# Scale-up of the Chemical Lift-off of (In)GaN-based p-i-n Junctions from Sapphire Substrates Using Sacrificial ZnO Template Layers

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## ABSTRACT

(In)GaN p-i-n structures were grown by MOVPE on both GaN- and ZnO-coated c-sapphire substrates. XRD studies of the as-grown layers revealed that a strongly c-axis oriented wurtzite crystal structure was obtained on both templates and that there was a slight compressive strain in the ZnO underlayer which increased after GaN overgrowth. The InGaN peak position gave an estimate of 13.6at% for the indium content in the active layer. SEM and AFM revealed that the top surface morphologies were similar for both substrates, with an RMS roughness (5 μm x 5 μm) of about 10 nm. Granularity appeared slightly coarser (40nm for the device grown on ZnO vs 30nm for the device grown on the GaN template) however. CL revealed a weaker GaN near band edge UV emission peak and a stronger broad defect-related visible emission band for the structure grown on the GaN template. Only a strong ZnO NBE UV emission was observed for the sample grown on the ZnO template. Quarter-wafer chemical lift-off (CLO) of the InGaN-based p-i-n structures from the sapphire substrate was achieved by temporary-bonding the GaN surface to rigid glass support with wax and then selectively dissolving the ZnO in 0.1M HCl. XRD studies revealed that the epitaxial nature and strong preferential c-axis orientation of the layers had been maintained after lift-off. This demonstration of CLO scale-up, without compromising the crystallographic integrity of the (In)GaN p-i-n structure opens up the perspective of transferring GaN based devices off of sapphire substrates industrially.

Keywords: (In)GaN p-i-n, ZnO, photovoltaic, LED, chemical lift-off, scale-up, substrate
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## 1. INTRODUCTION

Gallium Nitride (GaN) is a direct wide bandgap material which can be engineered into the ultraviolet (UV) range through alloying with Aluminium (i.e. AlGaN) and into the visible range through alloying with Indium (i.e. InGaN) [1]. Since the development of p-type GaN in the 1990s [2,3] a huge range of AlInGaN-based p-n junction devices has emerged, including light emitting diodes (LEDs) [4], laser diodes, high power/frequency electronics, photodetectors and, more recently, third generation photovoltaics (PV) [5]. Commercial production of such devices usually employs alternative substrates (such as c-sapphire or 6H-SiC) because native GaN substrates with appropriate cost/quality/size are not currently available in industrial quantities. Such non-native substrates bring constraints, however, including significant crystal lattice mismatch, differences in thermal expansion coefficients, poor thermal/electrical conductivity, rigidity, limited size and high cost levels compared with competing materials systems. These constraints severely impact the cost/performance profile of the final devices. Currently, therefore, there is considerable interest in the transfer of InGaN based junctions to alternative substrates. This could be, for instance, metal alloys for LEDs (so as to form vertical device structures with superior current distribution and thermal management [6]) or soda-lime glass substrates for PV (so as to keep cost levels low). In industry, this is currently achieved by means of laser lift-off [7]. In previous studies the authors reported how a less onerous chemical lift-off (CLO) approach, could be used to lift GaN thin films off of sapphire [8,9], silicon [10] and GaN [11] substrates. This method is based on sacrificial Zinc Oxide (ZnO) underlayers. ZnO is much more susceptible to chemical etching than GaN so it can be preferentially dissolved and act as release layers for the GaN. In this way transfer of GaN [12,13] (and a few mm² of a full p-GaN/i-InGaN/n-GaN structure [14]) from sapphire to a low cost soda lime glass by means was demonstrated. Subsequently, a modified CLO procedure,

which allowed the scale-up to quarter [11] and full wafer scale [16] for GaN thin film CLO, was developed. This study explores the feasibility of similar scaling-up of chemical lift-off for full (In)GaN-based p-i-n junctions.

