GaN Epitaxy on Melt Grown Thermally Prepared Bulk ZnO Substrates

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GAN EPITAXY ON MELT GROWN THERMALLY PREPARED BULK ZNO SUBSTRATES

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Electrical Engineering at Virginia Commonwealth University

by

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December 2004
I would like to thank my advisor, Professor Hadis Morkoç, for offering me the opportunity to work in such a well-equipped research group. His continual insight, inspiration and guidance are greatly appreciated.

I am indebted to Professor Daniel Johnstone and Professor Martin Munoz, who gave me a lot of helpful suggestions in my thesis. I also benefit from the discussions with many group members, especially Prof. Michael Reschchikov, Dr. Umit Ozgur, Dr. Norio Onojima and Dr. Vitaly Avrutin. Special thanks is given to Mr. Jeff Nause of Cermet Inc., who provided us with the bulk ZnO substrates.

I am especially grateful to my friends and co-workers, including Dr. Feng Yun, Dr. Chunli Liu, Dr. Yong-Tae Moon, Mr. Jinqiao Xie, Mr. Yun Zhang, Mr. Bo Xiao, Mr. Yi Fu, Ms. Lei He, and Mr. Steve Puntigan.

Finally, I would like to thank my parents for their selfless love and understanding, not to mention their support and encouragement.
# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ...........................................................................................................ii

ABSTRACT ..............................................................................................................................v

CHAPTER 1 Introduction ........................................................................................................1

Chapter 2 Preparation of ZnO substrate for epitaxy .............................................................5

2.1 Introduction.....................................................................................................................5

2.2 Thermal treatment of bulk ZnO substrate.....................................................................6

2.2.2 Experimental procedures.......................................................................................10

2.2.3 Results and discussion...........................................................................................11

2.3 Forming Gas annealing ...............................................................................................21

Chapter 3 Epitaxy of GaN on bulk ZnO substrate ...............................................................27

3.1 Introduction.....................................................................................................................27

3.2 Epitaxy of GaN on ZnO by RF nitrogen enhanced plasma ........................................30

3.3 Epitaxy of GaN on ZnO by ammonia .........................................................................37
3.4 Discussions ..............................................................................................................42

Chapter 4  The outlook of the GaN/ZnO based devices..............................................49

4.1 Potential application of GaN/ZnO based LEDs .......................................................50

4.2 Potential applications of AlGaN/GaN MODFETs on ZnO substrates ....................57

List of References.............................................................................................................64
ABSTRACT

GAN EPITAXY ON MELT GROWN THERMALLY PREPARED

BULK ZNO SUBSTRATES

By Xing GU, Master of Science

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Electrical Engineering at Virginia Commonwealth University

Virginia Commonwealth University, 2004

Major Director: Dr. Hadis Morkoç, Founders Professor in Department of Electrical Engineering and Physics Department

Different methods were developed for the preparation of bulk ZnO substrates. Remarkable improvement on the surface, optical and crystalline quality of the bulk ZnO substrate was achieved. ZnO substrates with an atomically flat surface exhibiting terrace-like features were used as a substrate for GaN grown by MBE. High-resolution x-ray diffraction and low temperature PL results show that similar high quality GaN layers can
be achieved on both annealed O-face and Zn-face ZnO substrates. The prospect of the
device applications of GaN epitaxy on ZnO, including AlGaN/GaN MODFET structure
on ZnO and GAN/ZnO based p-n junction were discussed.
CHAPTER 1
INTRODUCTION

Wide band-gap semiconductors such as those based on GaN and SiC have come to
the forefront in the past decade because of an increasing need for short wavelength
photonic devices and high-power, high-frequency electronic devices\(^1\). Another wide
band-gap semiconductor, ZnO, has also received extensive attention recently as a
candidate material for opto-electronic devices such as UV laser diodes and UV light
emitting diodes, mainly due to its relatively large exciton binding energy (60 meV)
compared with GaN (24 meV) and ZnSe (19 meV) and availability of high quality
substrates, which make ZnO a highly efficient photon emitter.

Many of the major problems which have hindered the progress in GaN and related
semiconductors can be traced to the lack of a suitable substrate material. Native GaN
substrates are still not available, mainly due to the large vapor pressure of N on GaN
coupled with a low solubility of N in the molten metal at reasonable temperatures and
pressures\(^2\). Conventionally GaN has been grown on sapphire and SiC, but both of them
suffered from its intrinsic shortcomings: Sapphire possesses neither a close lattice nor thermal match with GaN, the stresses created by these mismatches cause fractures that can make the GaN active region useless. Moreover, since sapphire is not conductive, the electrical contact cannot be placed at the bottom of the device until the very costly step of etching through sapphire is performed. In the SiC case the lattice and thermal mismatch with GaN is smaller, but the match is still not perfect due to the different stacking order with GaN, which make structural defects such as Inversion Domain Boundaries (IDB), Stacking Mismatch Boundaries (SMB) inevitable. Another consideration is that SiC is extremely expensive to produce.

Therefore, alternative substrates such as GaAs, Si, ZnO, LiGaO₂, MgAl₂O₄, MgO has been used for GaN epitaxy, among which ZnO is being considered as one of the most promising one. That’s because of the stacking order match and close lattice match between the GaN and ZnO. Due to the lack of large area and affordable GaN bulk substrates, ZnO remains the only isomorphic substrate for GaN epitaxy. Device design also can be relatively simple because ZnO substrates are usually conductive allowing vertical electrical injection in potential LEDs and lasers. Moreover, the integration of II-VI and III-V semiconductors into a single hetero-junction device enables the exploitation
of the many similarities and differences in the material properties (energy bandgap, dielectric constant, etc.) to create new devices exhibiting unique optical and electronic properties. The combination of GaN and ZnO would be particularly interesting since these materials share a lot of similar properties\textsuperscript{3,4}.

The research of GaN epitaxy on ZnO has been performed with mixed success. Pioneered research on GaN epitaxy on ZnO substrate suffered from a string of failed records.\textsuperscript{5,6,7} E.S.Hellman \textit{et.al.} worked on the GaN epitaxy on ZnO via molecular beam epitaxy (MBE) with both Zn-face and O-face in the same run. GaN layer has been grown with relative poor quality as identified by X-ray diffraction and photoluminescence (PL) measurement. Severe reaction between Ga and ZnO substrate is prominent as indicated from the Ga$_2$ZnO$_4$ peak from the X-ray 2theta-omega scan. Pessimistic conclusion was drawn by the report, mainly due to the thermal and chemical instability of the ZnO substrate.

It was in 1997 that Hamdani\textsuperscript{8} \textit{et.al.} made the first successful growth of GaN on ZnO substrate via reactive ammonia MBE. High quality of GaN has been confirmed from optical measurement. Another investigation on the effect of buffer layer from the same group\textsuperscript{9} indicated that In$_{0.2}$Ga$_{0.8}$N buffer improve the GaN epitaxy layer quality further,
probably due to a better lattice match. One major obstacle still remained is the poor preparation of the ZnO substrate, leaving a lot surface damages such as scratched induced from chemical mechanical polishing (CMP).

