Growth And Characterization Of Zno Based Semiconductor Materials And Devices

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GROWTH AND CHARACTERIZATION OF ZNO BASED SEMICONDUCTOR MATERIALS AND DEVICES

by

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A dissertation submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in the College of Optics and Photonics
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2013

Major Professor: Winston V. Schoenfeld
ABSTRACT

Wide band gap semiconductors such as Mg₅Zn₁₋ₓO represent an excellent choice for making optical photodetectors and emitters operating in the UV spectral region.

High crystal and optical quality MgₓZn₁₋ₓO thin films were grown epitaxially on c-plane sapphire substrates by plasma-assisted Molecular Beam Epitaxy. ZnO thin films with high crystalline quality, low defect and dislocation densities, and sub-nanometer surface roughness were achieved by applying a low temperature nucleation layer. The critical growth conditions were discussed to obtain a high quality film: the sequence of Zn and O sources for initial growth of nucleation layer, growth temperatures for both ZnO nucleation and growth layers, and Zn/O ratio. By tuning Mg/Zn flux ratio, wurtzite MgₓZn₁₋ₓO thin films with Mg composition as high as x=0.46 were obtained without phase segregation. The steep optical absorption edges were shown with a cut-off wavelength as short as 278nm, indicating of suitability of such material for solar blind photo detectors. Consequently, Metal-Semiconductor-Metal photoconductive and Schottky barrier devices with interdigital electrode geometry and active surface area of 1 mm² were fabricated and characterized. Photoconductor based on showed ~100 A/W peak responsivity at wavelength of ~260nm.

ZnO homoepitaxial growth was also demonstrated which has the potential to achieve very low dislocation densities and high efficiency LEDs. Two types of Zn-polar ZnO substrates were chosen in this study: one with 0.5° miscut angle toward the [1-100] direction and the other
without any miscut angle. We have demonstrated high quality films on both substrates with a low growth temperature (610°C) compared to most of other reported work on homoepitaxial growth. An atomically flat surface with one or two monolayer step height along the [0001] direction was achieved. By detail discussions about several impact factors for the epitaxial films, ZnO films with high crystallinity verified by XRD in different crystal orientations, high PL lifetime (~0.35 ns), and not obvious threading dislocations were achieved.

Due to the difficulty of conventional p-type doping with p dopant, we have explored the possibility of p-type doping with the assistance of other novel method, i.e. polarization induced effect. The idea is the sheet layer of two dimensional hole gases (2DHG) caused by the wurtzite structure’s intrinsic polarization effect can be expanded to three dimension hole distribution by growing a MgZnO layer with a Mg concentration gradient. By simulation of LED structure with gradient MgZnO structure, the polarization effect was found not intense as that for III-nitrides because the difference of spontaneous polarization between ZnO and MgO is smaller than that of GaN and AlN, and the piezoelectric polarization effect may even cancel the spontaneous polarization induced effect. We have grown the linear gradient MgZnO structure with Mg composition grading from 0% to 43%, confirmed by SIMS. Hall measurement did not show any p-type conductivity, which further indicates MgZnO’s weak polarization doping effect. However, the gradient MgZnO layer could act as an electron blocking layer without blocking holes injected from p layer, which is useful for high efficiency light emitters.
ACKNOWLEDGMENTS

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My wife, Yuan Chen, is the one I want to thank the most. She has encouraged me when I am down, inspired me when I discuss research with her, and made me feel I can be better every
single day. Finally, I would like to thank my father and mother for their unconditional love and steadfast faith in me.
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1. CHAPTER ONE: INTRODUCTION

There has been a great deal of interest in wide bandgap semiconductors, owning to their applications in the ultraviolet (UV) region. It’s well established that the UV region occupies the spectral region from 10 nm to 400 nm, which is highly ionizing radiation and activates many chemical processes.

The detection of UV radiation is very useful for civil and military applications, such as chemical and biological analysis (for example: ozone and most organic compounds), flame detection (fire alarms, missile warning, and combustion monitoring), optical communications in vacuum, emitter calibration (UV lithography), and astronomical study. ‘UV-enhanced’ silicon photodiodes are the most common detection methods for UV emission, due to well-established Si technology. However, Si-based UV photodetectors exhibit some limitations inherent to the intrinsic material properties, such as device ageing, low quantum efficiency in deep-UV range (due to SiO₂ passivation layer), and low sensitivity to low energy radiation (filters are needed to block out visible and infrared photons). UV photodetectors based on wide bandgap semiconductors (diamond, SiC, III-nitrides and II-IV compounds) can overcome the limitations listed above. Especially for GaN-based and ZnO-based ternary or quaternary compounds¹-³, their bandgap can be engineered⁴,⁵ by introducing other elements and thus exhibit intrinsic visible blindness (λ < 350nm) or even solar blindness (λ < 280nm).
Light emitting diodes (LEDs) based on wide bandgap materials are extremely useful for applications in air, water, and surface sterilization and decontamination, bio-agent detection and identification, UV curing, and some analytical instrumentation. Compared to conventional UV sources (a mercury lamp), UV LED is more compact, flexible, and energy-saving, and has tunable emission spectrum which allows for the fabrication of LEDs with different wavelengths. SiC, ZnSe, GaN and ZnO are available materials for making UV or blue LEDs. SiC-based LEDs have low intensity because SiC has an indirect bandgap. Although ZnSe-based materials have been grown at room temperature, the lifetime of ZnSe based LEDs and Laser diodes (LDs) are short, due to high defect density. The high-intensity GaN-based LEDs from UV to the yellow light region can be obtained by creating alloys of GaN (3.4eV) with AlN (6.3eV) and InN (2.0eV). Although GaN-based LEDs have been studied for more than 20 years, the GaN growth has a large number of defects due to the lack of inexpensive lattice matched substrate. To reduce these defects, the substrate such as sapphire requires a buffer layer and substantial pre-growth of GaN (one to several μm) prior to device growth so that the defects at the sapphire interface are far away from the region of interest. These growth procedures contribute to complexity and time and thus the cost of manufacturing. As a result, other materials should be investigated to generate more stable LED with a lower cost of production. ZnO is a promising material for this application and is the subject of our research.

ZnO has the following advantages compared to GaN,
1. Commercial large size ZnO substrates are available. High quality ZnO films can be grown at relatively low temperatures (less than 700°C). High quality homoepitaxial films have been obtained by a few groups recently.

2. ZnO has large exciton binding energy of 60 meV, which is more than two times larger than that of room-temperature (RT) thermal energy (25meV). This enables high intensity of near-band-edge excitonic emission at room and even higher temperatures. Laser emission from ZnO based structures at RT is reported.

3. ZnO is resistive to high energy radiation, making it suitable for space applications or any harsh and high-energy environment.

4. Etching of Zn is much easier than that of GaN, which cannot be wet-etched in conventional acid mixtures at safe temperature. ZnO can be easily etched by acids and alkalis at low temperature, providing great flexibility in the processing, designing and integration of electronic and optoelectronic devices.

5. The growth temperature of ZnO is much lower than GaN (~1000°C).

6. ZnO has the same crystal structure and close lattice parameters to GaN. High quality GaN films can be obtained by epitaxial growing on ZnO substrate. Hybrid LED based on p-GaN/n-ZnO can also be achieved, which solves the main hindrance of p-type doing for ZnO devices.

Although ZnO has so many advantages over GaN, ZnO based light emitters are still not commercially available. One of the main difficulties in the evolution of the device is p-type doping, which is indispensable for achieving high-efficiency ZnO based devices. Intrinsic
defects due to the oxygen vacancies, Zn interstitials, H and other impurities evolving in the ZnO material during growth form shallow and deep donor levels. As a result, intrinsic ZnO shows very strong n-type conductivity. The n-type conductivity can be easily improved by doping with Al, Ga and In. However, reliable p-type doing for ZnO is still not well developed. Another challenge for ZnO is the phase segregation with intermediate Mg composition when alloying with MgO due to different crystal structures of ZnO (wurtzite) and MgO (rocksalt cubic). This impedes the development of photodetectors in the solar blind region. A few research groups have been devoted to find ways to grow single phase MgZnO with intermediate Mg composition to make high response solar blind photodetector.
2. CHAPTER TWO: BACKGROUND

Most of the current technological applications of ZnO, such as transparent conductive electrodes for solar cells, piezoelectric devices, and gas sensors, have been made of polycrystalline films. These films have been grown by various simple deposition techniques, such as chemical spray pyrolysis, electrochemical deposition and sol-gel synthesis, requiring relatively low temperatures and covering large areas. Later attempts led to high-quality ZnO single crystal films prepared by Radio-Frequency (RF) magnetron sputtering and other growth techniques allowing a fine control over deposition procedure, such as molecular-beam epitaxy (MBE), pulsed laser deposition (PLD), and metal-organic chemical vapor deposition. Among them all, MOCVD and MBE are expected to lead to better ZnO films in terms of crystalline quality and impurity control, yet at the expense of slow growth rates and much more complicated and expensive setups. In the following sections, our focus is mainly on MBE growth for single crystal ZnO.

2.1 Plasma-assisted Molecular Beam Epitaxy

MBE was first invented in late 1960s by Bell Telephone Lab and it has been widely used in the growth of semiconductor thin films and nanostructured materials. There are a variety of growth techniques for MBE: gas source MBE, and its derivative using metal organic compounds; atomic layer epitaxy, and plasma assisted MBE (PA-MBE). Among all of them, PA-MBE has become the most common approach in the growth of ZnO thin films and other materials.
2.1.1 MBE system

The schematic for PA-MBE system is shown in Figure 1. The growth chamber is evacuated by a cryopump and the base pressure in the chamber is around $2 \times 10^{-10}$ Torr. The pressure during the growth for ZnO is typically $\mu$Torr. During the growth, the metallic elemental sources are held in pyrolytic boron nitride (PBN) crucibles and evaporated from standard Knudsen cells (K-cells). Oxygen is usually provided by a Radio Frequency (RF) plasma source (13.56MHz). The substrate is held on a manipulator which has a filament to control the temperature of the substrate and can also control the orientation of the sample. Typical growth temperatures are in the range of 300°C-800°C. To obtain high quality films, the substrate temperature, oxygen flow rate, metallic flux, and the pressure during growth are crucial and need to be optimized. The main advantage of MBE is its precise control of fluxes of each element and in situ diagnostic capabilities. The growth can be monitored by Reflected High-Energy Electron Diffraction (RHEED, monitoring the growth quality), Residual Gas Analysis (RGA, analyzing the pressure for each element) and laser reflectometry (monitoring the growth progress, such as growth rate and film thickness).
2.1.2 Growth Methods

Various substrates have been used for ZnO thin film growth such as ZnO, GaN, SiC, glass, Si, and ScAlMgO₄. Table 1 summarizes the lattice misfits of well-known substrates for ZnO thin films.

Sapphire substrates are the most popular because of the price and availability. In 1997 and 1998 Chen et al. reported ZnO epitaxial growth on (0001) sapphire substrates by using an oxygen microwave plasma source.¹⁸,¹⁹ The epitaxy process exhibited three-dimensional (2D) nucleation at the initial growth stage, followed by three-dimensional (3D) growth as indicated by RHEED.
Table 1. Lattice parameters of several substrates for ZnO.

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal structure</th>
<th>Lattice constant (nm)</th>
<th>Lattice mismatch (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>c</td>
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<tr>
<td>ZnO</td>
<td>Hexagonal</td>
<td>0.3246</td>
<td>0.5207</td>
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<td>MgO</td>
<td>Cubic/rocksalt</td>
<td>0.4216</td>
<td>-</td>
</tr>
<tr>
<td>GaN</td>
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<td>0.5185</td>
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</tbody>
</table>

The [2̅1̅1 0] orientation of ZnO aligns with the [1̅1̅00] direction of Al₂O₃, and the [1̅1̅00] direction of ZnO aligns with the [1̅2̅1 0] direction of Al₂O₃. This alignment corresponds to 30° rotation of the crystal orientation of the ZnO epilayer against the Al₂O₃ substrate, because the ZnO lattice aligns itself with the oxygen sub-lattice in Al₂O₃. By this 30° rotation, the lattice mismatch is reduced from around 32% to 18%. The presence of these domains leads to increased carrier scattering as exemplified by the typical low mobilities of 1 to 40 cm²V⁻¹s⁻¹. In order to eliminate the rotational domains observed in ZnO thin films grown on (0001) sapphire, (11̅2 0) sapphire substrates (a-plane) have been used for ZnO epitaxy. The lattice parameter c=1.299 nm of a-plane sapphire is almost exactly 4 times of the parameter a=0.3246 nm of ZnO, with a lattice mismatch less than 0.08% at room temperature (RT). Fons et al.²⁰,²¹ conducted an investigation
of ZnO epitaxy growth on a-plane (1120) sapphire. The resultant residual carrier concentration was decreased to $6 \times 10^{16} \text{cm}^{-3}$ with electron mobility over 120 cm$^2$/V$\cdot$s$^{-1}$. AFM revealed a root-mean-square (RMS) roughness of less than 0.4 nm.