## 2. EXPERIMENT

(In)GaN p-i-n structures were grown by MOVPE on both GaN- and ZnO-coated c-sapphire substrates. The GaN was a commercial template provided by Lumilog and the ZnO template was grown using pulsed laser deposition (PLD) from a sintered 5N target in a molecular oxygen ambient with a 248nm KrF excimer laser, as described elsewhere [16]. The GaN p-i-n MOVPE growth procedure was adapted in order to avoid the dissociation of ZnO commonly observed during conventional GaN MOVPE [17,18]. This was achieved by introducing dimethylhydrazine (DMHY) as an N source and $N_2$ as a carrier gas, as described elsewhere [9,13,19]. Figure 1 shows a schematic of the (In)GaN p-i-n structure with the nominal thicknesses, compositions and carrier concentrations.

| P+ GaN contact layer | 50 nm, $7e19cm^{-3}$ | P+ GaN contact layer |
|---|---|---|
| p-GaN | 200nm, $1e19cm^{-3}$ | p-GaN |
| GaN- NID | 30 nm | GaN- NID |
| 20 nm InGaN | 20nm, nominally 18% In | 20 nm InGaN |
| GaN- NID | 30 nm | GaN- NID |
| GaN:Si regrowth buffer | 200nm | GaN:Si regrowth buffer |
| ZnO | | GaN |
| c- sapphire | | c-sapphire |

Figure 1. A schematic of the GaN p-i-n structure grown on the ZnO and GaN buffered c-sapphire substrate (NID = non-intentionally doped).

The InGaN-based p-i-n structures were temporary-bonded onto glass supports using Apiezon W wax and then lifted off the sapphire substrate by preferential chemical etching away of the ZnO interlayer in 0.1M hydrochloric acid (HCl), as illustrated in figure 2.
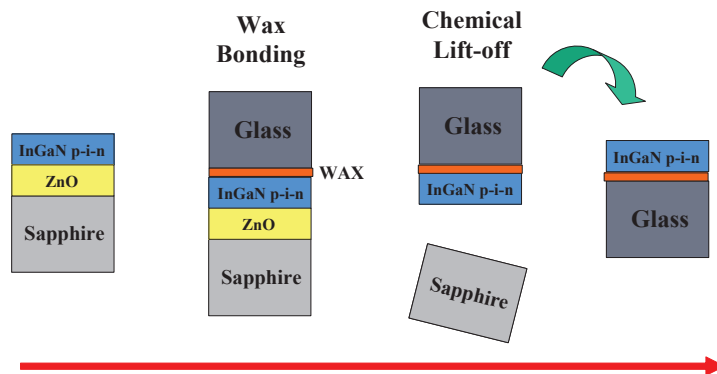


Figure 2. Illustration of the chemical lift-off process flow.

In this process, the ZnO interlayer plays two roles. It acts first as a crystallographic template for GaN epitaxial growth and second as a sacrificial release layer, which is selectively chemically etched (in an acid or alkali) so as to separate the GaN from the sapphire substrate. The glass substrate in this case is a temporary host, with the role of maintaining the integrity of the GaN layer by rigidifying the wax. Previous attempts at lift-off using only a wax support proved difficult to scale up because the flexible nature of the wax allowed the strain in the GaN to relax and cause cracking.

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

XRD studies of the ZnO template layer grown on c-sapphire by PLD revealed peaks characteristic of wurtzite ZnO. Figure 3 shows the XRD 2θ/ω scan and ω rocking curve for the (0002) peak.
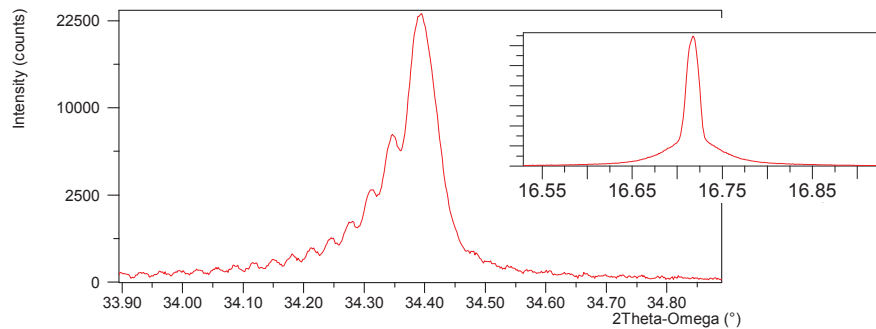


Figure 3. XRD 2θ/ω 2θ/ω scan and ω rocking curve (inset) for the (0002) peak of the ZnO layer grown on c-sapphire.