This work describes the development of GaN epitaxy on bulk, melt-grown ZnO substrates, with both oxygen-terminated (0001) direction (oxygen face), and zinc-terminated (0001) direction (zinc-face). The substrate preparation, epitaxial growth, and material characterization are explained. The combination of GaN/ZnO hetero-junction towards the device work is also covered.
CHAPTER 2

PREPARATION OF ZNO SUBSTRATE FOR EPITAXY

2.1 Introduction

The quality of the epitaxial layer depends not only on the growth conditions, but also on the substrate quality. Commonly, the surface of the commercial available substrates, i.e., sapphire, SiC and ZnO, contain a whole variety of defects that can disrupt the epitaxial layer growth and later be detrimental to device performance. The defects on the epitaxial layer, which can originate from both the bulk of the substrate and from the substrate preparation, need to be taken care of. While less effort could be expended to reduce the defects on the bulk substrate, we can control the substrate preparation to reduce the defects introduced from chemical polishing or cutting.

As the first step of the material growth, the substrate preparation deserves the extreme attention, since the mechanism of crystal growth is unambiguously determined by the structure of the substrate surfaces. In addition to a clean surface, a flat surface with
atomic steps is always desirable. The terrace surfaces are created by the vicinal atomic planes of the crystal lattice of the substrate. Two-dimensional (2D) nucleation may occur on the vicinal planes (the terraces) under proper growth conditions, where the flux of the constituent elements of the growing film is high enough to prohibit fast surface migration of the species adsorbed on the terraces. Therefore, the film may grow on the terraces in the layer-by-layer (Frank-van der Merwe mode) or layer plus island (Stranski–Krastanov mode) mode (if the strain energy of the film is high), which are preferable to the growers.

2.2 Thermal treatment of bulk ZnO substrate

2.2.1 Motivation of thermal treatment

Although being considered a promising substrate, and although mixed success have been achieved for GaN epitaxy on ZnO\textsuperscript{10,11,12,13,14}, the early studies employing ZnO as a substrate for GaN epitaxy suffered from the poor sample preparation of ZnO substrate\textsuperscript{10,11,12}. While mature pretreatment techniques have been established to remove the surface damage and produce terrace-like features for substrates such as sapphire\textsuperscript{15}, for a long time there has been no such established technique for ZnO substrate, with the
Figure 2.1 AFM image of as received O-face and Zn-face ZnO substrate
exception of one proprietary and complex mechanical polishing technique\textsuperscript{16}. The surface
damage on ZnO especially on O-face ZnO, shown in figure 2.1 (a), which is caused by
mechanical polishing needs to be removed in order to achieve highly efficient emission
from ZnO and high quality growth of GaN and its alloys. On the other hand, the Zn-face
ZnO is already very smooth as shown in figure 1(b), which is similar to the case of GaN
where Ga-polarity GaN tends to have a smoother surface, but still no terracing observed.

One difficulty in the ZnO surface preparation is that ZnO can react with both acid
and alkali rapidly, which makes a process based on wet chemical etching unlikely,
although it is widely employed in surface preparation of many other substrates. The
surface of O-face ZnO becomes rather rough only after 30 seconds etching in phosphoric
acid (85%), as shown in figure 2.2. The etching rate of Zn-face ZnO is much slower,
mainly attributed to the factor that the zinc face does not have unpaired electrons while
the oxygen face have, so that the Zn-face ZnO is not that chemically active as the O-face.
However, chemical etching can not help to improve the surface condition of the Zn-face
ZnO either.

While wet chemical etching process is difficult to be performed on ZnO substrates,
the thermal annealing process has shown that it can improve the surface condition by
Figure 2.2 AFM image of O-face ZnO substrate etched in phosphoric acid for 30 seconds.
itself. From literature it has been reported that annealing at some temperatures improves
the crystal quality and optical properties of ZnO layers grown on sapphire by MBE\textsuperscript{17} and
by MOCVD\textsuperscript{18,19}, and ZnO layers grown on silicon by reactive direct current sputtering
(DCS)\textsuperscript{20} and by RF magnetron sputtering\textsuperscript{21}. However, because spinel (ZnAl\textsubscript{2}O\textsubscript{4}) forms at
the interface between the sapphire substrate and the ZnO epitaxial layer during high
temperature annealing\textsuperscript{22}, and also Zn\textsubscript{2}SiO\textsubscript{4} with trigonal structure at temperatures higher
than 770\textdegree C on Si substrates\textsuperscript{20}, the annealing temperature is usually kept below 1000\textdegree C.
For ZnO bulk material used as substrates these constraints are not in effect and higher
temperature annealing can be employed even though prior belief had been that annealing
at temperatures above 800 \textdegree C would result in dissociation of the ZnO surface.

2.2.2 Experimental procedures

The ZnO substrates used were obtained from Cermet, Inc, both (0001) direction,
which is oxygen-terminated (oxygen face), and (0001) direction which is zinc-terminated
(zinc-face) were used. The details of the procedure employed are as follows: ZnO
substrates first underwent a chemical (solvent) cleaning procedure, in which the substrate
was cleaned in acetone using ultrasonic agitation for three minutes, followed by methanol,
again using ultrasonic agitation for three minutes, followed by a three minute rinse in
deionized water. The cleaned ZnO substrate was then placed in a programmable annealing furnace for annealing in atmosphere. Different annealing conditions were employed to converge on the optimum thermal treatment parameters. After the annealing process, ZnO was cleaned again using the wet cleaning procedure discussed above.

A Digital Instruments Dimension 3100 Atomic force microscope was employed to assess the surface morphology of the ZnO substrates before and after each thermal treatment. High-resolution X-ray diffraction (HRXRD) and low-temperature photoluminescence (LT-PL) were also employed to analyze the effect of high temperature annealing on the ZnO substrates.

2.2.3 Results and discussion

As we mentioned before, as-received O-face ZnO samples have surface damage such as scratches that must be removed prior to epitaxial growth. A series of annealing experiments have been done at different temperatures. AFM images of O-face ZnO annealed at 700°C, 800°C and 900°C for 1 hour are shown in figure 2.3. It is clear that with increasing annealing temperature, the surface domain size grew and the surface roughness improved from the 4.4nm of the as-received one to around 3 nm, but the
Figure 2.3 AFM images of O-face ZnO annealed for 1 hour at (a) 700°C (b) 800°C (c) 900°C
Figure 2.4 AFM images of O-face ZnO annealed for 1 hour at (a) 950°C (b) 1000°C
scratches still remained as those on the as received substrates. It seems that the ZnO molecules on the domain region migrate and make together at those annealing temperatures. However, higher annealing temperatures resulted in dramatic improvements.

Figure 2.4 shows AFM images of O-face ZnO annealed at (a) 950°C (b) 1000°C. The 950°C anneal temperature appears to be the threshold required to remove the scratches on ZnO. This can be explained by the fact that when annealed at high temperatures such as 950°C, enough thermal energy is given to the ZnO, and those ZnO molecules composing the domain area can therefore migrate a longer distance and move to a stable site to reduce the surface energy. Another plausible mechanism is the thermal decomposition of the ZnO domain region at high temperature, which can reduce the surface energy as well. Furthermore, ZnO annealed at 1050°C shows a terrace-like surface, which can facilitate smooth 2D growth and reduce column formation during the growth of GaN epilayers without the deleterious effects of a damaged substrate surface.

