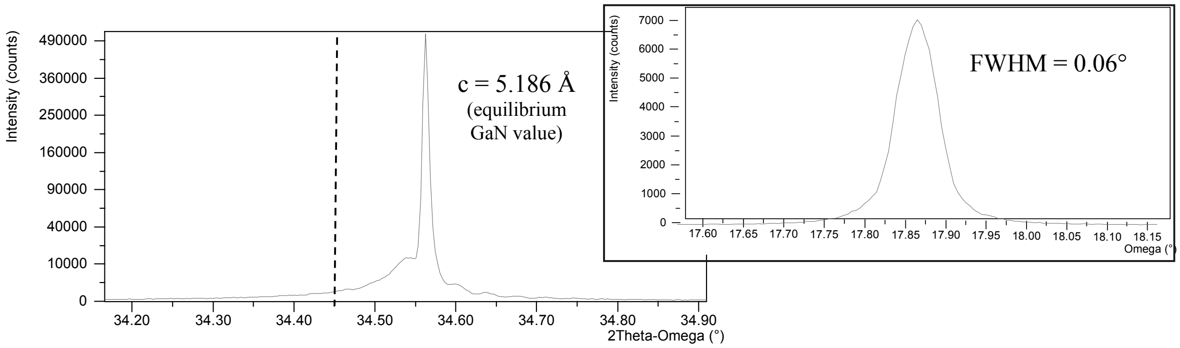

Figure 3: XRD 2θ/ω and ω scans around the (0002) peak for the ZnO grown on the bulk GaN structure (dotted line shows equilibrium ZnO (0002) peak position).

There is now a second, wider, peak of lower intensity straddling the bulk GaN (0002) peak in the 2θ/ω scan. This ZnO-related peak has Pendellösung fringes, which are indicative of a thin film with a relatively low surface roughness over the area of the X-ray beam spot. The fringe spacing gives an estimate of the ZnO film thickness at 235 nm, which is consistent with the SEM sectional image (Fig. 1). The ZnO peak position in the 2θ/ω scan does not correspond to that for equilibrium wurtzite ZnO (indicated by the dotted line) , however, and it would thus appear that ZnO is compressively strained by the underlying GaN substrate. The ω rocking curve for the ZnO (acquired just to the left of the GaN 2θ/ω peak where the ZnO peak is dominant) shows a FWHM value (of 0.06°), which is comparable with that observed for the GaN substrate and indicative of a very low dispersion in the crystallographic orientation about the c-axis.

Figure 4 shows XRD 2θ/ω and ω scans around the (0002) peak for the GaN/ZnO/GaN structure.

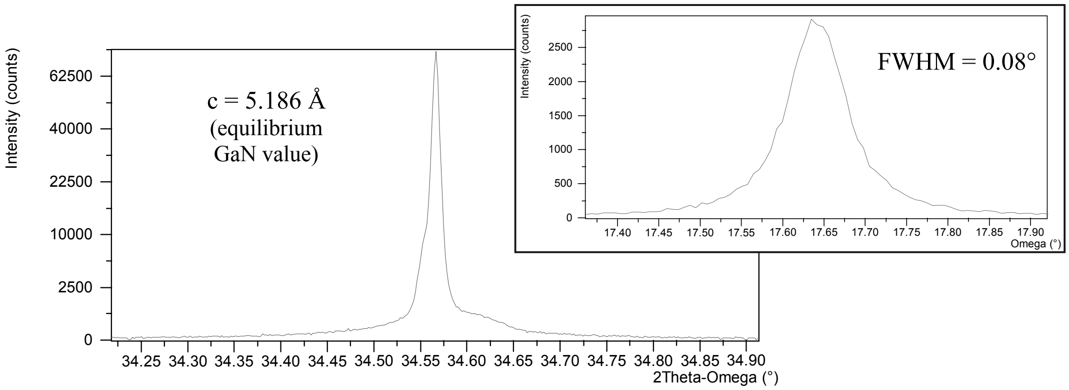

Figure 4: XRD 2θ/ω and ω scans around the (0002) peak for the GaN/ZnO/Bulk GaN structure.