The 2θ/ω peak position corresponds to a c lattice parameter of 5.211 Å (compared to a value of 5.206 Å for equilibrium wurtzite ZnO). This suggests that the ZnO was under slight compressive strain in the film plane. The peak also shows Pendellösung fringes, which indicate that the film had a relatively smooth surface over the scale of the XRD beam spot. The fringe spacing corresponds to a film thickness of ~280 nm. The ω rocking curve has a linewidth of 0.018°, which corresponds to a very strong preferential c-axis orientation along the growth direction. Figure 4 shows the XRD 2θ/ω scans for the (0002) peaks of the (In)GaN p-i-n structure grown on both ZnO/c-sapphire and GaN/c-sapphire.
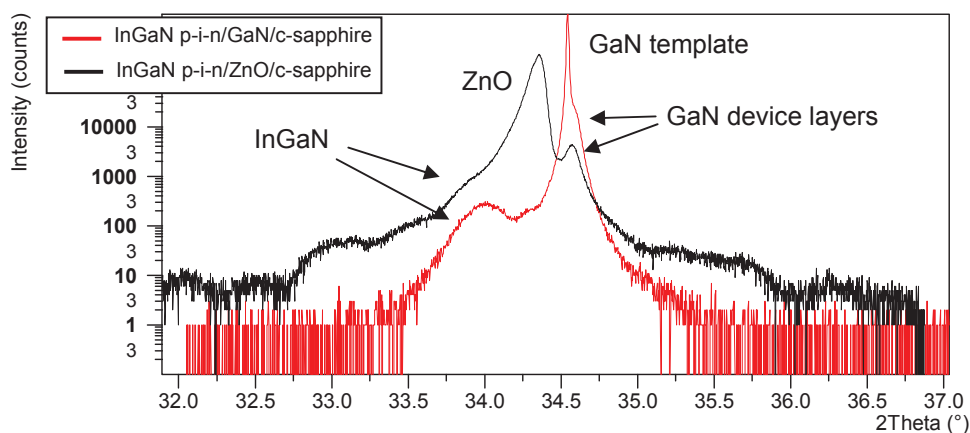


Figure 4. XRD 2θ/ω scans for the (In)GaN p-i-n structure grown on both ZnO/c-sapphire and GaN/c-sapphire.

The presence of ZnO, InGaN, GaN template and GaN device layer peaks can all be distinguished in the scans. The peaks do not show the Pendellösung fringes that were present in the scan for ZnO prior to GaN overgrowth, which suggests that surface roughness increased. The ZnO peak position corresponds to c lattice parameter of 5.216 Å. This indicates that the ZnO was under more compressive strain in the film plane than prior to the GaN growth. The GaN template peak corresponds to a c lattice parameter of 5.189 Å, which is close to the value of 5.186 Å typically expected for equilibrium wurtzite GaN. The peak position for the GaN device layers grown on the ZnO buffer layer corresponds to a c lattice parameter of 5.184 Å. The c lattice parameter for the GaN film grown on the GaN template appears quite similar but cannot be given precisely because the peak maximum is obscured by the tail of the neighboring GaN template peak. The peak position for the InGaN thin film grown on the GaN template layer corresponds to a c lattice parameter of 5.269 Å, which can be correlated to an indium content of ~ 13.6 at% in the active region of the device [20]. The c lattice parameter for the InGaN grown on the ZnO template appears quite similar but cannot be given precisely because the peak maximum is obscured by tail of the neighboring ZnO template peak.

Figure 5 shows SEM images of the structure grown on both the GaN and ZnO templates.
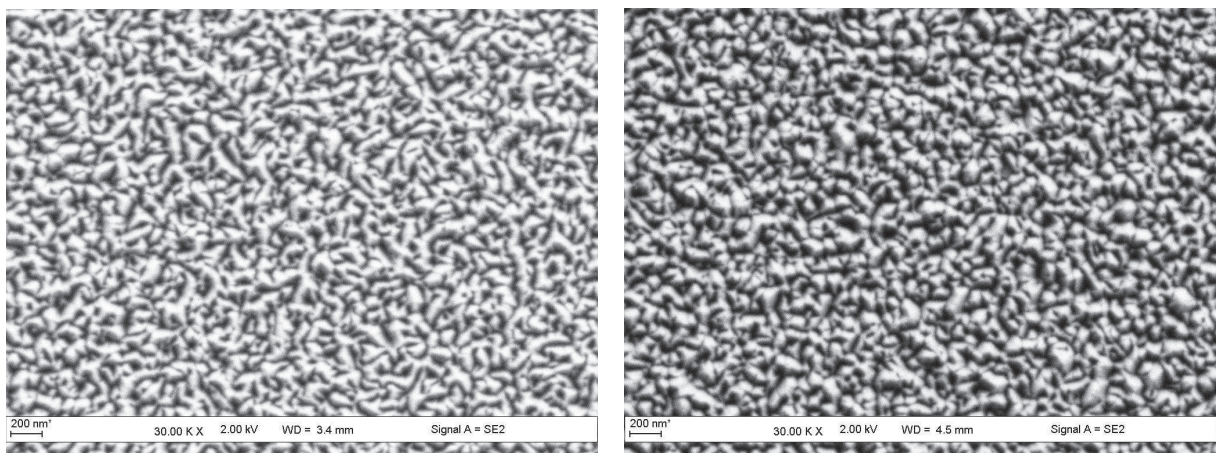