The results of different annealing times at 1050°C are shown in Figure 2.5. We can clearly observe that the terraces begin to form after 30 minutes. They coalesce and their
Figure 2.5 AFM images of O-face ZnO annealed at 1050°C for (a) 30 minutes (b) 1 hour (c) 2 hours (d) 3 hours
Figure 2.6 AFM images of Zn-face ZnO annealed at 1050$^\circ$C for 3 hours.
boundaries become straighter with increasing annealing time. Increasing the annealing
time to 3 hours results in the formation of straight and parallel terraces with a roughness
of only 0.6 nm. The height for the steps is around 0.5 nm, which corresponds to the
thickness of a ZnO bimonomer in [0001] direction. When the annealing temperature is
increased to 1100°C, the surface also becomes smooth, however no terrace-like surface
was observed.

The same trend is also clear for Zn-face ZnO substrates, which is already very
smooth (root mean square (rms)=0.12 nm). After annealing at 1050°C for 3 hours, the
surface roughness increased to the range of 0.5 nm, but the terrace-like features begin to
appear (Figure 2.6), which is indicative of a surface free of damage and is appropriate for
epitaxy.

HRXRD and LT-PL have also been employed to characterize the crystal and
optical quality of ZnO substrate before and after 1050°C annealing. Several observations
can be made. The multiple peaks appearing in the diffraction are attributed to small angle
grain boundaries present in the material. As the slit width for X-ray is reduced, the
number of peaks reduces, reaching just 2 for a slit width of 20 µm. (By reducing the scan
region, the number of small angle grain boundaries include in the scan region is reduces,
Figure 2.7 XRD rocking curve of ZnO (0002) reflection (O-face)
Figure 2.8 Comparison of 15K PL spectra of ZnO (O-face) substrate before and after annealing.
so only 2 peaks were observed.) By annealing at 1050 °C for 3 hours, the full width at half maximum (FWHM) of ZnO (0002) rocking curve has been reduced to 0.576 arcmin, from 1.302 arcmin before annealing, as shown in Figure 2.7. This improvement is speculated to be from increased dominance of the (0002) oriented ZnO grains, since it has the lowest surface energy\(^2\). Broadening from the strain at the interfaces between the (0002) grains and grains with other orientations may have been reduced with annealing as well.

In the LT-PL spectra a strong and sharp ZnO peak and its phonon replicas were found both before and after annealing (Figure 2.8). As in the case of the X-ray diffraction, the FWHM of ZnO exciton peak improved from 1.2 meV to 0.7 meV. However, a broad green band became evident after annealing. Two possibilities could be responsible for this: The first one is the out-diffusion of Hydrogen in ZnO during the high temperature annealing: Hydrogen which has been reported to passivate the radiative recombination centers giving rise to the green emission centered at 2.3eV\(^{24,25}\), will be removed from ZnO by annealing at a temperature of 700 °C or even lower\(^{26,27}\). This result is also in accordance with other optical research in ZnO which indicates that the hydrogen-related donors giving rise to the 3.364eV line in PL is thermally unstable and these donors will
be annealed out during the thermal process, leading to a reduction in the PL intensity\textsuperscript{28}. Another plausible reason is the formation of O-vacancy related complex, which introduces extra defects and therefore gives rise to the green band. This speculation is also supported by the well-known fact that when in the ZnO the equilibrium vapor pressure of O is smaller than Zn\textsuperscript{29}, therefore annealing of ZnO at high temperature for long time may cause the lose of O and forming O-vacancy related complex. From previous report it is indicated that after reduction treatment such as forming gas annealing the green band is enhanced\textsuperscript{28}, therefore the second explanation seems to be more plausible.

### 2.3 Forming Gas annealing

Forming gas, which is widely employed in industry for gas hypersensitisation of film, consists typically of 5\% to 10\% hydrogen and 90\% to 95\% nitrogen. As a kind of reduction treatment, the thermal treatment in forming gas has been observed to cause significant release of Zn vapor in ZnO powders and resulted in extra singly occupied oxygen vacancies (V\textsubscript{O}) giving rise to a green luminescence band in the PL spectra\textsuperscript{30,31}. 
In this study, we investigated the effect of forming gas annealing on the optical and crystalline quality of bulk ZnO. The ZnO substrate was cleaned in the same procedure described first, and then loaded into a quartz tubular annealing furnace. We used the forming gas composed of 95% nitrogen and 5% hydrogen, and the annealing temperature and time were set to 600 °C and 10 minutes, respectively. After annealing, the ZnO substrates were cooled down in the nitrogen ambient.

After the forming gas annealing, an obvious surface roughening occurred on those ZnO substrates, as shown in figure 2.9(a), which can be recovered by the high temperature annealing process we described before [figure 2.9(b)]. The surface roughening is suspected to be caused by the hydrogen in the forming gas, which is a strong reducing gas. Thus the damaged layer on the surface of ZnO can be effectively removed. This improvement of crystal quality at the surface is confirmed by the LT PL spectra which showed both a high optical efficiency (4 times higher than that before annealing) and narrower excitonic peaks. Furthermore, time-resolved photoluminescence (TRPL) measurement indicated an extended exciton life time for the forming gas annealed ZnO samples. Figure 2.10 shows the room temperature TRPL for both as
Figure 2.9 AFM images of (a) Zn-face ZnO after forming gas annealed (b) followed by 3 hours annealing in air.
Figure 2.10 Room temperature TRPL for both as received and forming gas annealed samples at an excitation energy density of 540 µJ/cm²
received and forming gas annealed samples at an excitation energy density of 540 µJ/cm².

The decaying TRPL data can be described by the following biexponential decay function:

\[ A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) \]

where \( \tau_1 \) is the faster decay constant and \( \tau_2 \) is the slower decay constant which are most probably related to the effective nonradiative and radiative recombination, respectively. \( A_1 \) and \( A_2 \) are the amplitudes for these two decaying components.