The 2θ/ω scan now shows evidence of a third peak being superposed on that of the ZnO/GaN scan with a relatively low intensity tail extending out on the right-hand-side of the main GaN peak. The Pendellösung fringes of the ZnO layer are now no longer visible. The ω rocking curve FWHM value (of 0.08°) is comparable with that observed for the GaN substrate (0.07º). This corresponds to a significant reduction in crystallographic dispersion relative to typical GaN layers grown on ZnO/sapphire.

Figure 5 shows the (112) peak ϕ scan and the (0002) peak reciprocal space map for the GaN/ZnO/GaN structure.

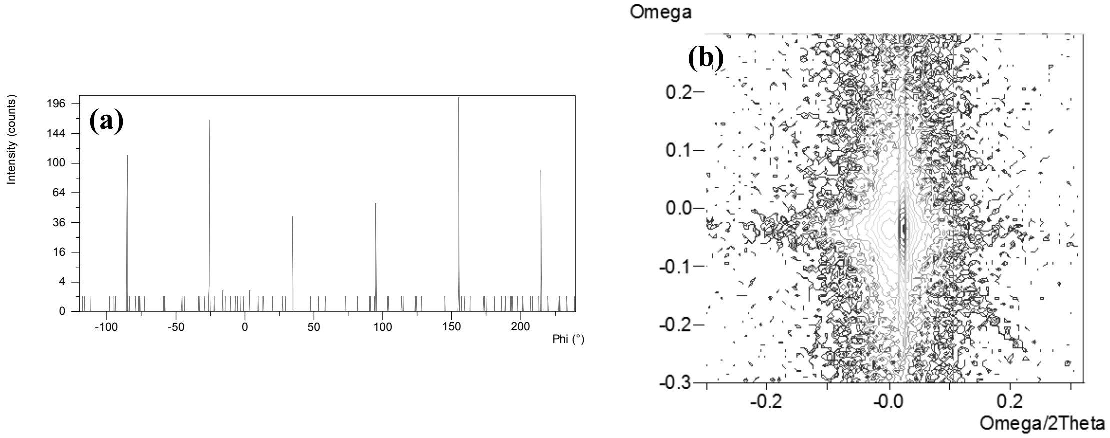

Figure 5: XRD a) (112) peak ϕ scan & b) (0002) peak reciprocal space map (log scale) for the GaN/ZnO/GaN structure

There is a single set of six, evenly-spaced, peaks in the ϕ scan, which is coherent with epitaxy in the six-fold wurtzite symmetry. Overall, the XRD studies suggest that the GaN epilayers grew epitaxially and were relatively strain free thanks to a compressively-strained ZnO underlayer which provided a lattice-matched template.

After the XRD characterization, the surface of the GaN layer was bonded onto a glass support using Apiezon W wax and the ensemble was immersed in a ~1M HCl solution so as do dissolve the ZnO interlayer and thus release the GaN overlayer from the freestanding GaN substrate. Figure 6 shows the progression of the subsequent chemical lift-off over time.