Figure 5: SEM images of the surface of the GaN p-i-n structure on both the GaN (LHS) and ZnO (RHS) templates.

The SEM images are comparable for both templates.
Figure 6 shows AFM images of the surface of the GaN p-i-n structure on both the GaN and ZnO templates.
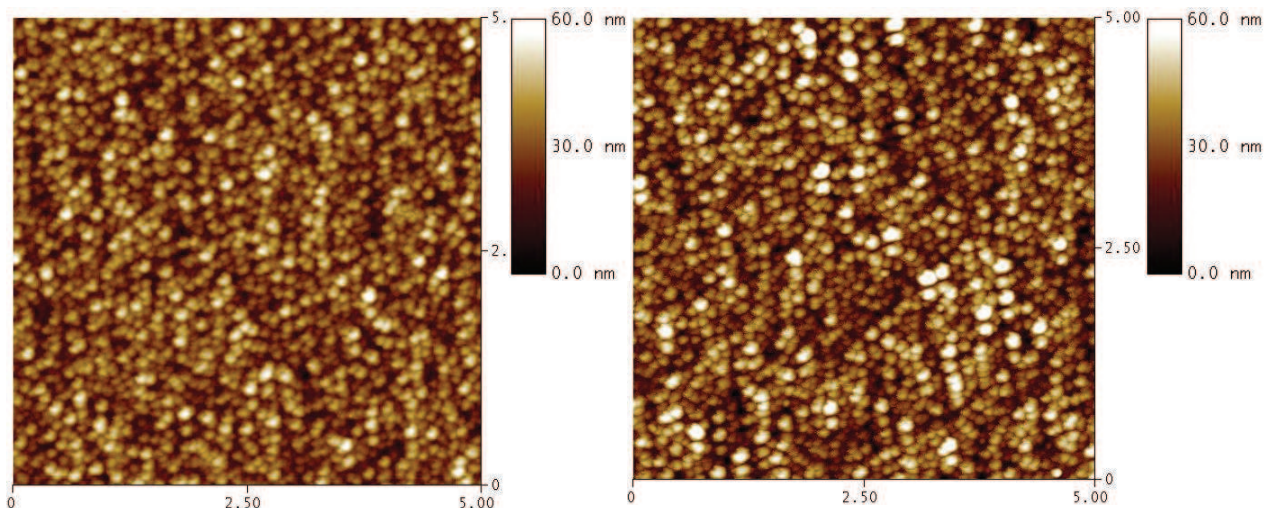


Figure 6 AFM images of the surface of the GaN p-i-n structure on both the GaN (LHS) and ZnO (RHS) templates.

The AFM images for the growths on the GaN and ZnO templates are relatively similar with root mean square (RMS) roughnesses (over areas of 5μm x 5μm) of 9 and 11 nm, respectively. This level of roughness is consistent with the lack of Pendellösung fringes in the XRD 2θ/ω scans. The AFM images also reveal that granularity is larger for the ZnO-templated sample, with a mean of ~40nm for the ZnO-templated sample vs ~30nm for the GaN templated sample.