The ratio of the slower decaying component to the faster decaying component, \( A_2/A_1 \), is a good indication of the dominant recombination mechanism. \( A_2/A_1 \), based on the TRPL measurement at 540 µJ/cm², is 0.094 for the as received ZnO and 2.54 for the forming gas annealed ZnO. This indicates a remarkable increase in the radiative recombination. This can be explained by the following: Zn vacancy complex introduced defects, which may govern the nonradiative recombination, can be effectively removed by forming gas annealing, which is in good accordance with the report of forming gas annealing on ZnO powders. This improvement in radiative recombination is well supported by the observation of the increase of the PL intensity for the forming gas annealed ZnO.
In summary, we reported different preparation methods which resulted in remarkable improvement on the surface, optical and crystalline quality of the bulk ZnO substrate. Forming gas annealing can remove the Zn vacancy complex introduced defects and therefore improve the optical and crystalline quality near the surface, but results in increased surface roughness. This can be solved by a high temperature annealing in the air, which dramatically improves the surface condition of ZnO and is effective for both as received and forming gas annealed ZnO. HRXRD and LT PL measurements also indicate the improvement of crystalline quality of ZnO after such a high temperature annealing process.
CHAPTER 3

EPITAXY OF GAN ON BULK ZNO SUBSTRATE

3.1 Introduction

When a thin film (thin film here means the thickness of the film is less than the critical thickness) with a small lattice constant is grown on a large lattice constant substrate, the film maintains an in-plane lattice constant of the substrate and is under a biaxially tensile strain. On the other hand, when a thin film (same definition as before) with a large lattice constant is grown on a small lattice constant substrate, the film maintains an in-plane lattice constant of the substrate and is under a biaxially compressive strain. Since layer composites with well defined electrical and optical properties require coherence of the in-plane lattice constant, biaxial strain is always present in such heterostructures. In a simplest model which assumes static interface, the critical thickness of GaN/ZnO can be calculated by the following expression:
\[ a_{\text{GaN}}^T = a_{\text{GaN}}[1 + (T - RT)\alpha_{\text{GaN}}] + \frac{t}{t_c} \left\{ a_{\text{ZnO}}[1 + (T - RT)\alpha_{\text{ZnO}}] - a_{\text{GaN}}(1 + (T - RT)\alpha_{\text{GaN}}) \right\}^{33} \]

where \( a_{\text{GaN}} \) and \( a_{\text{ZnO}} \) are the strain free a-axis length of GaN (0.318nm) and ZnO(0.325nm), \( a_{\text{GaN}}^T \) is the a-axis length of GaN at growth temperature, \( \alpha_{\text{GaN}} \) and \( \alpha_{\text{ZnO}} \) are thermal expansion coefficient along a-axis of GaN (5.59X10^{-6}K^{-1})\(^{34}\) and ZnO (4.75X10^{-6}K^{-1})\(^{34}\), T is the growth temperature, RT is room temperature, t and \( t_c \) are the thickness of GaN epilayer and critical thickness, respectively. Hamdani et.al has predicted a critical thickness of 8nm to 12nm of GaN/ZnO estimated using different elastic models under the same assumption\(^{35}\).

ZnO is considered as a promising candidate for GaN epitaxy mainly due to the fact that the lattice mismatch between GaN and ZnO is very small (\( \alpha \) for ZnO is 1.9% larger than \( \alpha \) for GaN). Therefore, the defects density caused by the misfit for GaN/ZnO is expected to be lower than other substrates such as sapphire. Another desirable aspect for ZnO substrate is that it is the only isomorphic substrate for GaN heteroepitaxy. Although, substrates such as SiC, although the lattice mismatch with GaN is relatively small compared to that with sapphire, the different stacking order makes the resulting structure defects such as inversion domain boundary (IDBs) and stacking mismatch boundary (SMBs) inevitable. A schematic of the formation of such kind of defects of GaN/SiC is
Figure 3.1 Schematic formation of stacking mismatch boundaries (SMBs) of GaN/SiC

(after$^{34}$)
shown in figure 3.1. Using the wurtzite structure substrate such as ZnO is expected to avoid such kind of structural defect. Besides the crystal structure, the thermal mismatch between the GaN and ZnO is also relatively small, which is about ½ of that between GaN and SiC.

Being considered as one of the most promising substrate for GaN, the approach of GaN epitaxy on ZnO has not achieved the expected results yet, with mixed success for GaN epitaxy on ZnO effort having been noted in the past.\textsuperscript{35,36,37,38,39} The surface preparation has been mentioned in literature as the main reason for the less than satisfactory results.\textsuperscript{35,36,37} Now that this bottleneck has been overcome by the thermal treatment that we introduced in the Chapter 2, it is worthwhile to revisit this exciting heteroepitaxy.

### 3.2 Epitaxy of GaN on ZnO by RF nitrogen enhanced plasma

GaN epitaxy on thermally treated ZnO substrates was performed in an SVT molecular beam epitaxy (MBE) system, which can employ both radio-frequency (RF) plasma enhanced nitrogen and ammonia as active nitrogen sources. Excellent surface condition of ZnO substrates is shown in figure 3.2 by reflection high energy electron diffraction (RHEED). Due to the reactivity between ZnO and ammonia as well as Ga,
Figure 3.2 RHEED pattern of ZnO substrates after thermal treatment
Figure 3.3 A series RFEED taken at the initial growth stage
first a thin low-temperature GaN buffer layer was grown with RF nitrogen plasma in order to initiate the GaN growth. Then the substrate temperature was raised and the main GaN layer was grown under a typical Ga-rich (N-limited) condition. The RF nitrogen flux was such that as to maintain a growth rate of 0.3 µm/h. RHEED was used to monitor the GaN quality in-situ. A sharp and streaky RHEED pattern was maintained throughout the entire growth process on both Zn-face and O-face ZnO, which is an indication of two-dimensional (2-D) growth mode. (Figure 3.3 is a series RHEED taken at the initial growth stage) This is a marked improvement in the RHEED image, compared with earlier results\(^4\), which we attribute to the surface preparation mentioned in the last chapter. Without such surface preparation, the RHEED patterns of the ZnO substrate are typically composed of weak and broken diffraction lines, and the RHEED patterns on the surface of grown GaN layers are also typically broken with poor resultant layer quality. A comparison to show the effect of the LT GaN buffer and preparation of ZnO on the quality of GaN epitaxy on O-face ZnO, in terms of PL measurement is shown in Table 3.1
Table 3.1 A comparison to show the effect of the LT GaN buffer and preparation of ZnO on the quality of GaN epitaxy on O-face ZnO in terms of PL measurement

<table>
<thead>
<tr>
<th></th>
<th>RT PL</th>
<th></th>
<th>LT PL</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>FWHM</td>
<td>Exciton/YL</td>
<td>FWHM</td>
<td>Exciton/YL</td>
</tr>
<tr>
<td>Without annealing of ZnO substrate, without LT GaN buffer</td>
<td>90meV</td>
<td>~3</td>
<td>Not measured</td>
<td>Not measured</td>
</tr>
<tr>
<td>Without annealing of ZnO substrate, with LT GaN buffer</td>
<td>71meV</td>
<td>~6</td>
<td>15.4meV</td>
<td>~500</td>
</tr>
<tr>
<td>With annealing of ZnO substrate and with LT GaN buffer</td>
<td>55meV</td>
<td>~15</td>
<td>12meV</td>
<td>~4000</td>
</tr>
</tbody>
</table>
Figure 3.4 RHEED reconstruction of (a) GaN/ZnO after growth (b) 2X2 reconstruction of GaN on Zn-face ZnO (c) 2X2 reconstruction of GaN on O-face ZnO
Upon cooling the substrate temperature down to 350°C a clear 2×2 RHEED reconstruction can be found on both Zn and O terminated ZnO (figure 3.4), which is an indication of Ga-polarity GaN grown on ZnO.