Considering the challenges of the substrate orientation and buffer layer, homoepitaxy of ZnO is the most efficient way to improve the overall properties of the Zn$_{1-x}$M$_x$O films. In principle, ZnO thin films can be epitaxially grown on single crystal ZnO substrates with reduced concentrations of threading dislocations, without contamination from the substrate, and without a thermal mismatch. However, only a few groups have reported on homoepitaxial growth of ZnO layers. This can be attributed to the current high price of ZnO substrates, and also insufficient knowledge about the surface preparation for epitaxial growth$^{22-24}$. High quality films can be obtained with even less than 2 nm roughnesses and are presented$^{23,25}$ and even with atomic flat surface$^{26-28}$.

2.1.3 Doping

Doping is a crucial factor for making high quality light emitters and photodetectors. For n-type doping, Zn or O atoms are substituted with atoms which have one more electron in the outer shell than the local atoms. Group III elements, aluminum, gallium and indium, are shallow and efficient donors by replacing Zn. Electron concentrations of $10^{20}$ cm$^{-3}$ have been obtained in Al-doped ZnO or Ga-doped ZnO, which even at room temperature result in a degenerate electron gas in the conduction band. The other option for n-doping would be to use Group VII elements to
replace the oxygen atom. However it has been less investigated for ZnO. For p-type doping, it was expected that the Group I and V elements are good acceptors by replacing Zn or O atoms with elements from Group I and V, respectively. Group I elements such as Li, Na, and K and also the Group Ib elements (Cu and Ag) are known as acceptors for ZnO. However, these acceptors might forms deep acceptors levels with ionization energies around a few hundred meV \(^{29,30}\), which would not be an efficient p type dopant. Group-I elements such as Li, may even form interstitials at high growth temperature due to their small atomic radii and thus behave like donors \(^{29,30}\). Elements like Na and K causes lattice strain, due to the larger bond length than that of Zn-O, resulting in defects such as donor-type vacancies. Most of the efforts are focused on p-type doping of ZnO with the Group V elements such as N, P, As, Sb, and Bi. It was found the hole concentrations by these p-type dopant were usually much lower than the dopant concentrations. This suggests that the dopant atoms not only form shallow acceptors, but also form deep acceptors and even donor type defects. Nitrogen is considered the best acceptor for p-type doping because of its shallow acceptor level predicted by theory \(^{31}\). LEDs with p layer of low hole concentrations \((10^{-16} \text{ cm}^{-3})\) was shown\(^{32}\). But no follow-up work has been shown for higher efficiency LEDs. Recent calculations based on density functional theory suggest that substitutional nitrogen is a deep acceptor\(^{33}\). P-type doping using nitrogen is hampered by a number of problems, some of which are a low solubility and the formation of complexes such as N\(_2\) and Zn\(_1\)-N\(_0\) which is donor type. A efficient p type doping requires breaking N\(_2\) species with plasma as much as possible to increase atomic nitrogen and reduce the density of molecular N\(_2\). Recently, Sb doping was demonstrated to be effective at p-type doping, although it may cause
large lattice distortions since the size of Sb is much larger than Zn or O atoms\textsuperscript{34,35}. LEDs based on p-type Sb-doped ZnO and n-type Ga-doped ZnO (ZnO:Ga) junctions with output power of 32nW at current of 60mA was demonstrated\textsuperscript{10}.

2.2 Characterization techniques

Characterization techniques for thin films are essential to determine the quality of the films. Generally, a high quality thin film should show good structural, morphological, optical and electrical properties. In our MBE system, there were two in situ measurements: RHEED and Laser Reflectometry. RHEED provides the crystal orientation and surface information during the growth. For example, the 2D growth usually shows straight lines on certain crystal orientation while the RHEED pattern for 3D growth has wider broken lines or spotty patterns\textsuperscript{18,19}. In Laser Reflectometry, the reflectance from the surface and the interface between the substrate and thin film is modulated by the thickness of the film due to the interference effect. The growth rate can be estimated by calculating the period of the oscillation.

After growth, more ex situ characterization methods are needed to determine the structural, morphological, and optical properties. Detailed information about these characterization techniques can be found easily on website or books\textsuperscript{36}. In brief, X-Ray Diffraction technique determines the crystal structure and orientation of the films by measuring full width of half maximum (FWHM) of the peaks observed and estimates the elemental compositions from the shifting of the peaks. Rutherford Backscattering (RBS) is used for compositional
characterization. Similarly, Secondary ion mass spectroscopy (SIMS) was also used to determine the composition, but also distribution of each element along the depth of the sample. Atomic Force Microscope (AFM) provides surface morphology by scanning the area under interest. Hall-effect measurement is used to test the electrical properties, whereas the carrier concentration, resistivity and mobility of carriers can all be obtained. PL measures the emission spectrum after optical stimulation. The spectrum provides the information about defects (and is enhanced by operation at extremely low temperature). By applying a pulsed laser as an excitation source, the system is called Time Resolved Photoluminescence (TRPL), which could even show the lifetime of the carriers and could be used to determine the defects more accurately.
3. CHAPTER THREE: MGZNO HETEROEPITAXIAL GROWTH

3.1 Introduction

Most effort focused on ZnO growth on sapphire is due to its relative low cost\textsuperscript{18}. However, there is a large in-plane lattice mismatch (18\%) between c-oriented (0002) ZnO and c-plane sapphire. Chen et al.\textsuperscript{18} reported the smallest full width at half maximum (FWHM) of x-ray diffraction (XRD) (0002) rocking curve (~18 arc sec). They found a 30° rotation in the crystal orientation of the ZnO epilayer on the sapphire substrate. MgO was used as a hetero-buffer between sapphire and the ZnO epi-layer to accommodate the lattice mismatch and eliminate the 30° rotation, thus improving the electrical and structural properties of the ZnO epilayers. Chu et al.\textsuperscript{37} demonstrated an epi-ZnO film with high mobility of 169.4 cm\textsuperscript{2}/VS and RMS roughness of 0.65nm, but with a broad FWHM XRD rocking curve (~200 arc sec). H\textsubscript{2}O\textsubscript{2} was used as oxygen precursor in MBE \textsuperscript{38}, resulting in a ZnO film with surface roughness of 0.2nm and FWHM of 30 arc sec. Most work demonstrating high quality ZnO optimizes one or two properties, while suffering with respect to other structural, optical or electrical properties. High structural, optical and electrical quality of ZnO films is necessary for ZnO LEDs with micro-watt output power. Here, we developed a low temperature growth method to obtain high quality ZnO thin films with low heat budget, high crystalline quality, low dislocation density, relatively high mobility and sub-nanometer surface roughness, suggesting possible efficient ZnO emitter growth on sapphire substrates.
3.2 Experimental procedure

ZnO was grown on (0001) α-Al₂O₃ (c-plane sapphire substrates) by plasma-assisted MBE³⁹. Base pressure in the growth chamber was ~2×10⁻¹⁰ Torr. Knudsen effusion cells were used to evaporate 6N-purity elemental Zn and 3N8-Mg with oxygen plasma generated by a radio frequency source at 13.6MHz. During the growth of ZnO layers, the pressure in the chamber was maintained around 3×10⁻⁶ to 5×10⁻⁶ Torr. To increase the homogeneity of heat conduction during the growth, 1µm of Titanium was deposited on the backside of the sapphire with a Temscal E-beam evaporation system (model FC-2000), as shown in Figure 2. The sample was thereafter degreased with iso-propanol and dried with a nitrogen gun. After this cleaning procedure, the substrate was immediately loaded on an indium free molybdenum holder and thermally cleaned at 600°C in a buffer chamber (10⁻⁹ Torr) for 4 hours before transferred to the growth chamber.

![Figure 2. Two inch Sapphire substrate with 1 µm Titanium deposition on the backside.](image)
Sapphire substrates pretreated with oxygen plasma have been reported critical for initial 2D ZnO growth in order to form an oxygen terminated surface\(^{18}\). Although the pre-treatment was largely used for growth of ZnO, the excess oxygen does accelerate the oxidation of metallic sources, i.e. Zn, in the MBE chamber especially when outgassing at high temperature under the oxygen environment, causing a measurable shift in the Zn flux over time. This, in turn, resulted in increased maintenance for the MBE chamber in order for replenishing the Zn source material. This oxidation during substrate pretreatment reduced the efficiency of growth and time between Zn source maintenances. Sapphire substrates discussed in this study were not treated with oxygen plasma, greatly improving the up-time of the system by reducing source oxidation and vacuum regenerative maintenance. The oxygen treatment may have not been necessary in this case because the sapphire substrates are already oxygen-terminated due to long exposure to air making the pre-treatment redundant.

3.3 **Optimization of growth conditions**

3.3.1 Growth rate calibration

In order to acquire the best quality of ZnO growth, prior literature suggests that the zinc and oxygen should be under stoichiometric conditions. Thus we first investigated and characterized the conditions for zinc and oxygen stoichiometry. The range of zinc and oxygen fluxes were determined by calculation of the growth rate changes versus the zinc and oxygen conditions, with growth rate being determined from laser reflectometry. The oscillation for one cycle corresponds to thickness change:
\[ d_T = \frac{\lambda}{2} \frac{1}{\sqrt{n_f^2 - \sin^2 \theta}} \]  

whereas the refractive index of the film \( n_f \) is 2.00337 for ZnO and 1.7375 for MgO; \( \theta \) is the angle between the laser beam and the substrates, which is 75°; \( \lambda \) is the wavelength of the laser beam (635 nm). For pure ZnO, the calculated thickness per cycle is \( d_T = 0.1809 \, \mu m \). One thing to note here is \( d_T \) is just an estimated value, since \( \theta \) is not always exactly 75° and the refractive index may change due to density of the films. Profilometer could be used for calibration of the calculated \( d_T \).

A growth rate calibration is needed for nucleation layer, which normally has a low growth rate. Figure 3 shows the reflectometry of ZnO low temperature (~350°C) growth with varied Zn cell temperature from 320°C to 355°C. One cycle was calibrated by profilometry to be 0.2 μm. The oxygen plasma power was fixed at 350 W. In the blue region, the oxygen flux was 2 sccm while in other region the flux was 1.5 sccm. The growth rate at oxygen flow rate of 1.5 sccm was obtained in Figure 4, which is almost linear relative to the Zn cell temperature.
Figure 3. Reflectometry of ZnO low temperature growth with varied Zn cell temperature. The oxygen plasma RF power was fixed at 350 W. The oxygen flow rate was 1.5 sccm except the blue region which is 2 sccm.

Figure 4. The growth rate v.s. Zn cell temperature with oxygen flux of 1.5 sccm and plasma power of 350 W at growth temperature of 350°C.

Then we need to calibrate the growth rate at high growth temperature of 510°C. Before that, a 25 nm ZnO nucleation layer was first grown and then annealed at 600°C for 10 minutes. The
oxygen plasma RF power was fixed at 350 W and the oxygen flow rate was 1.3 sccm. The resulted reflectometry curve is shown in Figure 5 and the corresponding growth rate is shown in Figure 6. The calibrated $d_T$ was 0.185 $\mu$m. Unlike growth of nucleation layer, we need higher Zn temperature in order to find the stoichiometric condition since a lot of work suggests stoichiometric condition is the best for ZnO growth on sapphire. It was found the stoichiometric condition at growth temperature of 510°C is Zn cell temperature between 370°C and 380°C, for oxygen flux of 1.3 sccm with RF power of 350W.

![Figure 5. Reflectometry of ZnO high temperature growth with varied Zn cell temperature. The oxygen plasma RF power was fixed at 350 W and the oxygen flow rate was 1.3 sccm.](image)
Figure 6. The growth rate v.s. Zn cell temperature with oxygen flux of 1.3 sccm and plasma power of 350 W at a growth temperature of 510°C.

3.3.2 Sequence of Zn and Oxygen

A good nucleation layer determines the quality of the growth. We first investigate the influence of the Zn source and Oxygen plasma source sequence on the surface morphology of ZnO films, as shown in Figure 7. The growth temperature was 350°C for nucleation and 600°C for ZnO high temperature growth layer. The Zn cell temperature was 360°C and oxygen flux was 1.5 sccm with RF power of 350W for nucleation layer. After 7 minutes growth of nucleation layer (about 25 nm thickness, we grew another high temperature (HT) growth layer on top of it. The Zn cell temperature was 350°C and oxygen flux was 1.3 sccm with RF power of 350W. The root-mean-
Figure 7. 5 μm× 5 μm AFM images of ZnO films grown on sapphire with (a) Zn source shutter open for 3 seconds before opening Oxygen source shutter , (b) Zn and O shutter open at the same time and (c) O source shutter open for 3 seconds before opening Zn source shutter.

square (RMS) roughnesses for Figure (a)-(c) were 6.93 nm, 9.31 nm, and 14.0 nm, respectively. It was found with Zn source shutter open for 3 seconds before opening Oxygen source shutter resulted in the best morphology. One explanation for this is the sapphire substrates should be oxygen terminated even when we don’t apply any oxygen plasma treatment. With Zn source opened first, Zn could form a good nucleation with about one atomic height step on oxygen terminated surface of sapphire and thus results a better morphology.