Figure 7 shows CL spectra for the GaN p-i-n structure on both the GaN and ZnO templates.
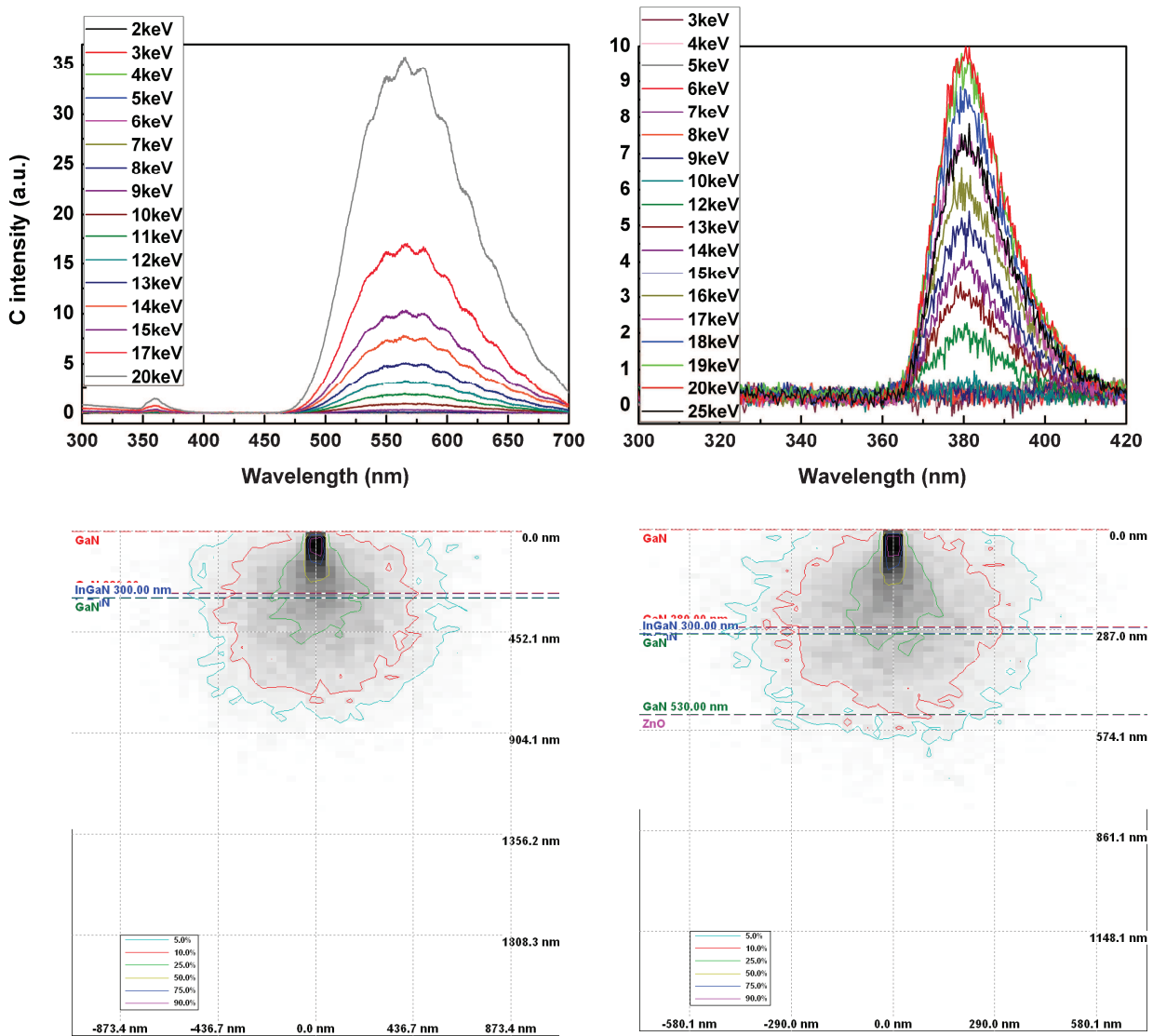


Figure 7 CL spectra (and Monte Carlo simulations at 12kV) for the GaN p-i-n structure on both the GaN (LHS) and ZnO (RHS) templates.

A relatively small GaN near band edge (NBE) UV emission peak and a broad defect-related visible emission band are observed for the structure grown on the GaN template . A strong ZnO NBE UV emission is observed for the sample grown on the ZnO template. The lack of a GaN signature is typical for samples grown on ZnO and has been linked to preferential carrier recombination in the ZnO because of the smaller bandgap compared with the GaN [8].

