

## ZnO Thin Film Templates for GaN-based Devices

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### ABSTRACT

GaN-based optoelectronic devices are plagued by a tendency to non-radiative transitions linked to defects in the active layers. This problem has its origin in a) intrinsic factors such as GaN's relatively low exciton binding energy (~24meV) and b) extrinsic factors including the poor availability of native substrates good enough to significantly suppress the defect density. Indeed, the 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 development of bulk GaN substrates of suitable quality has proven very difficult, a considerable amount of effort is also being directed towards the development of alternative substrates which offer advantages compared to those in widespread use (c-sapphire and 6H SiC). 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 paper, we discuss use of ZnO thin films as templates for GaN-based LEDs.

### 1. INTRODUCTION

The need for blue and UV solid-state emitters and detectors has propelled the investigation of wide bandgap semiconducting materials in recent years. Commercial applications typically include blue/UV LEDs for signage and lighting plus blue/UV lasers for data storage. Most of the materials development for these applications has centered around GaN (band gap~ 3.5 eV) , ZnSe (~2.9 eV), and 6H-SiC (~3.0 eV), with GaN and GaN-based alloys emerging as the clear winners, because SiC does not produce a sufficiently bright emitter and ZnSe is subject to defect formation under high current drive.

The development of GaN devices is currently hampered by the lack of suitable transparent lattice- and thermal-matching single crystal substrates. Hence, GaN has been grown on a variety of substrates, with most of the work being done using c-sapphire and 6H-silicon carbide. Each of these substrates offers advantages and drawbacks. 6H-SiC is conducting, but relatively costly. C-sapphire is relatively cheap and transparent, but it is electrically insulating. Moreover, the lattice match between GaN and both of these substrates generates strain in the epilayers: in the case of c-sapphire, there is compressive strain, whereas, in the case of 6H-SiC, there is tensile strain.

Another potential candidate for use as a GaN substrate is ZnO. Indeed, comparison of the crystalline properties of GaN and ZnO (as shown in Table I) suggests that the fit would appear better than c-sapphire or 6H-SiC. Besides having the same wurtzite structure, GaN and ZnO also have very small lattice mismatch and the same stacking order. For these reasons, stacking mismatch boundaries and inversion domain boundaries should not occur in GaN grown on ZnO. Furthermore, c-axis GaN/ZnO shows a much reduced mismatch in thermal expansion coefficient compared with GaN/6H-SiC or GaN/c-sapphire. Other key characteristics of ZnO, which predispose it for use as a GaN substrate, are its high transparency over the visible spectrum, its electrical conductivity and its amenability to chemical etching, which would allow selective removal of the substrate.

In view of the above it might now be asked why ZnO has not been widely adopted for use as a substrate for GaN. There are 3 main reasons for this:

1) high quality wide-area ZnO substrates have not been available in large volumes at a competitive price level.

2) the ammonia commonly used in Ga nitridation processes attacks the ZnO layer at temperatures over about 650C. Since GaN layers are typically grown at over 1000 C this is problematic.

3) ZnO evaporates in nitrogen ambient at temperatures over about 900 C. This conflicts with the high temperature bake under nitrogen commonly employed in GaN growth.

The first problem is now being resolved through developments in the quality of ZnO layers grown on sapphire such as those proposed by Nanovation. The second and third problems can be combated by avoiding a high temperature bake in nitrogen ambient at the start of growth and by commencing the GaN growth with a buffer layer at about 600 C before ramping up to over a 1000 C (see figure 1).

Formula	Name	Symetry	Point group	Space group	Stacking sequence (Wyckoff)	Lattice constant (Å)	Plane with nearest match to (0001) GaN	Effective a lattice constant (Å)	$\Delta a/a$ with GaN
GaN	Gallium nitride	Hexagonal	6 mm	P6 <sub>3</sub> mc(186)	AB (HH)	a=3.1891 c=5.1855	(0001)	3.1891	0%
6H-SiC	6H silicon carbide	Hexagonal	6 mm	P6 <sub>3</sub> mc (186)	ABCACB (CCHCCH)	a=3.081 c=15.117	(0001)	3.081	3.51%
Al <sub>2</sub> O <sub>3</sub>	Sapphire, corundum	Trigonal	$\bar{3}m$	R $\bar{3}C$ (167)		a=4.758 c=12.991	(0001) rotated 30°	2.747	16.09%
ZnO	Zinc oxide	Hexagonal	6 mm	P6 <sub>3</sub> mc (186)	AB (HH)	a=3.253 c=5.213	(0001)	3.253	-1.97%

Table 1: Comparison of crystal structures of GaN, 6H-SiC, c-Al<sub>2</sub>O<sub>3</sub> & ZnO (adapted from ref 1).

A reasonable number of groups have already worked on the growth of GaN on ZnO buffer layers using a wide variety of deposition techniques and a wide variety of substrates (1-7).