In general, four different bonding configurations are possible between the interfacial GaN on and ZnO. On the Zn-face the possibilities are Zn-Ga bonds or Zn-N bonds and on the O-face they are O-Ga or O-N bonds. Since both GaN and ZnO are polar materials, from electrostatic and bond strength considerations, the Zn (triply bonded to the O layer below) -N bonds and the Ga-O (triply bonded to the Zn layer below) bonds are most likely. This would imply that Zn-face and O-face substrates would lead to Ga- and N-polar GaN, respectively. However, our RHEED observations indicate that GaN layers are Ga-polarity regardless of the substrate polarity, i.e. 2x2 reconstructions on GaN grown either way. In an overly simplistic picture, one might be tempted to conclude that on the O-face ZnO, the O-N bonds form for polarity consistency. Moreover, one can also forward the argument that O-Ga covalent radii is larger than that for O-N bonds which would lead to a stronger interfacial bonding for the latter pair. However, this simplistic model assumes static interfaces which is definitely an assumption and deviates from the real situation: Abrupt Ga-O interface will contain an excess of 1/4 of an
electron/bond while Zn-N interface will be deficient by 1/4 of an electron/bond which will cause substantial electric fields, resulting in an unstable interface. It is very likely that several monolayers near the surface of ZnO could dynamically participate in atomic exchange, since charge build-up can be avoided by atomic mixing of interfacial layers such that number of electron-rich bonds equal to electron deficient bonds, and therefore opposite directions of dipoles for anion and cation are compensated. For example, Suzuki et.al has claimed the deposition of Ga-Polarity GaN on O-polar ZnO/MgO/Sapphire template. The polarity of GaN is characterized by conversion beam electron diffraction (CBED), and argue is forwarded that such a polar inversion occurs due to the formation of Zn$_3$N$_2$. Besides, in the case of epitaxy ZnO on GaN substrate, it has been reported that the interface bonding depends on the initial surface treatment, i.e. exposure to Zn metal first or exposure to Oxygen plasma first, and therefore lead to different polarity of ZnO grown on the GaN with the same polarity. In our case, the situation could be more complex since ZnO is much less chemical and thermal stable compared with GaN, which makes the complex reaction near the interface easier to occur.

3.3 Epitaxy of GaN on ZnO by ammonia
Ammonia was also used as the N-source after the ZnO surface was protected by an initial GaN layer grown with RF nitrogen plasma. Compared with the layers grown by RF nitrogen, the surfaces for the GaN layers grown with ammonia are rougher, which is typical of ammonia regardless of the substrate employed, probably due to the high mobility of species afforded by ammonia on the surface. However, GaN with better optical quality, as judged by photoluminescence (PL), was achieved by using ammonia as the N source when grown at the temperature of 690°C. Figure 3.5 shows the PL spectra taken at 15K of GaN grown on Zn- and O- faces of ZnO. Compared to our typical GaN layers grown on sapphire and SiC under similar growth conditions, GaN grown on ZnO (both on Zn- and O-faces) demonstrated very high radiative efficiency (18.8%) and weak yellow luminescence. The $V_{\text{Ga}}$-donor complex, isolated or bound to structural defects such as dislocations or SMB is believed to be the major source for yellow luminescence. The higher radiative efficiency and weaker yellow luminescence in GaN/ZnO compared to other substrates thus may evidence a reduction in defect density. The smallest full width at half maximum (FWHM) for the dominant GaN exciton peak at 15 K was 12 meV for GaN on O-face ZnO and 13.3 meV for that on Zn-face ZnO. Several earlier reports indicated that GaN grown on O-face ZnO was better in this
Figure 3.5 Comparison of LT-PL (15K) of GaN/ZnO on O and Zn face ZnO
respect. The present results demonstrate that by carefully controlling the growth parameters and using the new surface preparation method, the same good quality GaN can be achieved on Zn-face, too.

According to earlier reports\textsuperscript{38}, the spinel structure $\text{Ga}_2\text{ZnO}_4$ oxide can be easily formed between ZnO and Ga, as has been confirmed by X-Ray-Diffraction (XRD) $\theta$-2$\theta$ scans. Using a low temperature GaN buffer layer allowed us to avoid such kind of deleterious reactions, at least to the extent that can be discerned by our high resolution XRD scans. Indeed, only the GaN and ZnO peaks can be resolved, as shown in figure 3.6. Growth on Zn-face and O-face ZnO gave identical XRD results. Gil \textit{et al.}\textsuperscript{46} have built a theoretical model employing the Pikus and Bir Hamiltonian to fit the energy shift of the valence and conduction bands, taking into account the relaxation arising from thermal and lattice mismatch strain. They pointed out from optical measurements that GaN grown on sapphire and on ZnO is under compressive strain while that grown on SiC is under tensile strain. The thermal strain ($\varepsilon_{\text{th}}$) is:

$$\varepsilon_{\text{th}} = \frac{\Delta a_i(T) - \Delta a_s(T)}{\Delta a_s(T)}$$

where $\Delta a_i(T)$ and $\Delta a_s(T)$ are the variation of the lattice parameter between the growth temperature and room temperature for GaN layers and substrates, respectively.\textsuperscript{39}
Figure 3.6 HRXRD of GaN/ZnO 2 Theta-Omega Scan
The calculation of $\varepsilon_{\text{th}}$ using the temperature dependence of thermal expansion coefficient indicates that the thermal strain of GaN/ZnO is negative and GaN/SiC is positive, while the absolute value for GaN/ZnO is smaller. This indicates that the thermal strain of GaN/ZnO should be compressive while that of GaN/SiC should be tensile. These are in good accordance with our optical measurement that the exciton peak of GaN/ZnO was very slightly blue-shifted while for the exciton peak of GaN/SiC a red shift is clearly observable, although in the latter case the net compressive strain instead of tensile strain has been reported by some groups\textsuperscript{47,48} most probably due to residual compressive lattice mismatch stress. In GaN/ZnO the lattice mismatch is smaller (1.9\%) than that for GaN/SiC (3.54\%), so it is reasonable that the net strain in GaN/ZnO will not be turned into tensile one by lattice mismatch.