Figure 8 shows a schematic, plus corresponding photographs, of the chemical lift-off progressing across a quarter-wafer of the GaN p-i-n CLO for the ZnO-templated sample.
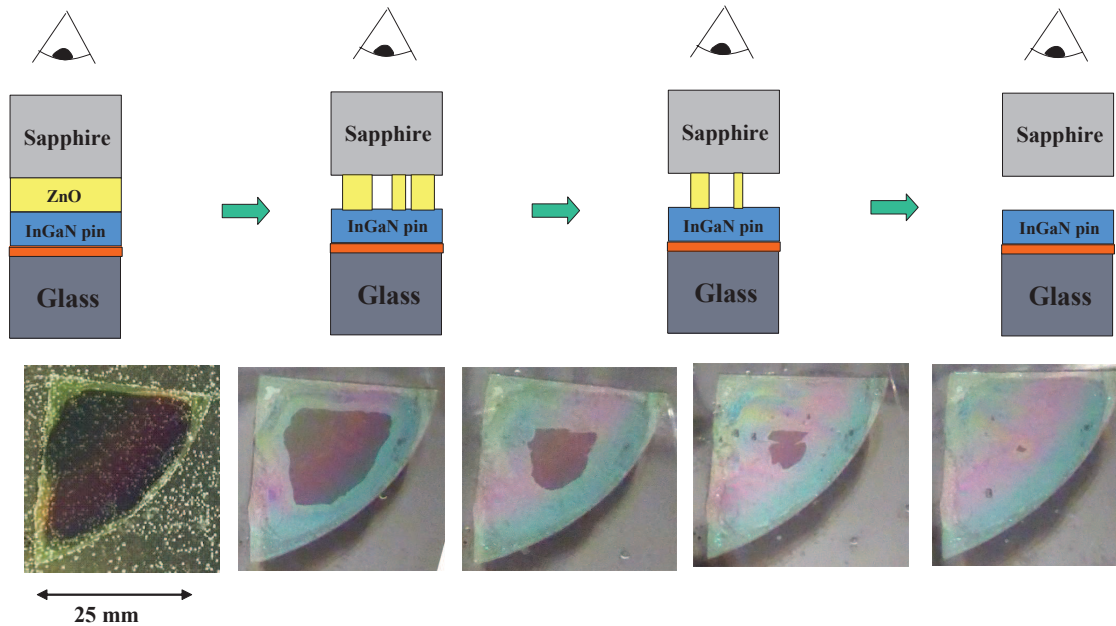


Figure 8. A schematic plus the corresponding photographs of the etching progress for the GaN p-i-n CLO from sapphire.

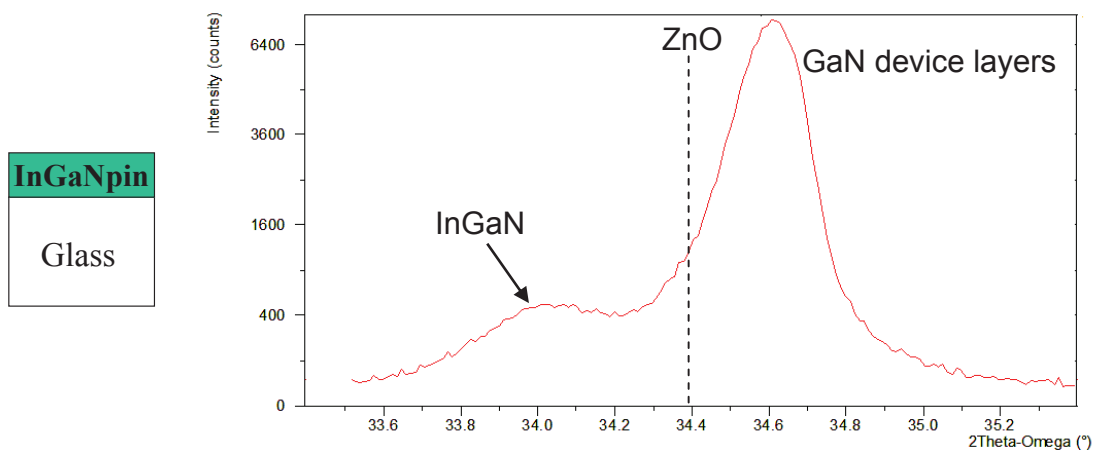Figure 9 shows the XRD 2θ/ω scan for the (0002) peak after CLO of the GaN p-i-n structure.



Figure 9 XRD 2θ/ω scans after CLO of the GaN p-i-n structure (with the position for the (absent) ZnO (0002) peak indicated).