3.3.3 Growth temperature

Most literatures have investigated the influence of growth temperature of the high-temperature (HT) growth layer on the properties of the films, without paying much attention to the influence of the temperature of low-temperature (LT) nucleation layer\textsuperscript{18,38}. To optimize the growth conditions, we studied the influence of the growth temperature on both HT growth layer and LT nucleation layer, as shown in Figure 8. We applied $T_{HT}$ from 450°C, since too low temperature
was not expected to provide good crystallinity. The growth procedure was same as mentioned before, except varying the growth temperatures. The relationship between RMS roughness and the growth temperature is shown in Figure 9.

![AFM images of ZnO films](image)

Figure 8. 5 μm× 5 μm AFM images of ZnO films under different growth temperature for low temperature nucleation ($T_{LT} = 300^\circ C$) and high temperature growth layers ($T_{HT}$).

<table>
<thead>
<tr>
<th>$T_{LT} = 300^\circ C$</th>
<th>$T_{HT} = 450^\circ C$</th>
<th>$T_{HT} = 500^\circ C$</th>
<th>$T_{HT} = 550^\circ C$</th>
<th>$T_{HT} = 600^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{HT} = 450^\circ C$</td>
<td><img src="image" alt="Image" /> (a)</td>
<td><img src="image" alt="Image" /> (b)</td>
<td><img src="image" alt="Image" /> (c)</td>
<td><img src="image" alt="Image" /> (d)</td>
</tr>
<tr>
<td>$T_{HT} = 500^\circ C$</td>
<td><img src="image" alt="Image" /> (e)</td>
<td><img src="image" alt="Image" /> (f)</td>
<td><img src="image" alt="Image" /> (g)</td>
<td><img src="image" alt="Image" /> (h)</td>
</tr>
<tr>
<td>$T_{HT} = 550^\circ C$</td>
<td><img src="image" alt="Image" /> (i)</td>
<td><img src="image" alt="Image" /> (j)</td>
<td><img src="image" alt="Image" /> (k)</td>
<td><img src="image" alt="Image" /> (l)</td>
</tr>
<tr>
<td>$T_{HT} = 600^\circ C$</td>
<td><img src="image" alt="Image" /> (m)</td>
<td><img src="image" alt="Image" /> (n)</td>
<td><img src="image" alt="Image" /> (o)</td>
<td><img src="image" alt="Image" /> (p)</td>
</tr>
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</table>
It was found higher growth temperature for LT nucleation layer $T_{LT}=350^\circ$C provides better morphology in general. Since the temperature already provided good morphology and the growth temperature for LT nucleation is not as crucial as that for HT layer, we didn’t investigate higher temperature for nucleation layer. A lot of literatures applied temperature for HT layer up to 700$^\circ$C. This is not the case here, as shown in Figure 8, the surface morphology deteriorated at
temperature above 550°C. From Figure 9, the best growth conditions is $T_{LT}=350°C$ and $T_{HT}=500°C$. It’s worth noting that the optimized condition is only for surface morphology. This condition does not necessarily mean good quality for other properties of the films, which we will discuss later. Since the lattice mismatch of ZnO and sapphire, there are always large dislocations found in the films. As shown in the inset of Figure 9, although both films showed good surface RMS roughness and even terrace steps were observed, there were lots of pits in the films growth with the best conditions under $T_{LT}=300°C$. However, the number of pits was largely reduced for the best growth condition under $T_{LT}=350°C$, which suggests high $T_{LT}$ reduce the number of defects.
3.3.4 Zn flux

We found the stoichiometric condition for ZnO films at growth temperature of 500°C is: Zn cell temperature of 370°C to 380°C with oxygen flux of 1.3 sccm and RF power of 350W, from Figure 6. Since most of the literature concludes the best growth happens at stoichiometric
condition, we started to investigate the Zn cell temperature at the stoichiometric point, in our case, with Zn cell temperature of 378°C. The AFM image was not as good as we expected, as shown in Figure 10 (d), with RMS roughness of 6.13 nm. This implies that we might need more oxygen rich condition. So we decreased the Zn cell temperature as shown in Figure 10. The roughness was largely improved at Zn cell temperature below 365°C and clear terraces were observed. We choose 350°C for Zn cell temperature in the following, since it provides a good morphology and higher Zn cell temperature accelerates the oxidation of the Zn cell.

3.4 Growth of ZnO

3.4.1 Typical growth conditions

After we did a systematic optimization of the growth conditions, we grew several films with the optimal conditions above. The typical growth conditions are listed in Table 2. The deposition of ZnO was monitored in situ by reflection high-energy electron diffraction (RHEED). Same as growth of GaN on sapphire that high quality films can be obtained by using a low temperature nucleation layer, a low temperature (LT) ZnO nucleation layer was first grown at 350°C on the sapphire substrate to act as nucleation layer.
Table 2. Typical growth conditions for ZnO

<table>
<thead>
<tr>
<th></th>
<th>Nucleation Layer</th>
<th>ZnO epi-layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth Temperature</td>
<td>350°C</td>
<td>500°C</td>
</tr>
<tr>
<td>Zinc temperature</td>
<td>360°C</td>
<td>350°C</td>
</tr>
<tr>
<td>Oxygen flow rate/Power</td>
<td>1.5sccm/350W</td>
<td>1.3sccm/350W</td>
</tr>
<tr>
<td>Growth rate</td>
<td>0.21μm/h</td>
<td>~0.15μm/h</td>
</tr>
<tr>
<td>Thickness</td>
<td>25nm</td>
<td>/</td>
</tr>
</tbody>
</table>

A growth rate around 0.21μm/h was achieved for nucleation layer as monitored by Laser reflectometry. Because the sapphire is oxygen terminated, Zn is preferred to form on the surface to combine with oxygen and thus have better migration ability. The Zn shutter was opened first for 3 seconds followed by the oxygen shutter. This sequence reliably generated terrace-step morphology. After 7 minutes, a 25 nm ZnO nucleation was formed on the substrate. The RHEED pattern of the nucleation layer, shown in Figure 11 (a), was initially spotty, indicating a roughening of the growth surface. The pattern gradually became a sharp streaky [Figure 11 (b)] pattern after annealing at 600°C for 30 minutes, indicating the nucleation layer was clean and flat after the annealing process. A subsequent high temperature (HT) ZnO layer was grown above the nucleation layer at 500°C. The Zinc and oxygen were kept at oxygen rich conditions at a low flux to assure a slow growth rate for HT ZnO layer, in this case, 0.15μm/h. This HT regime allowed for homogeneous diffusion of the adatoms and prevention of 3D growth. The RHEED
pattern after 500 nm HT layer was clearly streaky, indicating 2D growth, as shown in Figure 11 (c).

3.4.2 Characterizations

As shown in Figure 12, through optimization efforts we were able to demonstrate ZnO epitaxy with obvious terrace steps. The roughnesses was 0.938 nm for 5 μm × 5 μm AFM image and 0.384 nm for 1 μm × 1 μm. There were no pits observed on the AFM images, indicating fewer defects through the films. The triple-crystal $\omega$-$2\theta$ RC in the vicinity of ZnO (0002) reflection [Figure 13 (a)] is a smooth slightly asymmetrical (on the lower angle side) curve without interference fringes, with FWHM = 26 arc/s, corresponding to 640 nm vertical coherence length of the layer. This length is less in comparison with the total thickness of epitaxial layer ~ 940
Figure 12. AFM images of ZnO with roughness of: (a) 0.938 nm for 5 μm × 5 μm and (b) 0.384 nm for 1 μm × 1 μm.

nm, based on technological evaluation. ZnO 2θ angle peak position on the ω-2θ RC indicates that the elastic stress in this layer is almost fully relaxed by creation of edge dislocations.

All noted features clearly demonstrate an existence of closed dislocation loops with edge segments in the volume of epitaxial layer\textsuperscript{40}, created at the final stage of the defects creation procedure, after appearance of open dislocation loops and edge dislocations on the interface\textsuperscript{41,42}. These closed dislocation loops appear due to the structural transformation of point defects, continuously creating on the growth front: diffused inward and accumulated in pre-dislocation clusters above the interface, these point defects induce secondary elastic stress at the bottom of the layer, which finally transform accumulated point defects to closed dislocation loops\textsuperscript{41,42}.  

28
The density of created dislocation loops depends on the number of point defects, created on the growth front, i.e. perfection of growth conditions, and the energy of structural transformation of pre-dislocation clusters to dislocation loops, i.e. elastic properties of ZnO. The final length of these loops is determined by the duration of the growth procedure after nucleation of dislocation loops.
Figure 13. (a) triple-crystal $\omega$-2$\theta$ RC in the vicinity of ZnO (0002) reflection. Visual asymmetry of the RC is related to additional compressed elastic stress, induced by pre-dislocation clusters and closed dislocation loops; (b) triple-crystal $\omega$ RC of ZnO (0002) reflection. The inset is the magnified graph in the dashed area.
The thickness of the bottom sub-layer, filled out by closed dislocation loops may be roughly evaluated by the difference between the total thickness and the vertical coherence length of the layer, derived from the FWHM of the $\omega-2\theta$ layer peak. The left-side asymmetry of the $\omega-2\theta$ RC is related to additional compressed elastic stress, induced by pre-dislocation clusters and closed dislocation loops$^{43}$.

The triple-crystal $\omega$ RC measured on the maximum of the ZnO (0002) peak [Figure 13 (b)] is a convolution of the narrow curve (FWHM $= 13.3$ arc/s) and a wide diffuse base, related to the bottom structurally deteriorated sub-layer with a FWHM of $\sim 120$ arc/s. The FWHM of the (0002) ZnO peak (13 arc/s) is below the highest crystallinity reported to date in the literature (18 arc/s)$^{19}$. A LT nucleation layer is crucial on the interfacial region to absorb these defects and produces a smooth surface that enables the following 2D epitaxial growth. The RHEED pattern for nucleation layer indicates the morphology of the initial annealed growth is smooth, allowing the subsequent growth of a high quality epilayer. Direct evaluation of the density of dislocation loops from the FWHM of these peaks (narrow curve and wide diffuse base in Figure 13 (b) yields values of $\sim 1.7 \times 10^5$ cm$^{-2}$ and $1.6 \times 10^7$ cm$^{-2}$, respectively$^{44,45}$. Based on our understanding, the second number correlates specifically with the density of closed dislocation loops at the bottom of the layer, while the FWHM of the narrow central coherent peak directly correlates with the lateral coherence length ($\sim 4 \mu$m in this case), and not the density of dislocation loops$^{46}$. The narrow width of the central $\omega$ RC peak correlates with the crystalline perfection of ZnO layer, but not directly, real more complicated situation is described below$^{46,47}$. 31
Typical ZnO layer grown on Sapphire substrate has open primary and secondary threading dislocation loops (most probably, screw type), created at the initial stages of epitaxial growth. Created, these dislocation loops penetrate through entire epitaxial layer, following from the bottom interface to the growth front. In highly lattice-mismatched epitaxial structures the total density of these dislocation loops may be roughly evaluated $\sim 10^8$ cm$^{-2}$. True screw dislocation loops have no edge segments in the volume of epitaxial layer and do not affect vertical coherence of epitaxial layers (do not increase FWHM of the $\omega$-2$\theta$ RC). At rather low density they also do not affect lateral coherence of epitaxial layer and do not increase FWHM of the central coherent peak of the $\omega$ RC.

Edge dislocations appear on the interface immediately after creation of primary and secondary dislocation loops as a part of chain defects creation procedure to almost fully accommodate initial elastic strain and fully relax initial elastic stress. Despite the high density of these dislocations ($\sim 10^6$ cm$^{-1}$ or even more), located on the interface, they do not affect vertical and lateral coherence of epitaxial layers and do not increase FWHM of the $\omega$-2$\theta$ and $\omega$ RCs. Edge dislocations do not deteriorate ad-atoms migration on the growth front and do not deteriorate 2D epitaxial growth mode.

The creation of closed dislocation loops in the volume of the layer, just above the interface, is a final stage of defects creation process. But appearance of these ramified loops in the volume of
the layer may be significantly postponed by perfect growth condition, which slows down accumulation and transformation of point defects at the bottom of the layer\textsuperscript{42,43,48,49}. Created, closed dislocation loops rise up, following to the growth front with the lag, specified by growth conditions and elastic properties of epitaxial layer. In case of GaN layer it may reach 900 – 1000 nm\textsuperscript{50,51}, in case of AlN ~ 200 – 250 nm\textsuperscript{48,49}. The density of closed dislocation loops is \(\sim10^8\) cm\(^{-2}\), but usually they are non-homogeneously distributed in the volume of the epitaxial layer and can create a kind of dislocation clusters with large spaces between them, mostly free of extended crystalline defects. Overlapped, these defect-free areas may affect both, vertical and lateral coherences of epitaxial layers, or just vertical coherence of the layers. Elongation of x-ray radiation diffuse scattered around ZnO (11-24) diffraction spot along Q\(x\) direction instead of \(\omega\) direction (Figure 14) is related to the lateral correlation of closed dislocation loops and anisotropic distribution of induced elastic stress in the volume of ZnO layer\textsuperscript{51}. To directly confirm the suggested types, density and spatial distribution of crystalline defects, conventional cross-section TEM is desirable.
3.5 Growth of MgZnO

We have investigated different growth temperature from 370°C to 500°C for MgZnO and found the best growth temperature for is 430°C. This is consistent to several reports stating that reducing the growth temperature for MgZnO compared to ZnO growth improves the Mg incorporation and film quality. The resultant morphology (with very low Mg composition) is shown in Figure 15, with roughness of 0.497 nm which is a little higher than ZnO. We expected the roughness would deteriorate if the Mg ratio is higher since MgO is cubic structure while ZnO is wurtzite structure. More research work is needed to investigate the impact of Mg composition on the morphology.
Figure 15. AFM images of MgZnO with roughness of 0.497 nm for 1 μm × 1 μm

Table 3. Growth condition of MgZnO/ZnO/sapphire.