### 3.4 Discussions

Two important issues must be taken care of to realize high quality GaN epitaxy on ZnO. The first one is the disparity between the electronic configurations which exists during the formation of the heterointerface. Due to the change in valency occurring from one monolayer to the next as the III-V/II-VI interface is formed, interface states are
generated. Therefore, for the unreconstructed interface, interface states must exist, which are present as unsaturated electron bonds. Such unsaturated bonds can lead to substantial electric field in the interface, which may be released by either forming dislocations or by atomic mixing. Besides being a non-isoelectronic heterosystems, the III-V/II-VI semiconductors also belong to the class of semiconductors which form highly reactive interfaces. Moreover, the heterovalence will enhance the interdiffusion at the interface, i.e., Ga and N diffusion into ZnO while Zn and O diffusion into GaN, to compensate the charge imbalance and interface dipoles. A very likely product of interfacial reactions are the thermodynamically favored compounds of the form III$_2$VI$_3$. If the III$_2$VI$_3$ compounds are presented, the lattice mismatch between II-VI and the appropriate III$_2$V$_3$ semiconductor should be also considered. For example, the GaAs/ZnSe only has a 0.27% lattice mismatch, however, when Ga$_2$Se$_3$ interfacial layer is formed, the strain is magnified and a 4% mismatch is expected between the substrate and epitaxy layer. In ideal situation, the epitaxial relationships between GaN and ZnO are expected to be [0001] of GaN being parallel to [0001] of ZnO, and no discernible in plane rotation for strain reduction is expected, which happened when GaN was grown on some other substrates such as sapphire. However, if the initial layer is not grown at optimized condition, or
severe atomic mixing happened at the GaN/ZnO interface so that an interfacial layer of Ga$_2$O$_3$ or Zn$_3$N$_2$ (both of them have an Ia3 space group (cubic) with inversion symmetry) is formed, then we have to reconsider the epitaxial relationship. Let’s take the formation of Ga$_2$O$_3$ for an example. Ga$_2$O$_3$ has a lattice constant of $a=1.223$ nm and $b=0.304$nm$^{50}$. Since ZnO has a lattice constant of $a=0.325$nm, the lattice constant of Ga$_2$O$_3$ along the a axis ($[100]$) is around 4 times larger than that of ZnO. Therefore, it is suggested$^{50,51}$ that the epitaxial relationship between GaN/Ga$_2$O$_3$/ZnO becomes $\{21\bar{T}0\}_{\text{GaN}}\|[010]Ga_2O_3\|[21\bar{T}0]_{\text{ZnO}}$ (figure 3.7). The lattice misfit along the $[100]$ ($a=1.223$nm) and $[010]$ ($b=0.304$nm) axes of Ga$_2$O$_3$ with the $[01\bar{T}0]$ ($4\sqrt{3}a/2$) and $[2\bar{1}\bar{T}0]$ (a) direction of ZnO becomes 8.6% and -6.5%, and 10.7% and -4.7% with that of GaN. Moreover, due to the different lattice structure between Ga$_2$O$_3$ and ZnO (GaN), inversion domain boundaries are expected to occur. Therefore, it is of extreme importance to avoid such interfacial layer formation in order to exploit the structural advantage of ZnO substrate for GaN epitaxy.

Kobayashi$^{1}$ et al$^{52}$ recently reported the room temperature growth of GaN on ZnO substrate by pulsed laser deposition (PLD). It is indicated that although the surface of GaN grown at room temperature shows the clear step and terrace structure, it disappears
Figure 3.7 Schematic shown of epitaxial relationship between GaN/Ga$_2$O$_3$/ZnO (after $^{53}$)
with the increase of the growth temperature to 500°C and even lower. An argument is forwarded that this degradation in the surface morphology is probably related to the intermixing of atoms at the heterointerface at increased temperatures, due to the reaction between the ZnO substrate and III group nitrides.

Compared with GaN/Sapphire, the GaN grown on ZnO is relatively easier to peel off, especially for those GaN grown at relatively high temperatures. Besides the unsaturated interface bonding, the reason of the peeling off has also been speculated to be caused by the reactivity between the ZnO and ammonia, or by the thermal mismatch between GaN and ZnO. However, both of them seem not to be the true answer if we take the following facts into consideration: first, the GaN peels off at a relative high temperature even it is grown by RF nitrogen, which means the peeling off occurs in an ammonia free ambient, too. On the other hand, we have tried to raise the temperature of GaN/ZnO layer in the air, then the peeling off does not occur even the anneal temperature is 100°C higher than the peeling-off temperature of GaN/ZnO when growing in the MBE system. This observation denies the statement that thermal expansion could be the reason for the peeling off of GaN on ZnO. Actually, the thermal mismatch between the GaN and ZnO is reasonably small, which is only about 1/2 of that between GaN and SiC.
Although no conclusion has been drawn on this issue, several factors should be taken care of. A strong bonding at the interface is always preferable, as we discussed previously. Another factor we should be aware of is the fast decomposing rate of the ZnO substrate, especially in an oxygen free system such as MBE. Without the suppression of the oxygen ambient, the decompose of ZnO could be reasonably fast, and it is a potential reason that causes the GaN epitaxy on ZnO to peel off at high temperature in MBE system, while it remains intact when heated in atmosphere at the same temperature or higher.

Another issue people have to pay extra attention is the stability of the substrate itself. Unlike sapphire and SiC, the ZnO substrate is thermally and chemically unstable, which means that it is very difficult to be employed in epitaxial methods particularly those relying on high-temperatures or reactive ambient, such as MOCVD and HVPE. MBE seems to be the most promising approach due to the relatively low growth temperature and clean growth ambient. In case of the reactive MBE, ZnO can react with ammonia at temperatures higher than 600°C. However, the capability of growing GaN with RF plasma enhanced Nitrogen makes it possible to grow GaN without ammonia, or initiate the growth with RF nitrogen and then switch to ammonia growth.
Still we have to be aware of the thermal decomposition of the ZnO substrate. Our investigation by residual gas analyzer (RGA) indicated that the signal of the O and Zn increase dramatically when the substrate temperature is increased to 800°C, although considerable signal can be accumulated at a temperature much lower than that. The increase in the signal is believed to come from the thermal decomposition of the ZnO substrate.

In summary, ZnO substrates with an atomically flat surface exhibiting terrace-like features by high temperature annealing were used as a substrate for GaN grown by MBE. RHEED patterns showed that 2D epitaxial growth of GaN can be achieved on these thermally treated ZnO substrates. High-resolution XRD results indicated that the surface of ZnO could be protected from the reaction with either Ga or ammonia by employing a low temperature RF-nitrogen GaN buffer layer. The XRD method resolved the GaN diffraction from that of ZnO. Low temperature PL results show that similar high quality GaN layers can be achieved on both annealed O-face and Zn-face ZnO substrates.
CHAPTER 4

THE OUTLOOK OF THE GAN/ZNO BASED DEVICES

The integration of II-VI and III-V semiconductors into a single hetero-junction device enables the exploitation of the many similarities and differences in the material properties (energy bandgap, dielectric constant, etc.) to create new devices exhibiting unique optical and electronic properties. The combination of GaN and ZnO would be particularly interesting due to the materials share a lot of similar properties. Especially considering the difficulty in producing high-quality, reproducible p-type ZnO hinders the realization of ZnO homojunction, hetero $p - n$ junctions can be used instead of homo $p - n$ junctions in optoelectronic devices. The GaN/ZnO heterostructure would be a promising candidate for such applications, since growth of $p$-type GaN has been established and there is only a slight lattice mismatch of 1.9% between GaN and ZnO.
4.1 Potential application of GaN/ZnO based LEDs

Band-line-up data for the ZnO/GaN heterostructure is highly needed in optoelectronic device applications. Generally speaking, when a thin film with a larger lattice constant is grown on a smaller lattice constant substrate and the thickness of the film is smaller than the critical thickness, the films maintains an in-plane lattice constant of the substrate and is under a biaxially compressive strain. The band ordering in such a system is strongly strain dependent and usually type I band alignment is obtained. Similarly, when a thin film with a smaller lattice constant is grown on a larger lattice constant substrate and the thickness of the film is smaller than the critical thickness, the film is under a biaxially tensile strain and usually a type II band alignment is expected. (This principle works especially well for the Si/SiGe system)