Even though most of the GaN growths were performed on ZnO layers with relatively low crystal quality, there was a general consensus that use of a ZnO buffer layer leads to improvements in GaN film characteristics including crystallography, surface morphology, defect density, electrical properties, band structure & cracking.

Paradoxically, however, it was uniformly observed that the ZnO layer had evaporated, in spite of the use of a low substrate temperature during the initial stages of GaN growth.

The lack of a conclusive explanation for this paradox seems to have obscured the beneficial role of ZnO and hence hindered the adoption of ZnO as a buffer for GaN.

Furthermore, to the best of our knowledge, there has been no previous report of a GaN device made using a ZnO buffer layer.

In this work we report on our first demonstration of a GaN LED using a ZnO buffer layer as a template.

## 2. EXPERIMENT

ZnO thin films were grown in a home-made laser deposition system using a Coherent KrF excimer laser (248nm). During growth, pulse repetition rate was varied between 1 and 50 Hz. The laser spot was focused on high purity target to give a fluence of up to about 4 J/cm<sup>2</sup>.

High purity molecular oxygen (O<sub>2</sub>) was introduced for the growth. O<sub>2</sub> pressure during film growth was studied over the range between 10<sup>-6</sup> and 10<sup>-3</sup> Torr.

GaN films were grown using a horizontal flow low-pressure MOCVD reactor at Northwestern University. Details of the growth procedure as well as the LED processing steps are given elsewhere. Of note is the fact that no "low temperature" GaN buffer layer was used and no particular adaptation of the growth procedure was made for the presence of the ZnO buffer.

X-ray diffraction studies were conducted with a 4-circle Philips X-Pert MRD system.

Atomic Force Microscopy (AFM) was conducted in contact mode using a Park Scientific Autoprobe System.

### 3. RESULTS

#### 3.1 ZnO template layer

After optimizing each growth parameter, we were able to achieve ZnO thin films of relatively high crystal quality. Fig. 1a shows a typical  $\theta/2\theta$  scan. The relatively high intensity of the ZnO (0002) peak ( $\sim 34.4^\circ$ ) plus the narrow linewidth (220 arc.sec) indicate that the films were well crystallized and strongly c-axis oriented.

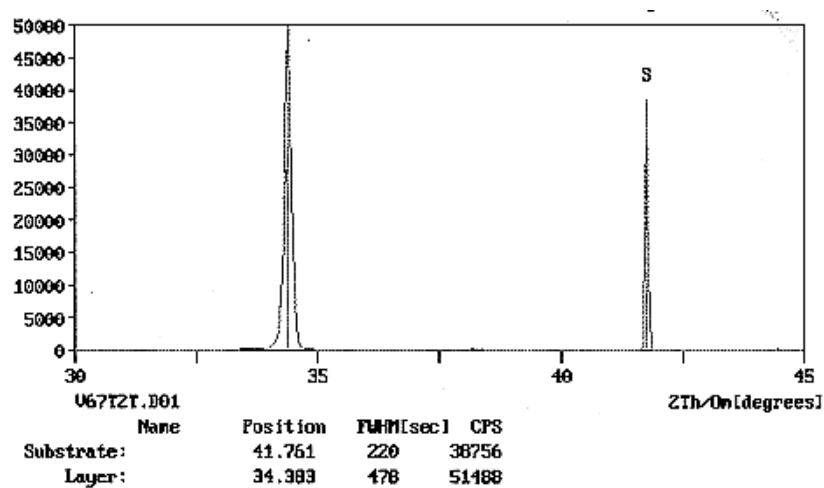


Fig.1a: X-ray diffraction  $\theta/2\theta$  X-ray diffraction spectrum of a typical ZnO thin film

The high crystal quality is confirmed by an omega rocking curve full-width-half-maximum of 240 arc.sec (Fig.1b) and a RMS surface roughness (over 4 square microns) of 7 angstroms (Fig.2).