<table>
<thead>
<tr>
<th>Thickness by Reflectometry</th>
<th>ZnO nucleation</th>
<th>ZnO buffer</th>
<th>MgZnO epilayer</th>
</tr>
</thead>
<tbody>
<tr>
<td>20nm</td>
<td>200nm</td>
<td>335nm</td>
<td></td>
</tr>
<tr>
<td>T_{GM}</td>
<td>350</td>
<td>500</td>
<td>430</td>
</tr>
<tr>
<td>T_{Zn}</td>
<td>360</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>F_{O2}</td>
<td>1.5sccm/350W</td>
<td>1.3sccm/350W</td>
<td>1.3sccm/350W</td>
</tr>
<tr>
<td>T_{Mg}</td>
<td>-</td>
<td>-</td>
<td>335</td>
</tr>
</tbody>
</table>
Figure 16. RHEED patterns of (a) Nucleation layer; (b) Annealing at 600°C for 5 minutes; (c) 200 nm ZnO buffer and annealed at 600°C for 10 minutes; (d) MgZnO and (e) MgZnO after baking at 500°C.
Rutherford Backscattering for MgZnO which shows Mg to Zn+Mg ratio is 9%.

The Mg concentration herein for MgZnO was 9% confirmed by Rutherford Backscattering, as shown in Figure 17. The growth condition for MgZnO is listed in Table 3 and the RHEED patterns during the growth were shown in Figure 16. It was observed that the RHEED pattern is streaky and straight after the growth, indicating good 2D growth.

The ω rocking curve (Figure 18) indicates the FWHM of the fitted curves were 17.5 arc sec and 548 arc sec, respectively. This suggests the primary dislocation loops is $N_{Pr.Disl.Loops} = 3.6 \times 10^5 \text{cm}^2$ while the secondary dislocation loops $N_{Sec.Disl.Loops}$ from $3.5 \times 10^7 \text{cm}^2$ (at the top) up to $3.1 \times 10^8 \text{cm}^2$ (at the bottom of the layer). Adding of Mg to solid solution noticeably affected crystal perfection of the epitaxial layers. Deteriorated crystal perfection for MgZnO significantly
affected shape and parameters of $\omega$ rocking curves and hence increased $Q_x$ width of both (0002) and (11-24) RSMs as shown in Figure 20 and Figure 21. This deterioration visually changed spatial distribution of diffracted spot on (11-24) RSM (elongation, related to $Q_x$ direction). We also did a photoluminescence on this film with a He-Cd laser (Figure 19), and a strong near-band-edge (NBE) emission at around 370 nm attributed to direct recombination of photogenerated carriers near the band edge is observed. The intensity of green band related to defects is relatively small, indicating that resultant films are of high optical quality with few oxygen vacancies/intrinsic defects which is suitable for device application. To further suppress this green band, purer Mg is required (99.98%) in the future for the light emitter applications.

Figure 18. $\omega$ rocking curve of ZnO/sapphire.
Figure 19. Photoluminescence of MgZnO/ZnO/sapphire

Figure 20. Reciprocal space mapping (RSM) of ZnO (11-24) for (a) ZnO and (b) MgZnO films grown on sapphire.

Figure 20. Reciprocal space mapping (RSM) of ZnO (11-24) for (a) ZnO and (b) MgZnO films grown on sapphire.
High Mg composition is crucial to achieve heterostructure for LEDs, but suffers from phase segregation when Mg composition is higher than 37%. By carefully designing the experiment parameters, we have achieved MgZnO layers with up to 46% of Mg as shown in Figure 22, with Cathodoluminescence (CL) spectra together with the results of optical transmission measurements. It can be seen that wurtzite $\text{Mg}_{0.46}\text{Zn}_{0.54}\text{O}$ layers have optical band of approximately 280nm, which is suitable for solar blind application. The transmission shows very
steep absorption edge and no other absorption edge was found, indicating no inclusions of cubic phase. This is verified by XRD characterization, which only shows (002) peaks of single crystal wurtzite $\text{Mg}_0.46\text{Zn}_{0.54}\text{O}$ epitaxial layers, as shown in Figure 23. It’s also worth to note that the grown $\text{Mg}_{0.46}\text{Zn}_{0.54}\text{O}$ layers had very low background concentration of $5 \times 10^{16}/\text{cm}^3$ which is beneficial for p-type doping and has the electron mobilities of $58 \text{ cm}^2/(\text{V·s})$. This intrinsic conductivity might be one of the reason that wurtzite MgZnO shows at least four orders magnitude higher of the photoresponsivity than that of cubic MgZnO in the solar blind region.

Figure 22. Room temperature cathodoluminescence (solid lines) and optical transmission (dashed lines) of MgZnO with Mg mole content from 0 to 46%.
Figure 23. XRD of (002) peak of Mg$_{0.46}$Zn$_{0.54}$O epitaxial layer.

Figure 24. AFM images of Mg$_{0.08}$Zn$_{0.92}$O with (a) and without (b) ZnO high-temperature. The RMS roughness is 0.206 nm (a) and 7.49 nm (b) for 1μm×1μm area.
Although the surface roughness does not influence the performance of photodetectors, a high quality films with good morphology is crucial for light emitters. We optimized the growth conditions for MgZnO and the morphology was found much better if we applied a high-temperature (HT) ZnO buffer layer first. Figure 24 (b) shows the AFM image for \( \text{Mg}_{0.08}\text{Zn}_{0.92}\text{O} \) with only regular low-temperature ZnO nucleation layer, where the surface RMS roughness is 7.49 nm. After applying a 200 nm HT ZnO buffer, as shown in Figure 24 (a), the surface morphology was significantly improved and the RMS roughness is only 0.206 nm, with clear aligned terrace steps and without any pits on surface.

3.6 Doping

To achieve efficient light emitters, n type doping and p type doping with high crystallinity and tunable electron/hole carrier concentrations are crucial. As mentioned in Chapter Two, group III elements are potential dopant for ZnO and among them, Al and Ga are proved to achieve a high carrier concentration with reasonable mobility\(^{52,53}\). In this study, we chose Ga for n-type doping of ZnO since the length of the covalent bond of Ga-O (1.92 Å) is closer to that of Zn-O (1.97 Å) than that of Al-O (2.7 Å).
Figure 25 and Figure 26 show the carrier concentration, mobility, resistivity and roughness as a function of Ga cell temperature for both ZnO and MgZnO (9% Mg) grown on sapphire. We successfully controlled n-type up to $4 \times 10^{19} / \text{cm}^3$ while maintaining a relatively high mobility above 60 cm$^2$/Vs. It was reported that as more Ga incorporated to the film, the mobility deteriorates. This is not the case here, as shown in Figure 25; the mobility does not deteriorate at all as the Ga cell temperature increases, indicating good electronic transport properties.
Figure 26. Resistivity and Roughness as a function of Ga cell temperature for both ZnO and MgZnO (9% Mg). For undoped ZnO, the roughness was about 0.678 nm and resistivity is 0.15233 Ohm·cm.

The RMS roughness, however, increased a lot by doping with Ga cell temperature above 500°C. Further optimization is needed to generate a relatively smooth surface for the doping layer.

We also investigated the crystallinity of doped films by XRD for on axis and off-axis scans. FWHM of these rocking curves indicate the dislocation densities. Extrapolation of FWHM value for a rocking curve rotated 90 degree from the surface normal (impossible to measure in practice) can be used to calculate edge dislocation density (twist), while the on axis scan is indicative of screw dislocations (tilt). Low screw dislocation density implies well ordering in the
growth direction while low edge dislocation density means high disordering in the c-plane. A shown in Figure 27, the (0002) is on axis scan (indicative of screw dislocations) and by fitting the curve with 90 degree orientation we would obtain the edge type dislocations. Figure 28 shows the FWHM for tilt and twist under difference Ga cell temperatures. The tilt corresponds to (0002) scan, indicative of screw type dislocations; while twist corresponds to the extrapolation of FWHM for a rocking curve rotated 90 degree from (0002) direction, indicating edge type dislocations. It’s observed that the density of edge type dislocation is much higher than the density of screw type dislocation. This is due to the large in plane lattice mismatch between the sapphire and epitaxial films. To suppress this dislocation, we need latticed matched substrates as discussed in next chapter.

Figure 27. FWHM of ω rocking curves with different orientation of scan.
In summary, we have successfully grown high quality ZnO and MgZnO on sapphire substrates. Resultant films have the highest demonstrated quality as compared to known published results. The growth temperature, sequence of Zn and O source shutter, and Zn/O ratio for both ZnO nucleation and buffer layer growth was optimized on sapphire, resulting in RMS roughness values down to 0.373 nm for 1 μm². Several characterization methods have been applied to reveal the quality of the epitaxial films. The FWHM for (0002) peaks was measured to be 13 arc sec and 17.8 arc sec for ZnO and MgZnO, respectively, indicating good ordering in the growth direction. The RSM provides some evidence of deterioration of crystal structure while doping with Mg. Ga doping was also demonstrated carrier concentration up to 4×10¹⁹ cm⁻³ with high motilities above 60 cm²/Vs. The large lattice mismatch between the substrates and epitaxial films.
caused relatively large edge-type dislocations all through the films. Lattice matched substrates are needed such as native ZnO, as discussed in the next chapter.
4. **CHAPTER FOUR: ZNO HOMOEPITAXIAL GROWTH**

4.1 **Introduction**

Although most ZnO epitaxial layers grown by molecular beam epitaxy (MBE) have been carried out on c- and a-plane sapphire substrates, the large lattice mismatch and thermal expansion coefficient mismatch between ZnO heteroepitaxial films and the sapphire substrates cause a high dislocation density of larger than $10^9$ cm$^{-2}$, leading to various kinds of donor-type defects. Such high residual carrier concentration ($\sim 10^{17}$ cm$^{-3}$) deteriorates the electron transport properties and makes the growth of p-type ZnO challenging. ScAlMgO$_4$ (SCAM) was thus applied to substitute sapphire as lattice-matched substrate for ZnO (0.09% mismatch) and nitrogen-doped p-type ZnO films have been successfully achieved by a repeated temperature modulation technique$^{32,55}$. However, SCAM substrates have several critical shortcomings: they are not commercially available and cleaving is difficult since the substrates easily peel off along the c-plane$^{56}$. Recently, single crystalline ZnO substrates have been grown by the hydrothermal method$^{57-59}$, providing a route to significantly suppress the defects caused by lattice and thermal mismatches. In this chapter, we have developed a relatively low temperature growth to obtain high quality ZnO thin films for efficient ZnO light emitter on ZnO substrates.
4.2 Experimental procedure

The ZnO homoepitaxial films were directly grown on Zn-polar ZnO substrates by PAMBE, using a radio-frequency (RF) oxygen plasma as the O source \( f_0 = 13.56 \text{ MHz} \), equipped with an electrostatic ion trap (EIT). Elemental Zn (6N) was evaporated from standard hot-lipped Knudsen cell. Oxygen flux was varied between 1.5 and 2 sccm and RF power was varied between 250W to 400W. Zn cell temperature was adjusted from 330°C to 360°C at a fixed growth temperature ranging from 580°C to 800°C. The chamber pressure during growth ranged from \( 5 \times 10^{-6} \) to \( 1 \times 10^{-5} \) Torr, depending on the Zn and O flux. The films were grown on single-crystalline (0001) ZnO substrates grown by hydrothermal method (Tokyo Denpa Co., Ltd). The Zn-polar surface was chosen for growth, since it has been reported that the RT excitonic emission from films grown on the Zn-polar face is 30 times stronger than that on O-polar surface and nitrogen incorporation (for p-type doping) is more efficient on the Zn-polar face. The substrates were cleaned using a hydrochloric acid solution for 30s to remove surface contaminations such as silica gel, and then rinsed in ultrasonic baths of acetone, isopropyl alcohol, and deionized water. Prior to growth, substrates were thermally cleaned at 700 °C for 30 minutes in an ultra-high vacuum chamber (~2×10^{-10} Torr). The thickness of the ZnO films in this study ranged from 300nm to 600nm.

The surface morphology of the homoepitaxial ZnO films was inspected by a Veeco Dimension 3100 atomic force microscope (AFM). The thickness of the film was measured by standard profilometry. X-ray diffraction (XRD) measurements were made with a Philips Panalytical Pro
Materials Research Diffraction system. Time-resolved photoluminescence (TRPL) measurements were carried out at RT using a doubled optical parametric amplifier operating at 250 kHz and giving ~100 fs pulses at 325 nm and with a fluence of 440 µJ/cm². Data was collected at the PL peak with a 10 nm bandwidth using a time-correlated single photon counting technique with ~30 ps resolution.