Although the above mentioned statement is only an approximate rule (i.e, it doesn’t work for AlGaN/GaN case, which follows the type I alignment), in GaN/ZnO case the band alignment does follow it, as demonstrated by ex-situ ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS) and calculation thereafter. Both the valence band and conduction band of GaN is higher in energy than the ZnO respective
bands. However, the exact amount of band discontinuity differs from report to report, depending on different calculation mode or experiment procedure employed. For example, a 0.6 eV of $\Delta E_{v}$ has been calculated based on the electron affinity rule$^{55}$, while the value is 0.24 eV when the valence band Schottky barrier height is used$^{56}$. XPS results on those thin ZnO grown on GaN via MBE and sputtering all confirms the type II alignment at the ZnO/GaN interface while the valence band of GaN being located above ZnO, but different $\Delta E_{v}$ (0.8eV for the MBE grown ZnO and 1.45eV for the sputtering ZnO) were reported. The latter one fits better for the calculation of T. Nakayama et.al., who employing the pseudo potentials ab initio calculation and get the average valance band offset of 1.6eV$^{57}$. The same report also points out that the offset value could vary from 1.0 to 2.2 eV due to different pretreatment during the initial growth stage, which may well be responsible for the disperse of the different results acquired. For example, the band offset will change depending on the different atomic configuration at the interface$^{58}$. Moreover, the offset value also depends on the strain state of the system. The strain in the interface could affect both the band gap and the electron affinity of the semiconductor. Figure 4.1 shows the n-GaN/n-ZnO band gap alignment, where the $\Delta E_{v}$ is taken as 1.45eV.
Figure 4.1 Scheme of i-GaN/n-ZnO band alignment

\[ \Delta E_v = 1.45 \text{eV} \]
\[ \Delta E_c = -1.55 \text{eV} \]
\[ E_c - E_f = 0.0 \text{eV} \]
\[ E_f - E_v = 1.85 \text{eV} \]
\[ E_g = 3.3 \text{eV} \]
\[ E_r - E_v = 3.3 \text{eV} \]
Figure 4.2 Scheme of p-GaN/n-ZnO band alignment
P-GaN and P-AlGaN have been taken to substitute for p-ZnO in terms of ZnO based opto-electronic applications, chiefly due to the difficulty in producing high-quality, reproducible p-ZnO. Considering p-GaN/n-ZnO combination, which has been reported already and Electroluminescence (EL) spectra has been measured. According to the band alignment (figure 4.2), $\Delta E_v$ and $\Delta E_c$ are comparable (for example, if we take $\Delta E_c = 1.55 \text{eV}$, then $\Delta E_v = (E_{gZnO} + \Delta E_c - E_{gGaN}) = 1.45 \text{eV}$) which means that the electrons could go over the barrier and come from n-ZnO into p-GaN, and holes could come from p-GaN into n-ZnO over the barrier when bias is added. Besides the doping concentration, the barrier height is another factor that determines the tunneling current density. While $\Delta E_c$ is slightly higher than $\Delta E_v$, we have to take the electron and hole effective mass into consideration. For example, we know that for a p-n homo-junction, the injection current of electron and hole can be expressed as:

$$J_n = q\mu_n (nE + \frac{kT}{q} \frac{\partial n}{\partial x})$$

$$J_p = q\mu_p (pE - \frac{kT}{q} \frac{\partial p}{\partial x})$$

respectively and the +,- is the indication of direction. Therefore, considering the junction with a similar electron and hole concentration, which of the two current components, $J_n$ or $J_p$, is dominant is mainly determined by the terms $\mu_n$ and $\mu_p$. For
semiconductors such as GaN or ZnO, the mobility $\mu$ can be approximated as $(\Sigma \frac{1}{\mu_i})^{-1}$, where $\mu_i$ is the mobility limited by different scattering mechanisms, providing that the scattering events are independent, meaning an electron would be undergoing one full scattering event before it may subjected to another and the scattering event is one where the distribution is energy independent. For example, from deformation potential scattering $\mu_{dp} \sim (m^*)^{-5/2} T^{-3/2}$ and from ionized impurity scattering $\mu_l \sim (m^*)^{-1/2} T^{3/2}$. For all the above mechanisms $\mu$ decreases with the increase of the effective mass $m^*$. A calculated value gives the heavy hole and light hole effective mass of GaN as 1.4 $m_0$ and 0.3 $m_0$\(^5\), while electron effective mass of ZnO is taken as 0.38$m_0$\(^6\)(for the electron effective mass of ZnO different values such as 0.50$m_0$\(^6\), 0.26$m_0$\(^6\) and 0.06$m_0$\(^6\) have been reported by different measurement or calculation methods in the past). Therefore, as the mobility from the polar optical phonon scattering (which is the dominant mechanism for GaN RT mobility) is concerned, the electron mobility in ZnO side will be much higher than the hole mobility in GaN side. As for research interest, researches hope that the electron-hole recombination happen on the ZnO side, which has an exciton binding energy of 60meV and the most efficient emitter
potentially. But from the discussion above we realize that the band alignment should be engineered in order to realize such a purpose.

An easy but effective method is to replace the p-GaN with p-AlGaN. We know that both GaN/ZnO and AlGaN/ZnO have type II band alignment, and therefore the barrier for holes $\Delta E_{\text{v}} = (E_{g\text{ZnO}} + \Delta Ec - E_{g\text{AlXGa}_{1-X}\text{N}})$, or $\Delta Ec - \Delta E_{\text{v}} = E_{g\text{AlXGa}_{1-X}\text{N}} - E_{g\text{ZnO}}$. Therefore, in order to enhance the holes current while suppress the electrons current, a larger value of $\Delta Ec - \Delta E_{\text{v}}$ is desirable. This can be achieved by replacing the p-GaN with p-AlGaN, which gives rise to the $E_{g\text{AlXGa}_{1-X}\text{N}}$. For example, an AlGaN with Al composition of 12% increases the band gap to 3.64eV, if we simply assume a linear relationship between the band gap and Al composition. By replacing the p-GaN with AlGaN, we enlarge the difference between the barrier for holes and the barriers for electrons, which will enhance hole injection and make it dominant in the current mode. A limitation of this method, however, is the realization of p-AlGaN, as it is well know that only for Al composition of around 12% or lower that good quality P-AlGaN can be achieved. Therefore, we can not design the band gap alignment as free as we wish. Another factor is by introducing the AlGaN the electron affinity is reduced for AlGaN compared with GaN, therefore increase the barrier for both electron and hole for a same amount. Finally, the exact band
discontinuity of the GaN/ZnO junction is still a subject of discussions. For example, if we take the $\Delta E_c$ as 1.55 eV and make a linear assumption of the $\chi_{\text{GaN}} - \chi_{\text{AlGaN}} = 0.3 \text{ eV}$, then the barrier for electron and barrier for hole for the $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$ is around 1.85 eV and 1.51 eV, respectively. If we take $\Delta E_c$ as 0.8 eV then the barrier for electrons and barrier for holes should be 1.1 eV and 0.76 eV, respectively.