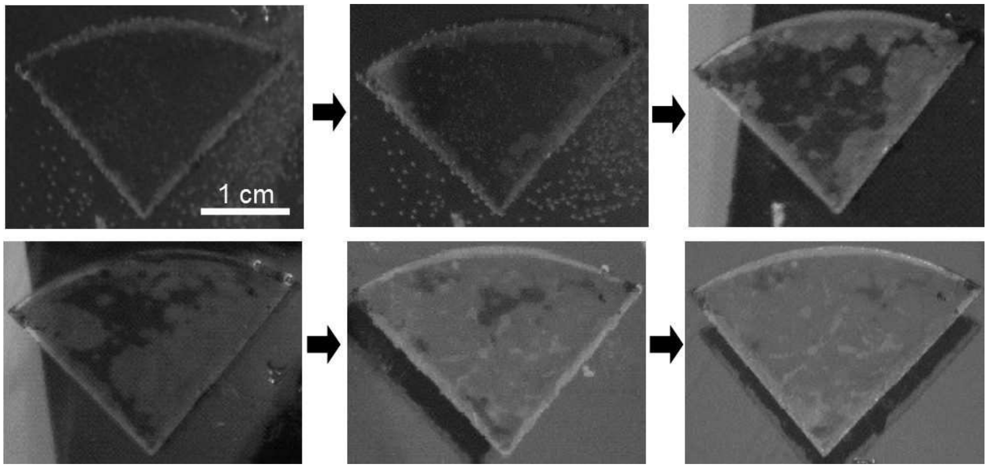

Figure 6: Photographs taken through the backside of the (immersed) GaN quarter-wafer showing a time sequence of the chemical dissolution of ZnO and the progressive detachment of the GaN substrate (sample is in ~1M HCl solution).

After the chemical lift-off, the bulk GaN substrate was cleaned chemically in an ultrasound bath, then rinsed and dried with compressed air before being reused as a substrate for another cycle of ZnO and GaN growth.
The XRD scans in Figure 7 indicate that the second cycle of ZnO growth on the reclaimed GaN substrate gave equivalent crystallographic quality to the first cycle (Fig. 3). There were no pronounced Pendellösung fringes, however, which suggests that the surface roughness may have increased.

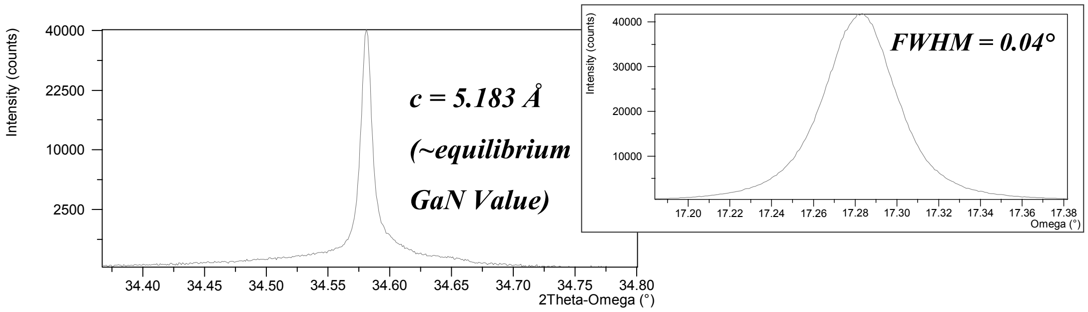

Figure 7: XRD 2θ/ω and ω scans of the (0002) peak for the ZnO layer on reclaimed GaN substrate.

The XRD scans in Figure 8 indicate that the second cycle of GaN growth was also of comparable crystallographic quality to the first cycle (Fig. 4).

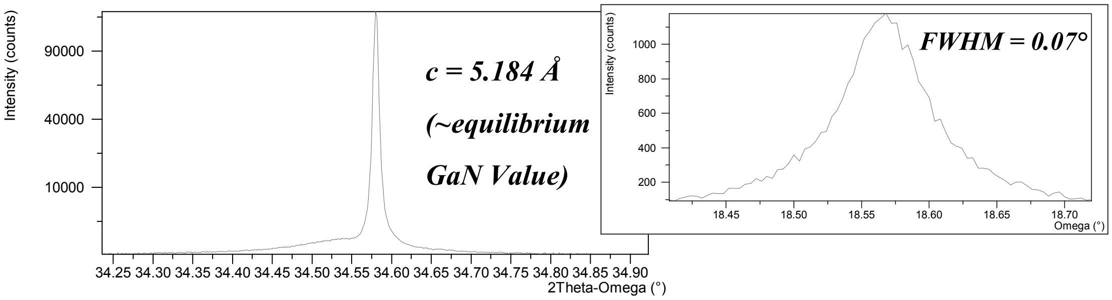

Figure 8: XRD 2θ/ω and ω scans of the (0002) peak for the GaN/ZnO/GaN (second cycle) shows comparable materials quality to the first cycle (Fig. 2).