### 4.3 Optimization of growth conditions

#### 4.3.1 Substrates

A few works have been done to optimize the growth conditions of ZnO homoepitaxial films grown on miscut ZnO substrates, specifically Zn-polar ZnO substrates with a miscut angle of 0.5° toward the [11̅00] direction \(^{28,56}\), since it was found that miscut ZnO substrate is beneficial to achieve ZnO films with atomic flat surface with one or two atomic height \(^{28,56}\). Yet growth on non-miscut ZnO substrates has not shown such step-and-terrace surface morphology and the surface root mean square (RMS) roughness is also larger compared to the growth on miscut substrates \(^{63-66}\). There are also other problems for growth on non-miscut ZnO substrate: pits were generated during the growth. Y. Sawai et. al attributed this to different numbers of dangling bonds per edge atom on two types of edges \(^{67}\), as shown in Figure 29. Since the ZnO surface is usually terminated by O atoms, the step edge is stable along the m-plane, whereas only O atoms construct this termination edge. As a result, one type of edge has two dangling bonds while type B edge has only one dangling bonds per edge atom.
Since more dangling bonds tend to bond with Zn more easily, type A edge will grow faster and thus results in pits/defects on the surface. Herein most of our work is focus on growth on Zn-polar ZnO substrates with a miscut angle of 0.5° toward the [11̅00] direction. Yet no one have successfully grown atomic flat surface on non-miscut ZnO substrates, we will demonstrate excellent growth on non-miscut samples after optimizing the growth condition at the end.

4.3.2 Surface Morphology

The quality of the epitaxial films includes structural, optical, electrical and morphological properties. Among them, morphology is the first option we need to optimize. We first tried to grow ZnO on Zn-polar ZnO substrates with the optimized conditions we identified for ZnO on sapphire. We found the resultant films were very rough with a growth rate three times faster than growth on sapphire. This is because each O atom on a Zn-polar ZnO surface has three dangling bonds along the c-axis, while each O atom on an O-polar ZnO surface has just one dangling bond along the c-axis\(^6\). It was clear that the surface mobility and growth kinetics of homoepitaxial
ZnO is very different than that on sapphire, and the high growth rate likely causes the surface roughing due to 3D growth.

We later found from recent publications that it is preferred to grow under O-rich or stoichiometric conditions on ZnO substrates\textsuperscript{28}. Under O-rich conditions the Zn-polar surface should be smooth because Zn adatoms bonded to O atoms on O-terminated surface are stable due to three bond configuration. In contrast, under Zn-rich conditions, the surface can become rougher from 3D growth because the Zn adatoms bonded to O atoms are unstable. Unfortunately, after we tried growing under O-rich conditions with all other conditions same as growth on sapphire, the surface morphology is still not improved a lot. Realizing we needed to improve the surface quality, better zinc migration was required to shift from 3D growth to 2D growth. To achieve this, we increased the growth temperature from 500°C to 700°C while remaining under oxygen rich conditions. This was successful with a greatly improved surface morphology and terraces, as shown in Figure 30. However, this surface morphology is still not satisfactory, further optimization is needed. One thing worthy to mention here is we hadn’t optimized all the growth condition yet at this point, especially no surface preparation was applied to the substrates.
We also tried titanium deposition on the back side (O polar face) of ZnO substrate for better heat conduction homogeneity. In this way, we were able to reduce the growth temperature from 700°C to lower than 600°C. Figure 31 shows the AFM for c-plane ZnO with 0° and 0.5° miscut towards m-plane. It was observed although the roughnesses were improved, there are still large pits for non-miscut samples [Figure 31 (a)] and the bunched steps observed for miscut samples [Figure 31 (b)]. Although Ti coating reduced the growth temperature, it was found that the color of the Ti coated side changes and the Ti thickness was reduced to more than half of its original value. This is probably because during several hours’ growth, the Ti evaporates or peels while reacting with oxygen and ZnO substrate under O rich condition. The photoluminescence shows two peaks located at 377nm (ZnO) and 405nm, as shown in Figure 32. The peak at 405 nm may
be related to ZnTiO$_3$ which has a bandgap at 3.06eV. All these problems may cause the heat inhomogeneity for the growth after. Therefore, we continued growing without Ti coating.

Figure 31. AFM images: (a) ZnO (C plane with no miscut to m-plane) with roughness of 0.297nm; (b) ZnO (C plane with 0.5° miscut to m-plane) with roughness of 1.23nm.
4.3.3 Preparation of substrates

In previous discussions, surface preparation only includes rinsing with acetone, isopropanol and de-ionized water, which could help to remove the organic contaminations on the surface. However, this kind of surface preparation was not enough to clean the surface contaminations of ZnO substrates such as inorganic particles and thus resulted in a low quality surface. A well-defined substrate surfaces should satisfy the following requirements \(^{62,68}\): (1) no metallic and other particles exists on the surface, (2) surface degradation after polishing should be removed, and (3) atomic flat surface should be achieved. There are usually several steps for the manufacture to process single crystalline (0001) Zn-polar ZnO substrates: chemo-mechanically
polishing (CMP), high temperature annealing and CMP. Silica particles was found captured by Zn(OH)$_2$ on the ZnO surface originating from alkaline polishing solution during CMP. Since Si is known as a good donor in ZnO and it might migrate into the epitaxial film during growth, careful wet etching should be applied to remove the Si residual.

The etching of ZnO substrates has been studied by several literatures. Too long etching causes hexagonal pits on surface (Figure 33) and too short etching causes incomplete removal of Silica residual. We etched the substrates by a hydrochloric acid solution (pH = 0.024) for 30 s, rinsed in ultrasonic baths of acetone, isopropyl alcohol and deionized water, exposed to UV-ozone for 5 minutes and then immediately loaded into the chamber.

![Figure 33. 3 minute etching of ZnO substrates](image)
The UV-ozone exposure here was used to remove the carbonate groups (CO$_3$ groups) and carboxyl groups (-COOH groups) which causes an abnormality of the substrate surface and in turn deteriorates the flatness of epitaxial film.

Figure 34 (a) shows the AFM image for ZnO epilayer grown on ZnO substrates after etching$^{72,73}$. The surface is very rough with root mean square (RMS) roughness of 9.31 nm. Since Zn-polar surface is more chemically inert than O-polar surface$^{70}$, the O-polar surface could be very rough and inhomogeneous during the etching for Zn-polar surface, as shown in Figure 35. To improve the surface morphology, we protect the O-polar surface with photoresist during etching process [Figure 34 (b)]. The surface morphology was greatly improved (RMS roughness of 0.307 nm) with step height of 0.26 nm or 0.52 nm aligning the [1100] direction, corresponding to one or two monolayers of ZnO along c-axis.

![AFM images](image)

Figure 34. AFM images (5 × 5 μm$^2$) of ZnO films grown after etching the substrates (a) without and (b) with protecting O-polar surface.
To further investigate the influence of surface treatment on the quality of epitaxial films, we grew several films with and without surface treatment before optimizing the growth conditions. Figure 36 is the box-and-whisker plot for PL lifetime of several ZnO films grown on ZnO substrates at growth temperature of 640°C. It is obvious that the PL lifetime with etching of substrates were higher, with median values for samples without and with etching of substrates of 34 ps and 71 ps, respectively. This indicates the Si and other contaminations on the surface may migrate into films and forms donor-type point defects during the growth, which deteriorate the PL lifetime. With the etching treatment, the density of these contaminations was reduced and thus PL lifetime was improved.
4.3.4 Impact of Oxygen source parameters

Great effort has been applied to improve the quality of the ZnO homoepitaxy by studying the impact of the miscut angles\textsuperscript{28}, buffer layers\textsuperscript{66}, polarization of the substrates\textsuperscript{64}, growth temperature\textsuperscript{23,28} and flux ratio of the elemental sources\textsuperscript{28,64}. However, no literature has yet reported on the impact of oxygen for ZnO homoepitaxy on the surface morphology, structural properties and optical properties. Most literature reports on homoepitaxy growth with a high oxygen flux of 3 standard cubic centimeters per minute (sccm) at high growth temperature (above 800°C) and they are able to achieve step flow growth through an increase in surface migration length\textsuperscript{28}. However, there are several challenges with these growth conditions. First, high growth temperature restricts N incorporation for p-type doping of ZnO, since the sticking coefficient of N atoms is inversely proportional to the growth temperature\textsuperscript{74}. Second, high
growth temperature also accelerates deterioration of the substrate heater, especially for growth in a high oxygen flux environment. Third, since ZnO homoepitaxial growth happens at an O-rich condition, high oxygen flux promotes the oxidation of metallic sources. Therefore, growing in a low temperature range with a reduced oxygen flux is highly beneficial for ZnO homoepitaxial growth by MBE. To date, there are very few publications\textsuperscript{64,66} reported on low temperature growth of ZnO homoepitaxy, and none of these have demonstrated terrace steps and good photoluminescence (PL) lifetime.

Figure 37(a) – (c) shows the surface morphology evolution grown under different Zn flux at fixed oxygen flux (1.5 sccm) and RF power (300W)\textsuperscript{72}. The growth temperature was 610°C. The root mean square (RMS) roughnesses for (a) – (c) were estimated to be 8.8nm, 2.44nm and 0.379nm, respectively. Very dense hexagonal pits or holes were formed on the surface as shown in Figure 37 (a), indicating higher Zn flux (T_{Zn}=350°C) causes surface roughening due to 3D nucleation and growth. Figure 37 (b) shows better morphology by applying less Zn (T_{Zn}=340°C), but with large terrace steps of about 4.4 nm in height, suggesting step bunching at the terraces.
Under lower Zn conditions ($T_{Zn}=330^\circ C$), in Figure 37 (c), the surface morphology improved considerably and the RMS roughness was close to that of the ZnO substrate (~0.242 nm). However, even though the surface was very smooth [Figure 37 (c)], terrace steps were not well-defined. These results indicate that oxygen rich conditions are preferred for good surface morphology at low temperature growth$^{65}$. This is in contrast to high growth temperature, where surface morphology is found to be uninfluenced by Zn/O rich conditions$^{28}$ since the migration length of Zn adatoms is much larger at higher growth temperature.
In an attempt to realize clear terrace steps, we increased the oxygen flux to 2 sccm with a growth pressure of \( \sim 1 \times 10^{-5} \text{Torr} \). Lots of pits (\( \sim 3.5 \times 10^8 \text{ /cm}^2 \)) [Figure 37 (d)] and hexagonal shaped beads (\( \sim 7.5 \times 10^5 \text{ cm}^2 \)) (inset in Figure 38) with diameter of about 1.5\( \mu \text{m} \) were formed on the surface. After growth, the film thickness was measured to be negative (-100--200 nm). This indicates that at low growth temperature, increasing the oxygen flow to 2 sccm results in an etching rate of the surface by the plasma larger than the growth rate. By increasing oxygen flow rate, more oxygen was produced, including the ionized oxygen (i.e. O\(^+\), O\(^-\), O\(_2^+\), O\(_2^-\)), ionized
ozone\textsuperscript{75} and neutral oxygen, among which the ionized oxygen could be the source of etching the surface\textsuperscript{76}.

To reduce the etching effect while keeping high oxygen flux, we applied a bias on the EIT, which deflects the ionized oxygen species. The trap voltage was optimized by exposing the heater filament directly to the oxygen plasma, and collecting the current generated from the ionized oxygen. More ionized oxygen was deflected if higher power was applied. The EIT voltage was optimized to 440V which is just above the voltage required to deflect all the ionized oxygen. Reasonable growth with a 400 nm thickness was achieved and the RMS roughness was 0.333nm, indicating the neutral oxygen species are the source adatoms bonded to Zn. Figure 38 shows the TRPL signal of the ZnO films grown with and without EIT for oxygen plasma. The data was fitted with a single exponential decay function $I(t)=I_0 e^{-t/\tau_{PL}}$, where $\tau_{PL}$ is the PL lifetime. The PL lifetime for the sample with EIT voltage of 440V was 217 ps, which is twice of that for sample without any EIT voltage (109ps). This indicates microstructure damage by the oxygen plasma induces defects that deteriorate the PL lifetime. For comparison, we also showed the PL lifetime for the best film grown with oxygen flux of 1.5sccm [Figure 37 (c)]. The PL lifetime of this sample was only 48 ps, indicating high oxygen flux is needed for large PL lifetime.
Figure 39. AFM images (2 × 2 μm²) of ZnO films grown with Zn cell temperature of (a) 360°C, (b) 350°C and (c) 340°C under oxygen flux of 2sccm and RF power of 300W, with EIT voltage of 440V. (d) RMS roughness as function of Zn cell temperature for different oxygen flow rate. Note for oxygen flow rate of 2 sccm the EIT voltage of 440V was used.