### 4.2 Potential applications of AlGaN/GaN MODFETs on ZnO substrates

The GaN-based heterojunction system possesses many of the highly coveted characteristics needed for high power devices. GaN itself possesses a large band gap of 3.4 eV, a very high breakdown field ($3 \times 10^6$ V cm) and an extremely high peak ($3 \times 10^7$ cm s) and saturation velocity ($1.5 \times 10^7$ cm s)\textsuperscript{64}. These properties in combination with the high band offset and the high electron mobility observed in AlGaN/GaN heterostructures ($2019$ cm$^2$ V. s.)\textsuperscript{65}, promise an excellent microwave power performance of GaN-based heterojunction field effect transistors. Due to the strong chemical bonds in the semiconductor crystal, GaN-based devices also have bright prospects in high temperature operation and applications under radiation exposure. Furthermore, the wurtzite crystal
structure of group-III nitrides is highly piezoelectric, offering device design possibilities which is not accessible with those GaAs and InP based semiconductors.

The electronic devices in nitrides system are still in their early stages and currently most of the GaN-based MODFET structures are realized on sapphire or SiC substrate. At present the best devices are demonstrated on SiC substrates with excellent thermal conductivity. However, high resistive SiC substrates are very expensive, and high quality versions of them are not available to many of those in the field of high power devices. This leaves sapphire as the mainstream substrate for GaN based FETs unless favorable developments take place on the SiC realm. Besides the material degradation caused by the large lattice and thermal mismatch between GaN and sapphire, another issue that hinders the performance of the GaN based FET on sapphire substrate is the moderate thermal conductivity of sapphire, which adversely affects the higher power performance of those electronic devices.

ZnO substrates offer a promising alternative for GaN based FETs with competitive economic features: On the one hand, it offers nearly ideal structural and lattice constant match; on the other hand, ZnO has a room temperature thermal conductivity of approximately 60 W/m K \(^6\) (different values have been reported on the thermal
conductivity of ZnO. Actually, this value depends on the quality and preparation of the ZnO. i.e., using the high temperature annealing we mentioned in Chapter2 will cause a significant increase in the thermal conductivity), which is twice that of sapphire. The thermal conductivity of ZnO is expected to reduce at high temperatures, i.e., Olorunyolemi et.al has reported that the thermal conductivity reduced from 60 W/m K to 60 W/m K when the temperature was increased from RT to 1000°C\(^67\). What is more important, ZnO is less chemically resistant and not as hard a material as either sapphire or SiC, thus enabling the ZnO substrate to be easily removed after device fabrication. It can be selectively removed paves the way to mounting the active device region on a substrate with excellent thermal conductivity, such as polycrystalline and high resistive AlN which is commercially available.

Figure 4.3 is a schematic diagram of an AlGaN/GaN MODFET structure on ZnO substrate. Similar to GaN epitaxy, the growth is initiated with a low temperature GaN buffer layer grown by RF nitrogen to minimize the reaction between Ga and ZnO. Since the ZnO substrate is conductive and also takes O leaching from the ZnO substrate into consideration, an Mg-doped buffer is necessary to achieve high-resistive GaN buffer. AlGaN/GaN modulated doped structure can therefore be grown on the GaN:Mg buffer.
<table>
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<td>60 nm</td>
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<tr>
<td>ZnO substrate</td>
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Figure 4.3 Schematic diagram of an AlGaN/GaN structure on ZnO substrate
On the other hand, we should be aware of some intrinsic properties of ZnO substrate, i.e., its conductivity, which require extra attention compared with those FET prepared on conventional substrate such as sapphire. For example, the characterization of mobility of AlGaN/GaN structure grown on ZnO is complex. The mobility of the upper structure can not be measured directly and two-layer mode has to be employed for the calculation. If we assume that $t_1$ and $t_2$ are the thickness, $d_1$ and $d_2$ are the conductivity, $R_{H1}$ and $R_{H2}$ are the Hall constant of ZnO substrate and GaN epilayer respectively, then the Hall constant for the two-layer structure (that is what we measured) will become

$$R_{H} = R_{H1} \frac{t_1}{t} (\frac{\sigma_1}{\sigma})^2 + R_{H2} \frac{t_2}{t} (\frac{\sigma_2}{\sigma})^2$$

in the low magnetic field limit, where $t = t_1 + t_2$, $\sigma = \frac{t_1}{t} \sigma_1 + \frac{t_2}{t} \sigma_2$

However, we have to notify that the thickness of the ZnO substrate is much greater than that of the epilayer grown by MBE. If we assume $t = 300t_2$ and $d_2 = 3d_1$, then we will get

$$R_{H} = R_{H1} \frac{t_1}{t} (\frac{\sigma_1}{\sigma})^2 + R_{H2} \frac{t_2}{t} (\frac{\sigma_2}{\sigma})^2 = R_{H1} + \frac{3}{100} R_{H2}$$

This means that for the mobility we measure, most of it comes from the contribution of the ZnO substrate instead of the upper AlGaN/GaN structure. Therefore, a 3% deviation in the measurement of $R_{H1}$ (ZnO) would lead to an approximately 100%
deviation of $R_{H2}$ (epilayer). In order to make accurate Hall mobility characterization and calculation, it should be guaranteed that either the substrate is not that conductive (make $\sigma_1 << \sigma_2$, stands for high resistive ZnO) or the GaN epilayer has a thickness comparable to the substrate (make $t_2 \sim t_1$). To grown thicker GaN layer require the assistance of other epitaxy technique with much higher growth rate, such as HVPE.

Two issues have to be given ample attention on this structure, especially regarding the characteristic of the ZnO substrate: One is that the growth temperature of the AlGaN should not be as high as the researches use in sapphire. Increasing the temperature would result in an increased O-background doping as well as causing the potential peel off. Therefore, adding an insulating dielectric layer such as Si$_3$N$_4$ or SiO$_2$ under the gate would be a reasonable idea to reduce the potential leakage current caused either from the Mg-doped buffer and/or from the AlGaN grown at a reduced temperature (the low surface mobility of the Al adatoms usually requires a higher growth temperature of AlGaN compared with GaN by MBE). Another factor is the effect of the Mg-doped GaN buffer on the performance of the device. Mg-doped GaN confinement layer can effectively block the carrier leakage into the ZnO substrate and makes the FET structure on ZnO possible. However, the GaN channel grown on such doped buffer is also
expected to suffer from the degradation of crystalline quality. Adding an Mg-doped GaN into the MOCVD grown AlGaN/GaN FET on sapphire causes around a 4.5 times reduction in the channel current. Therefore, low concentration of Mg-doped GaN buffer is desirable to enhance the device performance, which requires a high efficient Mg doping while without creating too many structural defects. Bhattacharyya et.al. has just reported a p-type doping at relative high temperature (using extremely Ga-rich condition, and claimed a 10 times increase of the Mg doping efficiency (1% to 10%). The effectiveness of this method on ZnO substrate should be examined, however, since higher growth temperature may lead to an increased O leaching level as well. Other effective dopants, especially those with deeper levels such as C or Fe, may also be used to obtain semi-insulating GaN to realize better performance devices on ZnO substrate.
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