Figures 9 and 10 show SEM and AFM images of the GaN surface after the second cycle of GaN/ZnO growth.

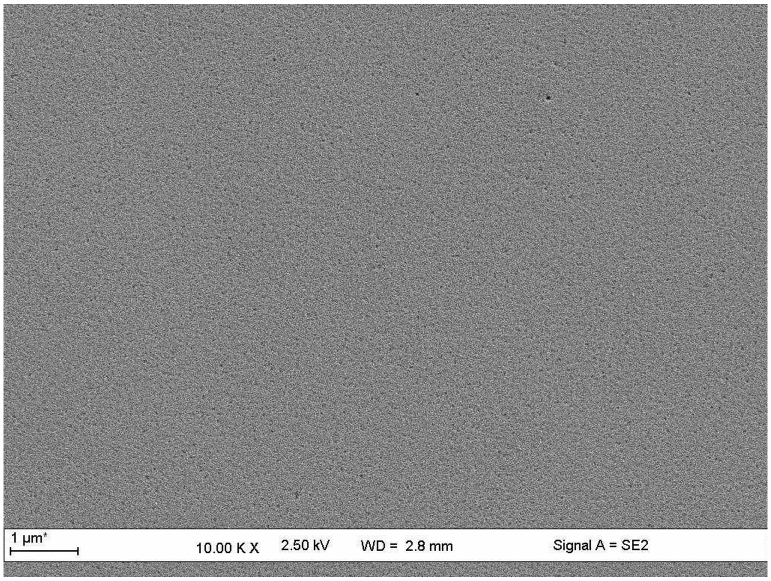

Figure 9: SEM image of the surface of the GaN/ZnO bilayer after recycling of the GaN substrate

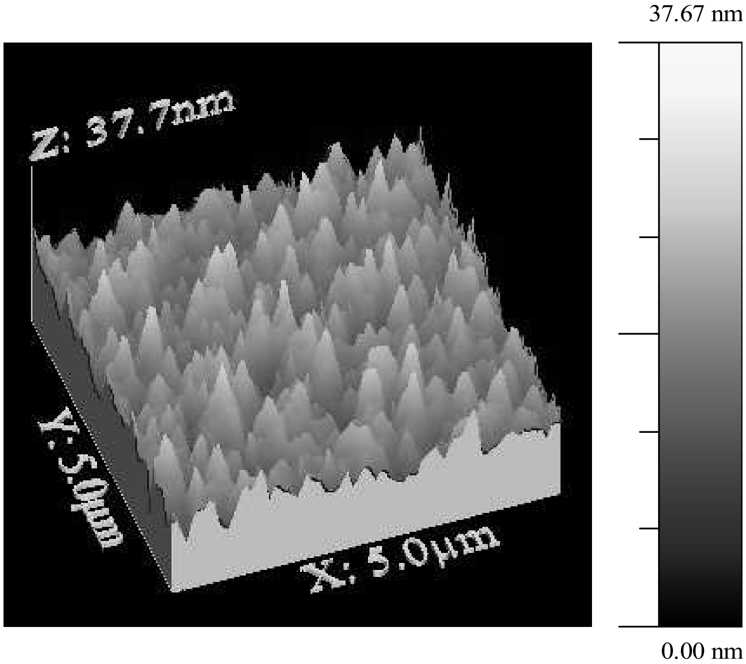

Figure 10: 5µm x 5 µm AFM scan of the surface of the GaN/ZnO bilayer after recycling of the GaN substrate

The SEM image shows that the surface is free of cracks and relatively homogeneous on the tens of microns scale. The AFM study of a 5 micron x 5 micron area revealed a peak-to-valley of 23 nm and a root mean square roughness of 3.8 nm.