Figure 39 (a) to (c) shows the AFM images of ZnO grown at oxygen flux of 2 sccm with optimized EIT voltage. Compared to ZnO films shown in Figure 37, the terrace steps were more obvious. However, the less O-rich conditions as shown in Figure 39 (a) resulted in more inhomogeneous distribution of steps. When the Zn cell temperature was decreased to 340°C [Figure 39 (c)], under a more O-rich condition, the surface morphology was greatly improved with step height of 0.26 nm or 0.52 nm aligning the [1100] direction, corresponding to one or
two monolayers of ZnO along c-axis. This is comparable to ZnO homoepitaxy growth at high growth temperature of above 800°C \(^{56}\) and much improved in comparison to those reported that were grown at low temperature \(^{65,66}\). The RMS roughness values of ZnO homoepitaxial epilayers are shown as a function of Zn cell temperature for different oxygen flux, in Figure 39 (d). The RMS roughness was considerably improved for higher O flux (2 sccm), with values as low as 0.277nm being achieved, compared to that of substrate (0.242 nm). Unlike growth at high temperature, surface roughness changes remarkably with changes in Zn/O ratio, indicating an O-rich condition is necessary at low growth temperature for good surface morphology.

Figure 40. X-ray diffraction (a) \(\omega\) scan with triple axis measurement and (b) coupled scan over \(\omega\) and 2\(\theta\) with crystal analyzer removed, of (0002) ZnO diffraction peaks of the ZnO epilayer.
The most attractive feature for MBE is its high vacuum and very few impurities inside the chamber. Impurities can come from various sources such as the sample holder, the heater, the chamber wall, the metallic sources, or the oxygen source gas. Impurities in the forms of Zn vacancy complexes are known as non-radiative centers (NRCs) that diminish the light emission from LEDs or LDs and cause short PL lifetime and low internal quantum efficiency. Although other growth methods have been applied for ZnO homoepitaxy, none of them have demonstrated a reasonable PL lifetime (a few hundreds of picoseconds) for ZnO thin films due to challenges in impurity control. To determine the impact of oxygen source purity on our ZnO homoepitaxial films, we grew samples using two different oxygen purities. Figure 40 shows X-ray diffraction curves of (0002) ZnO diffraction peaks of the ZnO epilayers grown on ZnO substrates with oxygen source purities of 4.5N and 6N. Figure 40 (a) is a scan over ω using a triple axis detector to give a high resolution but only for single peak. The measured full width at half maximum (FWHM) for growth with 4.5N oxygen and 6N oxygen were 17.3 arc sec and 18.2 arc sec, respectively. This is comparable to the FWHM of the ZnO substrates (17.6 arc sec), indicating high crystallinity for both films. To observe more potential features in XRD, a coupled scan setup over ω and 2θ with the triple axis crystal removed was executed, as shown in Figure 40 (b). A strong (0002) ZnO peak is observed from the 4.5N oxygen sample, accompanied by a very weak peak at 2θ=37.25°. In contrast, no such peak at 2θ=37.25° was present in the XRD from the sample grown with higher purity oxygen (6N). The PL lifetime for 4.5N oxygen was found to be lower than 50 ps compared to 217 ps grown with 6N oxygen, indicating low purity oxygen introduces more NRCs which reduced the PL efficiency. To identify the potential source
of the impurities, we considered the many impurities existing in the oxygen source bottle, such as CO, CO₂, H₂, H₂O, and N₂. By comparing these impurity concentrations in the oxygen bottle of different grades listed by the vendor, it was found that CO, CO₂, and N₂ are especially higher in concentration (more than one order magnitude) in 4.5N oxygen than in 6N oxygen. Therefore, the week peak at 37.25° may be attributed to some compounds composed by Zn, C, N, and O. Further investigation revealed that this peak fits very well to the peak position for Zn(CN)₂, suggesting this as the impurity complex in the epilayers that is also significantly reducing PL lifetime. Our study clearly indicates that higher purity oxygen is needed to achieve good PL properties in ZnO epilayer when growing in the lower temperature regime.

Normally before growth, the metallic source need to be heated up and oxygen plasma need to be ignited. The time between oxygen plasma ignition and growth should be long enough to stabilize and achieve a stable 2D nucleation on the surface. Figure 41 shows (0002) and (1012) X-ray diffraction ω-rocking curves of ZnO films grown 20 minutes (sample I) and 1 hours (sample II) after igniting oxygen plasma. In order to show more features here we used a double axis measurement for ω-rocking curves, whereas the resolution of the setup is not high enough to accurately measure the width but good enough to see the trends. The actual value of width should be smaller. Although both samples showed excellent surface morphology, the crystallinity of sample I was much better, as shown in the inset of Figure 41 which gives the value of width for full width at half maximum (FWHM), full width at one-tenth maximum (FW0.1M) and full width at one-hundredth maximum (FW.01M). For (0002) direction, the
width is generally larger for sample II and broadened faster by observing from the slope. And for (10\bar{1}2) direction, the value of width for sample II shows a much larger slope. The broadening of the width for sample II indicates long-time heating in the oxygen plasma atmosphere could deteriorate the crystal quality and maybe induce more defects inside the films. To verify this, we took a TRPL measurement on the two samples and the measured PL lifetime for sample I and II were 56 ps and 220 ps, respectively, indicating shorter time after igniting oxygen plasma is better for less defects and higher PL lifetime.

Figure 4.1. (a) (0002) and (b) (10\bar{1}2) X-ray diffraction ω-rocking curves of ZnO films grown 20 minutes and 1 hours oxygen after plasma on. The inset shows the value of FWHM, FW0.1M and FW0.01M.
We later measured the FWHM for different orientations of ω-rocking curves (a double axis measurement) of ZnO film grown with 6N oxygen, as shown in Figure 42. As discussed in Chapter 3, higher FWHM means greater variation in lattice constants in planes parallel to that axis, which in turn means more dislocations. Tilt, which is directly proportional to screw dislocations, is extracted from the (002) axis. The higher the FWHM of the (002) axis, the more screw dislocations. Twist, which is directly proportional to edge dislocations, is extracted from a scan 90° from surface (impossible, but extrapolated from examining trend of higher and higher off-axis scans). The higher the FWHM of off axis scans, the more edge dislocations. It was observed here the FWHM for each axis does not change a lot and maintain at a few tens of arc sec, which indicates very low dislocation density.
Figure 43 shows the reciprocal space mapping of ZnO film grown on ZnO substrate. The θ and ω orientation might have some offset. Spread in ω represents mosaic nature of material, meaning the wider the ω at a certain 2θ, the more polycrystalline. Spread along the diagonal, ω-2θ, represents a wide variation of lattice spacing; this sample is pretty good in this regard. The epilayer was lattice matched to the substrate ZnO since there was no other spot in the RSM, indicating the epilayer is matched to the ZnO substrate pretty well.
4.3.5 Growth temperature

To further improve the PL lifetime, we varied the growth temperature from 580°C to 660°C and studied TRPL signal of the ZnO films, as shown in Figure 44 (a)\textsuperscript{72}. The data was fitted with a single exponential decay function $I(t) = I_0 \exp(-t/\tau_{PL})$, where $\tau_{PL}$ is the PL lifetime. $\tau_{PL}$ as large as 0.38 ns was obtained at a low growth temperature of 580°C, which was about 6 times higher than that grown by other methods \textsuperscript{67,78}. Figure 44 (b) shows the PL lifetime and growth rate as a function of growth temperature. It was found the growth rate was decreasing drastically with increasing of growth temperature. But at growth temperature higher than 640°C, the growth rate was very low and did not change a lot with temperature. In the same way, the PL lifetime decreased with increasing of growth temperature until 640°C, indicating lower growth temperature is preferred for high PL lifetime. To explain this, we draw a graph in the inset in Figure 44 (b) which shows the curve of PL lifetime versus growth rate. The curves can be fitted nicely with a linear relationship $\tau_{PL} = 1.41R$, where $R$ is the growth rate with the unit of μm/h, indicating high growth rate is beneficial for high PL lifetime. Generally, the PL lifetime is dominated by the non-radiative lifetime ($\tau_{NR}$) and thus lower $\tau_{NR}$ results in lower PL lifetime. The results herein indicate that the concentration of NRCs which come from impurities is significantly decreased by growing with a high growth rate. To explain this, consider the growth as a competing process between impurities migration and growth rate. At lower growth temperature, the impurities inside the substrates migrate more slowly into the epilayer, while the epilayer is growing at a higher rate so that the impurities density gradually decreases from the
substrate surface toward the epilayer. Therefore, the epilayer has less impurities and thus higher PL lifetime.

Figure 44. (a) TRPL signal of the ZnO films grown at different growth temperature. (b) Growth rate and PL lifetime as a function of growth temperature. The inset in (b) shows a plot of PL lifetime versus growth rate.
4.4 Growth on non-miscut substrates

A few works have been done to optimize the growth conditions of ZnO homoepitaxial films grown on miscut ZnO substrates, specifically Zn-polar ZnO substrates with a miscut angle of 0.5° toward the [1\bar{1}00] direction\textsuperscript{28,56}, since it was found that miscut ZnO substrate is beneficial to achieve ZnO films with atomic flat surface with one or two atomic height\textsuperscript{28,56}. Yet growth on non-miscut ZnO substrates has not shown such step-and-terrace surface morphology and the surface root mean square (RMS) roughness is also larger compared to the growth on miscut substrates\textsuperscript{63-66}. There are also other problems for growth on non-miscut ZnO substrate: pits were observed on surface due to different numbers of dangling bonds per edge atom on two types of edges whereas one edge tends to grow faster than the others\textsuperscript{67}. Even with very small miscut angles (0.1°) toward the [1\bar{1}00] direction, the surface roughness was much higher and bunched steps were observed\textsuperscript{28}. In this section, ZnO films were grown on Zn-polar non-miscut ZnO substrates at low growth temperature range (610°C) by plasma-assisted molecular beam epitaxy (PAMBE)\textsuperscript{80}. The influence of oxygen plasma power, Zn source flux, and growth temperature on the surface morphology of the ZnO films was investigated.

4.4.1 Experiments

The growth condition is very close to that mentioned in previous section. Elemental Zn (6N) was evaporated from standard hot-lipped Knudsen cells with adjusted cell temperature between 330°C and 350°C. Oxygen flux was fixed at 2 sccm and RF power was varied from 250W to 400W. The chamber pressure during the growth ranged from $5 \times 10^{-6}$ to $1 \times 10^{-5}$ Torr, depending
on the Zn and O flux. The films were grown on single-crystalline (0001) ZnO substrates grown by hydrothermal method (Tokyo Denpa Co., Ltd), processed with high temperature annealing and chemo-mechanically polishing (CMP). Non-miscut ZnO substrates with a miscut error of around ± 0.08° toward the [1100] and [1120] direction was used. The substrates were slightly etched with a hydrochloric acid solution, which removed surface contaminations such as silica gel. After rinsing with acetone, isopropyl alcohol and deionized water, the substrates were exposed to UV-ozone for 5 minutes and immediately loaded into the chamber. Prior to growth, substrates were thermally cleaned at 700 °C for 30 minutes in an ultra-high vacuum chamber (~2×10^-10 Torr). The thickness of the ZnO films in this section ranged from 200nm to 600nm.

4.4.2 Results and discussions

Figure 45 (a) shows atomic force microscope (AFM) image of non-miscut ZnO substrates. The triangle pits with depth of one to three monolayers (typically 0.26nm to 0.78nm) along c axis were found on the surface, which might be induced during the CMP. The surface root mean square (RMS) roughness for the substrate was measured to be 0.23 nm. Various growth temperatures ranging from 500°C to 800°C were also applied with no EIT voltage applied for oxygen plasma. It has been shown that high growth temperature (typically 700°C to 800°C) is beneficial for growth to achieve excellent morphology. Figure 45 (b) is AFM image of ZnO films grown at a high growth temperature of 750°C with RMS roughness of 0.55 nm. Although terrace steps with one atomic height (~0.26nm) was clearly shown in the image, two types of defects were found on the surface. One consisted of some small triangle pits which inherit from the pits on the substrates.
Another type consisted of big hexagonal pits with diameter of around 90 nm and depth ranging from 5 nm to 16 nm which are attributed to the oxygen plasma etching species.

To eliminate these etching effects, the EIT voltage of 440 V was applied to the RF oxygen plasma source, which could deflect the ionized oxygen plasma species and reduce the surface etching. Figure 43 shows the AFM images of resulted ZnO epitaxial films grown with different oxygen plasma power. The growth temperature was 610°C and the growth was kept at a low Zn flux condition where Zn cell temperature was 330°C. In general, the terrace steps were obviously observed under different oxygen plasma power conditions. Figure 46 (a) shows a relatively irregular surface at lower oxygen plasma power of 250 W, exhibiting meandering and step coalescence\textsuperscript{81}. This result indicates that the step-flow growth mode was not retained at low plasma power.
Figure 46. (a)-(d) show (2 × 2 μm²) AFM images of ZnO epitaxial films grown with different RF oxygen plasma power of 250, 300, 350 and 400 W, respectively. (e) Cross-sectional height profile of ZnO film grown with plasma power of 400 W.
By increasing the oxygen plasma power, the steps distribution was more regular with up to two monolayer heights of steps and less step coalescence was found [Figure 46 (b) and (c)]. At plasma power of 400 W, as shown in Figure 46 (d), the step edges were straight and regularly spaced apart, and the steps were always of monolayer height. The surface RMS roughness and growth rate as a function of plasma power is shown in Figure 47. The roughness was decreased as the power increased, and was below the roughness of ZnO substrate at higher oxygen plasma power. There are several oxygen plasma species: ionized atomic oxygen (O⁺), neutral atomic oxygen (O), ionized molecular oxygen (O₂⁺) and some other species with very small amount (such as ozone).
Figure 48. AFM images (10 × 10 μm²) of ZnO epitaxial films grown with Zn cell temperature of: (a) 330°C and (b) 350°C.