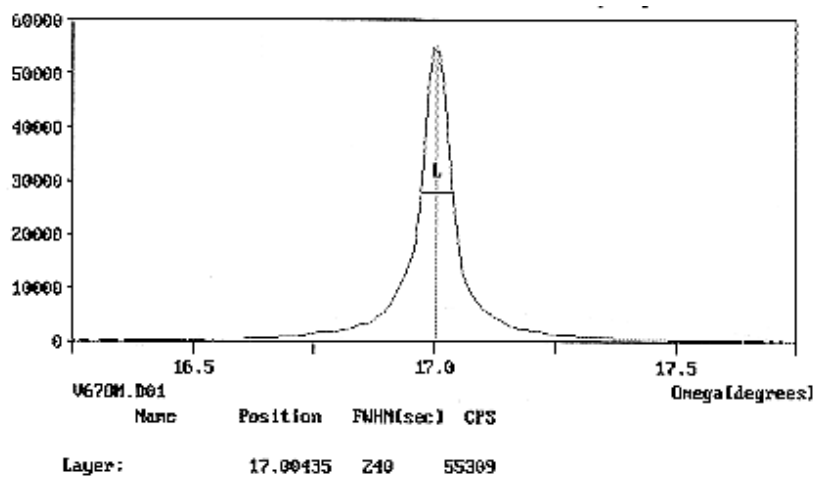


Figure 1b: X-ray diffraction rocking curve of (0002) peak of typical ZnO film

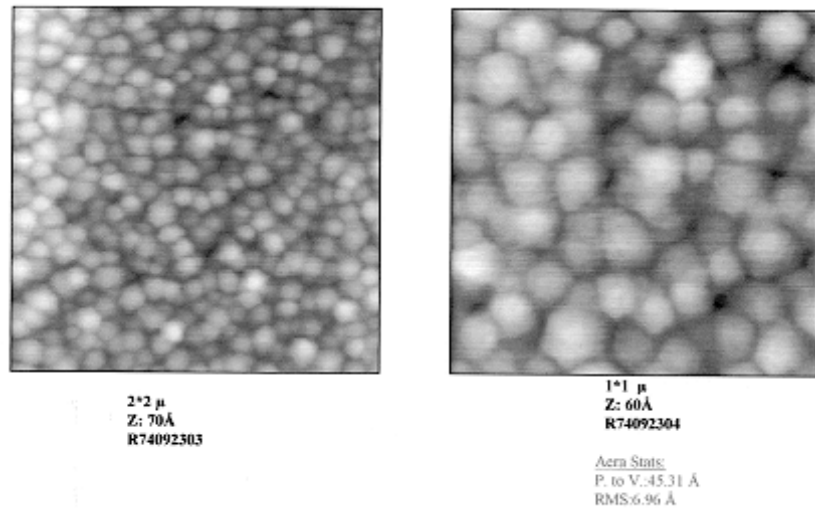


Figure 2 AFM contact mode images of typical ZnO film grown.

Film thickness was typically 70 to 100 nm and no evidence of particles was observed in AFM or Scanning Electron Microscope (SEM) images.

### 3.2 GaN based LED grown using ZnO template layer

The characteristics of the LED are shown below (Fig. 3). After device fabrication, no evidence of the ZnO layer was found, so it was assumed that it was dissolved during the GaN growth procedure.

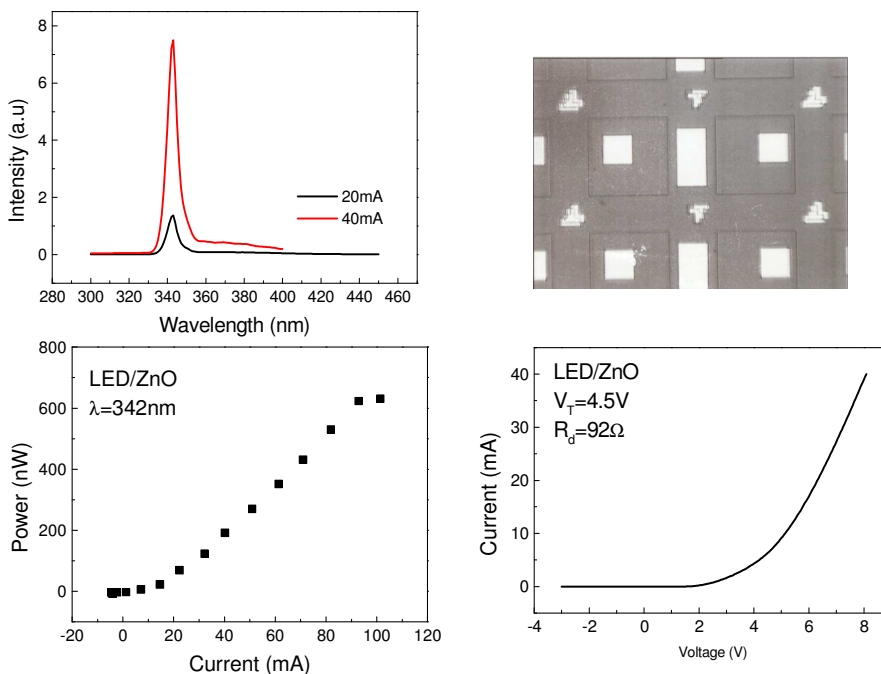


Figure 3: Characteristics of the GaN LED grown using a ZnO buffer layer on c-sapphire.

## 5. CONCLUSIONS

In this paper, we presented the results of a GaN based LED fabricated using epitaxial ZnO template layers. These results were obtained in 2002 with state-of-the-art ZnO layers on c-sapphire and a standard (non-optimised for ZnO) MOCVD recipe for the growth of GaN. To the best of our knowledge, this is the first report of a GaN LED grown using a ZnO buffer layer.

Subsequent literature review suggests that an improved device will be obtained if we employ

- a) a low temperature (<600C) stage at the start of the GaN growth
- b) higher quality ZnO layers.

Our subsequent work on ZnO has led to a breakthrough in the crystal quality of our ZnO layers which now have (0002) omega rocking curves better than an order of magnitude smaller which will facilitate superior quality next-generation GaN on ZnO.

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