CL spectra are shown as a function of accelerating voltage for ZnO/GaN (Fig. 11a) and GaN/ZnO/GaN (Fig. 11b) after recycling of the GaN substrate.

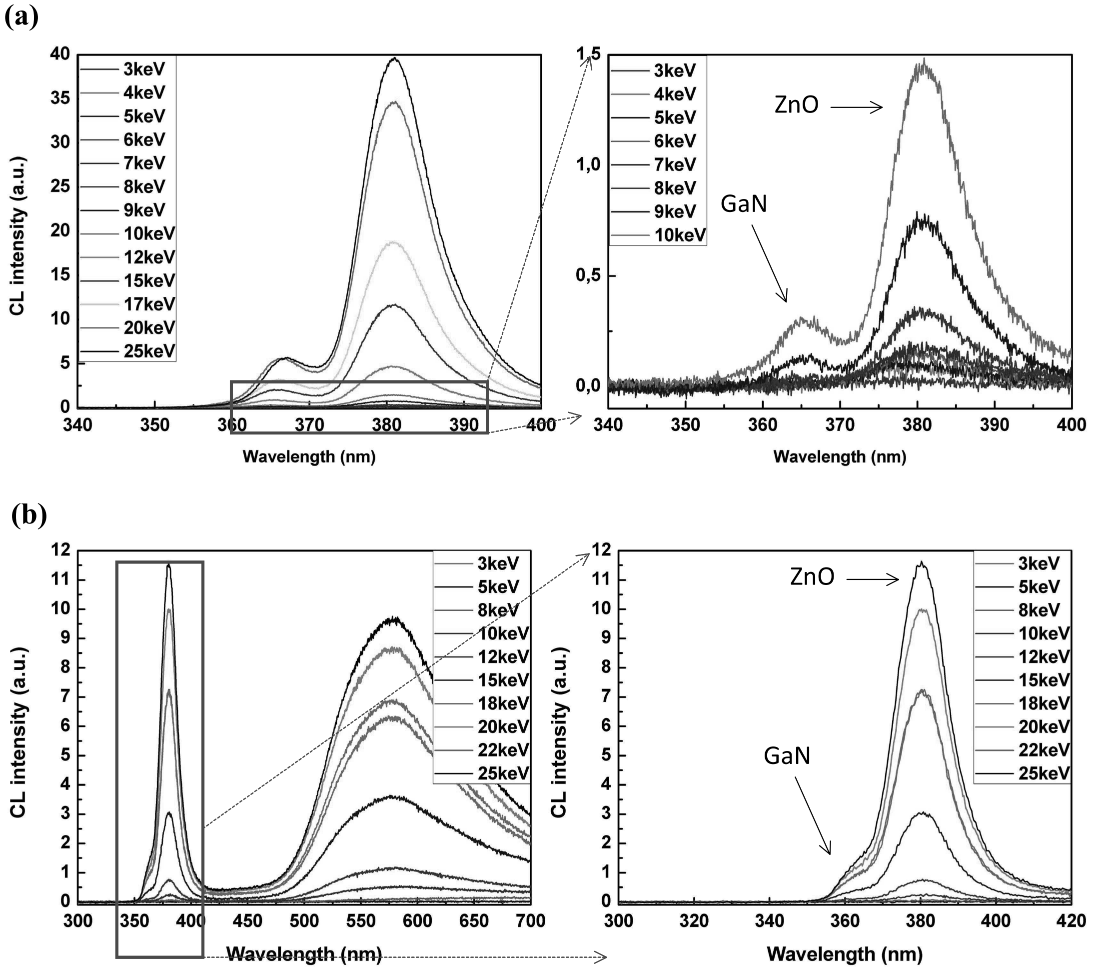

Figure 11: Cathodoluminescence at room temperature of a ZnO/GaN sample (top) and a GaN/ZnO/GaN sample (bottom) showing both the ZnO (at 380nm) and GaN (at 365nm) peaks.