As the power increases, the densities of these plasma species (O, O* and O₂*) increase, providing more oxygen rich conditions. Since such oxygen rich condition is beneficial for promoting step-flow growth for ZnO homoepitaxy at low temperature, higher oxygen plasma power resulted a better morphology. It was also found that O is the source adatoms forming ZnO films and ionized oxygen species contributes to the etching. As the plasma power increases, both O/O* and O/O₂* increase, indicating more contribution from growth than the etching effect on the surface. As a result, the growth rate increased as the power increased, as shown in Figure 47.

Figure 48 shows the 10 × 10 μm² AFM images of ZnO films grown with a high oxygen plasma power of 400W and two different Zn cell temperatures of 330°C (Sample I) and 350°C (Sample II). The growth rates for Sample I and II were 29.0 nm/h and 37.8 nm/h, respectively. Although the RMS surface roughnesses for both samples were relatively low (0.181 nm for Sample I and
0.434 nm for sample II), it was found Sample I had a more homogeneous surface morphology than Sample II.

Figure 49. AFM images (2 × 2 μm²) of ZnO epitaxial films grown with (a) Zn cell temperature and oxygen plasma power of 330°C and 300W, respectively, at growth temperature of 580°C; Zn cell temperature and oxygen plasma power of 350°C and 400W, respectively, at growth temperature of (b) 580°C and (c) 550°C. (d) Growth rate and RMS roughness as a function of growth temperature.
To explain this, consider at lower Zn flux the Zn adatom surface diffusion rates to step edges are higher than adatom arrival rates, then adatoms coverage on terraces are relatively low and the interaction between each adatom can be ignored, resulting the flow of steps across the surface and a homogeneous morphology [Figure 45 (a)]. At higher Zn flux, however, the adatom arrival rates increases and could be higher than adatom diffusion rates. In this case, more interaction between these adatoms happens and clustering occurs more frequently [Figure 45 (b)].

Figure 46 (a) shows AFM images with same growth condition as that shown in Figure 43 (b) except the growth temperature was 580°C here. By comparing two samples, it was found at lower growth temperature the Zn diffusion length was largely reduced and thus the hexagonal islands formed. This implies we need carefully investigate the influence of growth temperature to maintain good surface morphology. Figure 46 (d) shows the curves of the growth rate and RMS roughness as a function of growth temperature. The Zn cell and plasma power were kept at 350°C and 400 W, respectively, for a relatively higher growth rate. It was found at growth temperature equal or higher than 580°C, the surface RMS roughness was low and even smaller than the substrates (0.23 nm). Figure 49 (b) is a represented AFM imaged for growth at 580°C with RMS roughness of 0.11 nm. Higher growth temperature is not necessary since it restricts p-type doing with N incorporation and accelerates the deterioration of MBE system components in the oxygen growth environment. Besides, the growth rate increased with reduced growth temperature, so growing in the low temperature range will provide a reasonable growth rate. At temperature lower than 580°C, the surface morphology deteriorated a lot and the RMS roughness
was 27 nm at growth temperature of 550°C, as shown in Figure 49 (c). These results indicate growth temperature of 580°C is best to achieve relatively high growth rate while maintaining good surface morphology.

Figure 50 shows the PL spectra for ZnO films grown on Zn-polar ZnO substrate at 610°C under oxygen flux of 2sccm and RF power of 300W. The Zn cell temperature was 340°C, and EIT with 440V bias was applied. Figure 50 (a) shows the TRPL signals with PL lifetime as high as 380 ps, indicating high quality ZnO films and low concentrations of NRCs. To verify this, both room temperature PL and low temperature PL were taken in Figure 50 (b). A strong NBE emission at around 378 nm attributed to excitonic recombination was observed, as shown in Figure 50 (b). No green band (475nm-580nm) related to defects were observed even in a log scale, indicating few intrinsic defects and oxygen vacancy. The inset in Figure 50 (b) shows PL spectrum measured at 13K. The PL spectrum was dominated by neutral donor bound exciton emissions (D₀X) at 3.357 and 3.358 eV, with several emissions near band edge. A strong emission line was observed at 3.373 eV, which is assigned to the recombination of A-free exciton (Fₑ₋). This emission line was only half of the intensity of D₀X, comparing to other work which shows at least more than one orders lower emission. This result further suggests that there are fewer NRCs and thus long PL lifetime.
Figure 50. (a) TRPL signal and (b) room temperature PL spectrum of the ZnO films grown at 610°C. The inset in (b) shows the low temperature (~13K) PL spectrum.

4.5 **N-type Doping**

We investigate the feasibility of Ga doping with Ga cell temperature of 480°C. Atomically flat surface was obtained easily by incorporation with Ga, with a RMS roughness of 0.086 nm, as shown in Figure 51. This indicates Ga might act as a surfactant which helps to improve the surface morphology. Since ZnO substrates are conductive, we were not able to determine the electrical properties simply by Hall effect measurements. Figure 51 (c) is a Secondary Ion Mass Spectrometer (SIMS) depth scan of this film. The Ga concentration was measured to be
\( N_D = 3 \times 10^{19} \text{cm}^{-3} \) and the electron concentration was calculated to be \( n_0 = 2.09 \times 10^{18} \text{cm}^{-3} \) as discussed in the following.

Fermi-Dirac distribution function which defines the probability that an energy level \( E \) is occupied is \(^8\):

\[
f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{K_0 T}\right)}
\]

where \( E_F \) is the Fermi level energy, \( K_0 \) is Boltzmann constant \((1.3807 \times 10^{-23} \text{J} \cdot \text{K}^{-1})\) and \( T \) is the temperature which is 300K considering room-temperature here. Note here we does not approximate the equation (2) by Maxwell-Boltzmann function since the conditions \( E - E_F \gg K T \) might not be true here.

Density of states in the conduction band is:

\[
g_c(E) = 4\pi V \frac{(2m_n^*)^{3/2}}{h^3} (E - E_c)^{1/2}
\]

where \( V \) is the volume of the crystal investigated, \( m_n^* \) is the effective mass at the bottom of conduction band \((0.24m_0, m_0 = 9.109383 \times 10^{-31} \text{kg})\), \( h \) is the plank constant \((6.626 \times 10^{-34} \text{J} \cdot \text{s})\), and \( E_c \) is the energy level of bottom of conduction band.
Figure 51. (a) and (b) AFM image of Ga doped ZnO thin films on non-miscut ZnO substrates and (c) the corresponding SIMS scan for Ga concentrations.

The density of electrons in the conduction band $dN$ with energies between $E$ and $E + dE$ is:

$$dN = f(E) g_c(E) dE$$

By substituting Equation (2) and (3) into the functions above

$$dN = 4\pi V \frac{(2m^*_e)^{3/2}}{h^3} (E - E_c)^{1/2} \frac{1}{1 + \exp\left(\frac{E - E_F}{k_0 T}\right)} dE$$

(4)
Assume $\Delta E = \frac{E - E_c}{K_0T}$; $\Delta E_F = \frac{E_F - E_c}{K_0T}$ and effective density of states in the conduction band $N_c = 2\frac{(2\pi m^*_nK_0T)^{3/2}}{h^3}$ which is $2.95 \times 10^{18} \text{cm}^{-3}$ for ZnO (a little smaller than that calculated in Ref$^{83}$ whereas they use $m^*_n = 0.29m_0$). Therefore, form Equation (4), the density of electrons in the conduction band $dN$ with energies between $E$ and $E + dE$ in the unit volume is

$$dn = \frac{dN}{V} = \frac{2N_c}{\sqrt{\pi}} \left(\frac{\Delta E}{1 + \exp(\Delta E - \Delta E_F)}\right)^{1/2} d\Delta E$$

(5)

After integral of Equation (5), we can obtain the electron carrier concentrations $n_0$ in the conduction band:

$$n_0 = \int_0^{\Delta E'_c} \frac{2N_c}{\sqrt{\pi}} \left(\frac{\Delta E}{1 + \exp(\Delta E - \Delta E_F)}\right)^{1/2} d\Delta E$$

(6)

where $\Delta E'_c = \frac{E'_c - E_c}{K_0T}$ and $E'_c$ is the energy level at the top of conduction band.

For charge neutrality,

$$n_0 = p_0 + n^+_D$$

(7)

where $p_0$ is the hole concentration and $n^+_D$ is the ionized donor concentration

$$p_0 = N_v \exp\left(\frac{E_p - E_v}{K_0T}\right)$$

$$= N_v \exp\left(\frac{E_F - E_c + E_c - E_v}{K_0T}\right)$$

$$= N_v \exp\left(-\Delta E_F - \frac{E_c - E_v}{K_0T}\right)$$

(8)

The bandgap $E_c - E_v$ is 3.3 eV and $N_v = 2\frac{(2\pi m^*_hK_0T)^{3/2}}{h^3}$ was calculated to be $1.137 \times 10^{19} \text{cm}^{-3}$ with $m^*_n = 0.59m_0$. 

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\[ n_D^+ = \frac{N_D}{1 + 2 \exp\left(\frac{-E_D - E_F}{K_0 T}\right)} \]

\[ = \frac{N_D}{1 + 2 \exp(\Delta E_F - \Delta E_D)} \]  

(9)

where \( \Delta E_D = \frac{E_D - E_C}{K_0 T} \) and Ga donor ionization energy \( E_C - E_D = 53 \, meV \).

From Equation (6)-(9), we get \( \Delta E_F = -0.123 \) and we are able to obtain \( n_0 = 2.09 \times 10^{18} \, cm^{-3} \) by substituting the value of \( \Delta E_F \) to Equation (6).

4.6 Summary

ZnO films were grown on Zn-polar ZnO substrates with 0.5° miscut toward the [1\overline{1}00] direction by PA-MBE. An atomically flat surface with one or two monolayer step height along the [0001] direction was achieved by low temperature growth (610°C) using 2 sccm oxygen flow rates. Such low growth temperature is beneficial for p-type doping of ZnO and reduces the deterioration of MBE system components in the oxygen growth environment. Surface treatment such as wet etching was found crucial to achieve a higher PL lifetime. A short-time interval between growth and oxygen plasma ignition was found necessary for excellent crystallinity and high PL lifetime. EIT of the oxygen source was found necessary in order to circumvent oxygen flux etching of the surface at high oxygen flow rates. The less etching results in a higher growth rate and less defects in the films under high oxygen flux. Impurities such as C and N in the 4.5N oxygen gas source introduced a satellite XRD peak attributed to Zn(CN)\_2 with short PL lifetime observed from the ZnO epilayers. Use of higher purity 6N oxygen was found to reduce
impurities in the films, eliminating the satellite XRD peak and improving the PL lifetime to 217 ps. The growth rate was changed from 0.02μm/h to 0.246 μm/h by varying the growth temperature in the low temperature range from 580°C to 660°C, and PL lifetime as high as 0.35 ns was achieved. The relationship of growth rate and PL lifetime was found to follow a linear trend, suggesting a high growth rate is preferred for high PL lifetime since the films contain lower concentrations of point defects which would act as NRCs.

ZnO thin films were also grown on Zn-polar non-miscut ZnO substrates by PA-MBE. With an EIT for oxygen plasma, the etching effect was significantly reduced and atomically flat surfaces with one monolayer step height along the [0001] direction were achieved at a low growth temperature of 610°C. Higher oxygen plasma power and lower Zn flux were found necessary to achieve a better step-flow growth mode with a more homogeneous surface morphology. It was found the growth rate and RMS roughness decreased with increased growth temperature, and the RMS roughnesses were lower than that of the substrate at growth temperature higher than 580°C. Since low growth temperature is beneficial for p-type doping, reduces the deterioration of MBE system components, and gives a relatively high growth rate, growth at a low temperature range but higher than 580°C is preferred to achieve good morphology.

When doping the film with Ga, we found Ga act as a surfactant which improves the surface morphology considerably. The carrier concentration was calculated to be $2.1 \times 10^{18} \text{cm}^{-3}$ from a
SIMS scan. This indicates an efficient LED or LD structure with perfect interfaces between the active layer and n-type doping layer can be obtained.
5. CHAPTER FIVE: LIGHT EMITTING DIODES BASED ON POLARIZATION INDUCED DOPING

5.1 Introduction

ZnO suffers from the doping asymmetry problem, meaning it can be easily n-type doped but not p-type\textsuperscript{84,85}. While there are already commercially available GaN based LEDs and LDs, the application of ZnO is still limited to n-type or intrinsic devices due to the lack of practical and efficient p-type doping. The difficulties of p-type doping arise several studies for different dopant. Group-I elements with small atomic radii (i.e. Li) tend to form interstitials which act as donors. Group-I (Na, K) and V (P, As) with larger bond length than that of Zn-O induce lattice strain, forming defects such as donor-like vacancies. N is considered the most promising p-dopant since it has the similar atomic radius and electronegativity as O\textsuperscript{31,86}. Several groups have demonstrated LEDs with N-doping by MBE\textsuperscript{32,87,88} but with very low hole carrier concentrations and low mobilities. More detailed review about ZnO-based LEDs can be found in some literatures\textsuperscript{89}.