After CLO the ZnO peak (which was the strongest prior to lift-off (see Fig. 4)) is no longer present and the InGaN peak position can now be properly discerned. A corresponding c lattice parameter of 5.269 Å can hence be estimated. This is comparable to that measured for the InGaN on the GaN template and thus also matches to an indium content of ~ 13.6 at% in the active region.

Omega rocking curve linewidths for the (0002) peak were ~1.1° and 1.5°, respectively, before and after the chemical lift-off. The slight increase could be due to some imperfect bonding to the temporary host at the edge of the sample.

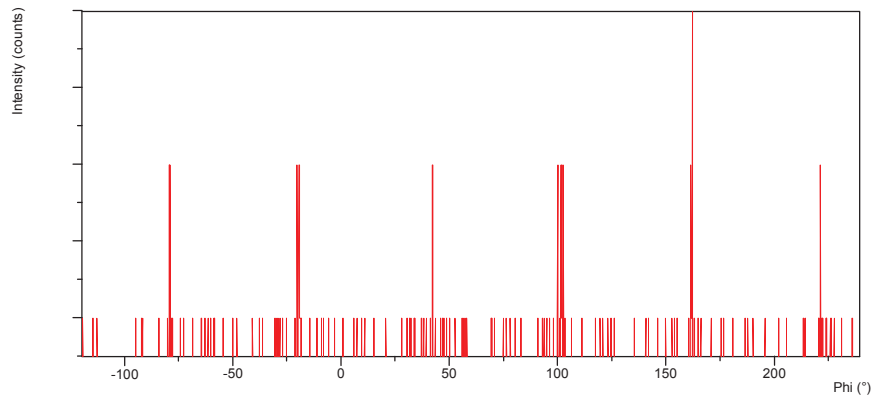Figure 10 shows the (112) phi scan for the (In)GaN p-i-n after CLO.



Figure 10 (112) phi scan for the (In)GaN p-i-n structure after CLO

The figure shows a single set of 6 peaks with a spacing of 60°, which is characteristic of wurtzite 6 fold symmetry. This implies (a) that there was epitaxy of the (In)GaN on the ZnO template and (b) that the integrity of the structure had been maintained after the lift-off process.


# 4. CONCLUSIONS


(In)GaN p-i-n structures were grown by MOVPE on both GaN- and ZnO-coated c-sapphire substrates without any evidence of ZnO back-etching. XRD studies of the as-grown layers revealed that a strongly c-axis oriented wurtzite crystal structure was obtained on both templates and that there was a slight compressive strain in the ZnO underlayer which increased after GaN overgrowth. The InGaN peak position for the growth on the GaN template gave an estimate of a 13.6at% indium content in the active layer. SEM and AFM revealed that the top surface morphologies were similar for both substrates with an RMS roughness (5 μm x 5 μm) of about 10 nm. Granularity appeared slightly coarser for the device grown on ZnO, however (40nm for the device grown on ZnO vs 30nm for the device grown on the GaN template). CL revealed a weaker GaN NBE UV emission peak and a stronger broad defect-related visible emission band for the structure grown on the GaN template. Only a strong ZnO NBE UV emission was observed for the sample grown on the ZnO template. The lack of a GaN optical signature typical for samples grown on ZnO and has been linked to preferential carrier recombination in the ZnO because of the smaller bandgap compared with the GaN.

The rigidification of the apiezon W wax host by bonding to a glass support allowed demonstration of successful quarter-wafer CLO of the InGaN-based p-i-n structures from the sapphire substrate without cracking or curling by selectively dissolving the ZnO in 0.1M HCl. XRD studies conducted after the CLO revealed that both the epitaxial nature and the strong preferential c-axis orientation of the layers had been maintained. The lattice parameters for the GaN and InGaN peaks were similar to those observed for growth on GaN templates and the scans no longer showed any trace of ZnO such that the InGaN peak position could be clearly discerned. The corresponding c lattice parameter of 5.269 Å is comparable to that measured for the InGaN on the GaN template and thus also matches to an indium content of ~ 13.6 at% in the active region. Omega rocking curve linewidths for the (0002) peak were ~1.1° and 1.5°, respectively, before and after the CLO. The slight increase could be due to some imperfect bonding to the temporary host at the edge of the sample. This demonstration of CLO scale-up without compromising the crystallographic integrity of the (In)GaN p-i-n structure opens up the perspective of transferring GaN based devices off of sapphire substrates industrially.
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# ACKNOWLEDGEMENTS

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