In both cases a strong ZnO near-band edge (NBE) peak is present at low accelerating voltage and a NBE contribution from the GaN substrate emerges as the accelerating voltage increases. The lack of a distinct GaN signal from the GaN film in the GaN/ZnO/GaN sample may be due to preferential carrier recombination in the ZnO due to the smaller bandgap.

4. CONCLUSIONS

Free-standing (0002)-oriented GaN substrates (ϕ = 2") were coated with ~200 nm of ZnO and used as templates for the growth of GaN thin films. SEM and AFM revealed that the GaN films had a relatively homogenous surface morphology with an RMS roughness (5 µm x 5 µm) of less than 4nm. XRD studies revealed compressively strained ZnO growth on the GaN substrates and the reproduction of the substrate rocking curve for the GaN overlayers, after only a hundred nm of growth (indicating that the GaN films had superior crystallographic quality compared to those grown on sapphire or ZnO/sapphire substrates). Quarter-wafer areas of GaN were then lifted off from the GaN substrate by selective chemical etching of the ZnO in dilute HCl. The expensive GaN substrates were then reclaimed/reused (without the need for polishing) in a second cycle of ZnO and GaN growth, which gave similar XRD, SEM, CL and AFM results to the first cycle.

Using the above approach, the GaN substrate is not consumed in the production process (Fig. 12) and the substrate costs per growth run can potentially be compressed to industrially-viable levels as a result of being divided over multiple fabrication cycles. This is a very attractive perspective because the expected result of substituting free-standing GaN substrates for non-native sapphire substrates is a breakthrough in output power per wafer and cost per lumen. There may even be the possibility of eliminating LED efficiency droop at higher injection currents through the adoption of non-polar GaN substrate orientations.

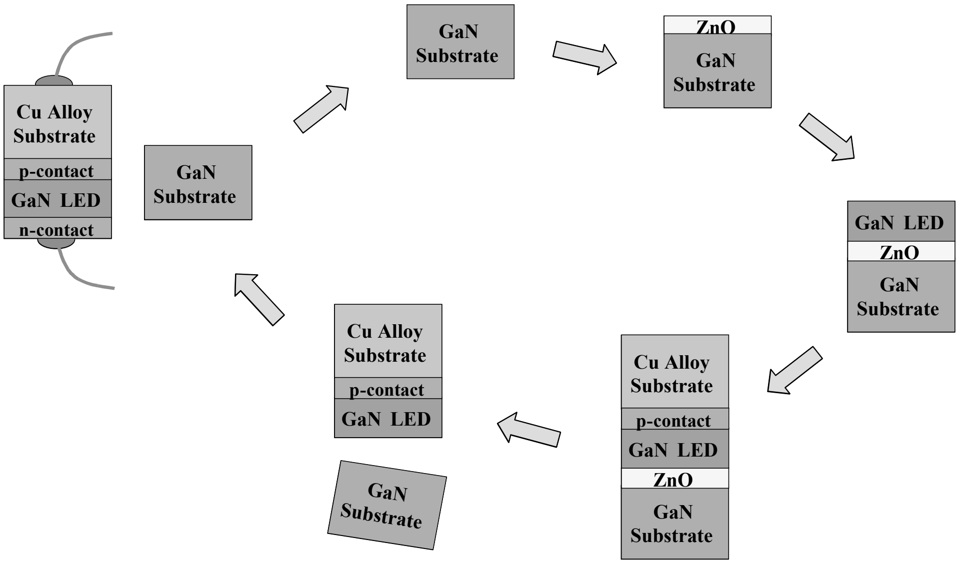

Figure 12: Process flow illustrating a potential chemical lift-off and GaN substrate multiple reclaim cycle for the development of novel devices such as vertical LEDs.

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