A few recent theoretical studies show controversial results about N doping. While experimentally Look et al. used photoluminescence to estimate N-related acceptor ionization energy of 170-200 meV\textsuperscript{90}, several works have indicated N-related defects N\textsubscript{O} are deep acceptors with high ionization energy of 0.4 eV to 1.3 eV\textsuperscript{33,91-94}. N\textsubscript{2} molecules at oxygen sites (N\textsubscript{2})\textsubscript{O} which have lower formation energy than N\textsubscript{O}, even compensate the N acceptors\textsuperscript{95}. A few investigations have been performed to demonstrate p-type doping by minimizing the N\textsubscript{2}/N ratio\textsuperscript{96,97}. The
simulations above, however, are based on the bulk model simulations without considering the growth process, such as polar face dependence and the influence of the gas pressure. Liu et al. discussed the origin of the p-type conductivity in N-doped ZnO on Zn-polar face and provided some ideas about doping methodology.

It is difficult to conclude whether p-type doping of ZnO is feasible or not since the reliability of p-type ZnO and the doping mechanism remains controversial. There are not many clues about how to design a growth process to optimize the p-type doping. Although the simulations might miss some important unknown factors for p-type doping, it is also rare to find any continuous experimental work after researchers demonstrated ZnO-based LEDs. To summarize all these works, there are two things which might be true for optimizing the growth conditions: (1) minimizing the N2/N ratio and (2) growing on Zn-polar surface. In this chapter, we will investigate a new route with polarization induced doping to assist p type doping.

5.2 Background of polarization induced doping

To circumvent the challenges faced with the traditional doping which causes low hole carrier concentrations, one possible approach was introduced recently by polarization induced doping for III-nitrides. Group III nitrides, i.e. GaN, AlN and InN have been attracted lots of attention for applications in high-power electronic and optoelectronic devices. Heterostructures based on group III nitrides, such as GaN, AlN, and InN have unique polarization properties compared to classical III-V and II-VI semiconductor heterostructures. The polarization is due to
strong spontaneous and piezoelectric polarizations that significantly modify electronic band diagrams of heterointerfaces and multilayered structures.

Extensive work studying the electron densities in undoped AlGaN/GaN HEMT structures\textsuperscript{102,103} has revealed an interesting phenomenon. A correlation has been observed between the large interface electron densities of AlGaN/GaN and the spontaneous and piezoelectric polarization of these materials\textsuperscript{104,105}. This results in a large electric field in the barrier layer of the AlGaN. Also, it has been observed that interesting phenomenon occur with these materials as a result of utilizing a graded junction configuration as opposed to a more common sharply defined heterojunction. AlGaN has larger spontaneous polarization than GaN which continues to increase as the Al composition increases. This results in the growth of films with fixed space charge density described by $\rho_{sp} = -\nabla \cdot \vec{P}(\vec{r})$. Ga polar growth with an internal grading from GaN to AlGaN results in a net positive space charge in the graded layer and attracts negative charge carriers (electrons) from available sources (remote dopants, interface states, etc.). This phenomenon results in the formation of a three-dimensional electron slab that has recently been demonstrated experimentally\textsuperscript{105}. The results also indicate the creation of a three-dimensional space charge region leading to the accumulation of a very high free electron concentration without the need for dopant atoms. Another group reported using grading techniques to create a negative space charge and have demonstrated significantly enhanced doping effectiveness with Mg atoms for creating p-type materials\textsuperscript{98}. Additionally, the bulk-like graded layers mentioned
above have realized very high electron mobility of the two-dimensional electron gas observed at the heterojunction interfaces.

The polarization induced doping concept has quickly generated much interest for its ability to provide p-n junction performance without traditional extrinsic impurity doping. A great deal of interest has been applied to ZnO for its superior properties over Si and III-nitrides. However, its inability to be stably p-doped has limited its application. With the recent advancement of polarization induced doping, an opportunity to mitigate the existing extrinsic p-type doping stability in ZnO exists and needs experimental investigation to determine if it might show similar promise as observed in the III-nitrides. On the other hand, there are little work on both spontaneous and piezoelectric polarization effects in MgZnO/ZnO structures. In this effort we investigate MgZnO/ZnO structures and gradient MgZnO/ZnO to explore the feasibility of using graded layers of MgZnO for p-type doping in these materials.

5.3 Simulations

First we need to investigate the feasibility of polarization induced doping at the interface of Mg$_x$Zn$_{1-x}$O and ZnO along c-axis. The amount of the bound polarization induced sheet charge density $\sigma$ is given by

$$\sigma = -\nabla P$$

(10)

where $P$ is the polarization fields across the boundary.
Assume the physical properties of ZnO and MgO have linear relationship except that calculated in recent literature\textsuperscript{106}, then

lattice constants:

\begin{align*}
a(x) &= (0.029x + 3.254)10^{-10}m \\
c(x) &= (-0.111x + 5.206)10^{-10}m
\end{align*}

(11)
(12)

elastic constants:

\begin{align*}
C_{13}(x) &= (4x + 84)GPa \\
C_{33}(x) &= (55x^2 - 9x + 176)GPa
\end{align*}

(13)
(14)

piezoelectric constants (MgO: $e_{33} = 0.14C/m^2$):

\begin{align*}
e_{31}(x) &= (-0.23x - 0.55)C/m^2 \\
e_{33}(x) &= (-1.1x + 1.24)C/m^2
\end{align*}

(15)
(16)

Table 4. Calculated parameters for MgZnO/ZnO with Mg composition of 0.3

<table>
<thead>
<tr>
<th>Top/bottom layer</th>
<th>Polar face</th>
<th>Stress</th>
<th>$P_{SP}$ for top $10^{-6}$ C/cm$^2$</th>
<th>$P_{PE}$ $10^{-6}$ C/cm$^2$</th>
<th>$\sigma$ $10^{-6}$ C/cm$^2$</th>
<th>$\sigma$ For AlGaN $10^{-6}$ C/cm$^2$</th>
<th>Carrier type</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgZnO/ZnO X=0.3</td>
<td>Zn</td>
<td>Relaxed</td>
<td>-6.11</td>
<td>0</td>
<td>0.81</td>
<td>1.6</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>Relaxed</td>
<td>6.11</td>
<td>0</td>
<td>-0.81</td>
<td>-1.6</td>
<td>h</td>
</tr>
<tr>
<td>MgZnO/ZnO X=0.3</td>
<td>Zn</td>
<td>Compress.</td>
<td>-6.11</td>
<td>0.56</td>
<td>0.25</td>
<td>2.69</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>Compress.</td>
<td>6.11</td>
<td>-0.56</td>
<td>-0.25</td>
<td>-2.69</td>
<td>h</td>
</tr>
<tr>
<td>ZnO/MgZnO X=0.3</td>
<td>Zn</td>
<td>Tensile</td>
<td>-5.3</td>
<td>-0.61</td>
<td>-0.2</td>
<td>-2.5</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>Tensile</td>
<td>-5.3</td>
<td>0.61</td>
<td>0.2</td>
<td>2.5</td>
<td>e</td>
</tr>
</tbody>
</table>
spontaneous polarization (MgO: \(-0.080\) C/m\(^2\)):

\[
P_{SP} = (-0.027x - 0.053)\text{C/m}^2
\]  \hspace{1cm} (17)

piezoelectric polarization \(^{104}\):

\[
P_{PE} = 2\frac{a_{\text{bot}} - a_{\text{top}}}{a_{\text{top}}} (e_{13} - e_{33} \frac{c_{13}}{c_{33}})_{\text{top}}
\]  \hspace{1cm} (18)

Since \(e_{13} - e_{33} \frac{c_{13}}{c_{33}}\) is negative for all compositional range of MgZnO, \(P_{PE}\) is negative for tensile strain and positive for compressive strain, respectively. The negative sign of \(P_{SP}\) means the polarization direction is opposite to the Zn-polar direction. The calculated parameters for Zn-polar and O-polar MgZnO/ZnO are listed in Table 4. It was found for O-polar direction MgZnO/ZnO will form two-dimensional hole gases (2DHG) and for Zn-polar direction ZnO/MgZnO will form 2DEG, which is similar to that of AlGaN. However, the polarization induced bound charge \(\sigma\) for II-oxides is about one order lower than that of III-nitrides. One reason for this is the difference of the spontaneous polarization between MgO and ZnO is only \(0.027\) C/m\(^2\) while for GaN and AlN it is \(0.052\) C/m\(^2\). This results in relatively weaker polarization induced effect. Another reason is the in-plane lattice constant \(a_0\) of MgO is larger than that of ZnO (Table 5), resulting in the opposite effect as opposed to that caused by the spontaneous polarization, as shown in Figure 52.
Table 5. Lattice constants of wurtzite ZnO, MgO, AlN and GaN, where $a_0$, $c$, $u$ are the in-plane and out-plane lattice constants and the internal parameter, respectively.

<table>
<thead>
<tr>
<th>wurtzite</th>
<th>$a_0$</th>
<th>$c$</th>
<th>$u$</th>
<th>$c/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>3.283</td>
<td>5.095</td>
<td>0.388</td>
<td>1.552</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.254</td>
<td>5.206</td>
<td>0.380</td>
<td>1.6</td>
</tr>
<tr>
<td>AlN</td>
<td>3.112</td>
<td>4.982</td>
<td>0.380</td>
<td>1.601</td>
</tr>
<tr>
<td>GaN</td>
<td>3.189</td>
<td>5.185</td>
<td>0.376</td>
<td>1.626</td>
</tr>
</tbody>
</table>

Figure 52. Bound polarization induced sheet charge with the directions of spontaneous polarization and piezoelectric polarization.

For the gradient structure, software called “1D Poisson” was used to calculate the bound charge. The structure for this simulation was a simple PIN ZnO LED with gradient MgZnO as p type layer, as shown in Figure 53. Since the software requires fitting with a 2nd polynomial for total
polarization, both spontaneous polarization [Equation (17)] and piezoelectric polarization [Equation (18)] were considered and the fitted the polarization equations is shown in the following.

For Zn polar direction, gradient from low Mg composition to high Mg composition

\[
P_{PE} = (-0.0028229x^2 + 0.020426x + \text{constant}) \text{C/m}^2 \quad (19)
\]
\[
P_{\text{total}} = (-0.0028229x^2 - 0.00657397x - 0.053) \text{C/m}^2 \quad (20)
\]
Gradient from high Mg composition to low Mg composition shows fitting with almost the same trend.

![Structure of PIN ZnO LED with gradient MgZnO as p type layer.](image)

Figure 53. Structure of PIN ZnO LED with gradient MgZnO as p type layer.
Similar equation can be derived for O polar direction, with opposite direction:

\[ P_{SP} = (0.027x + 0.053)C/m^2 \]  \hspace{1cm} (21)

\[ P_{PE} = (0.0028229x^2 - 0.020426x + \text{constant})C/m^2 \]  \hspace{1cm} (22)

\[ P_{total} = (0.0028229x^2 + 0.00657397x + 0.053)C/m^2 \]  \hspace{1cm} (23)

Polarization induced doping has been demonstrated recently for both n and p conducting regions for III-Nitrides, even without introducing impurity dopants\textsuperscript{105,107}. However, as we discussed above, the polarization effect of ZnO is smaller than that of GaN. Here different acceptor concentrations were investigated for p type gradient structures, as shown in Figure 54. For all structures, the conduction band acts as an electron blocking layer. But the bending of valence band was also observed for lower acceptor concentration, i.e. \(10^{16} \text{cm}^{-3}\), resulting in a hole blocking layer. It was also observed that holes are compensated if the acceptor concentrations are too low. Therefore, higher acceptor concentration is beneficial for electron blocking and holes distribution in the gradient layer.
Figure 54. (Left) Bandgap and (Right) carrier concentrations for Gradient structures with acceptor concentration ranged from $10^{16}$cm$^{-3}$ to $10^{19}$cm$^{-3}$. Here the thickness of the gradient structure is 100nm.

Figure 55 shows the impact of thickness on the band structure and distribution of carriers. Thin gradient layer (i.e. 50nm) causes bending of valence band and more depletion of holes. Therefore, a thickness for gradient layer larger than 100nm is preferred for efficient p type doping.
Figure 55. (Left) Bandgap and (Right) carrier concentrations for Gradient structures with thickness of 50nm, 100nm, and 200nm, respectively. Here the acceptor concentration of the gradient structure is $2 \times 10^{17} \text{cm}^{-3}$.

Figure 56 (a)-(d) shows the ZnO PIN structure with only spontaneous polarization (ZnO structure I) and both spontaneous polarization and piezoelectric polarization (ZnO structure II). The peak polarization induced holes concentrations are (ZnO structure I) $6.7 \times 10^{17} \text{cm}^{-3}$ and (ZnO structure II) $1.5 \times 10^{17} \text{cm}^{-3}$, but ZnO structure II has shallower holes distribution range, indicating week polarization effect. On the other hand, the polarization induced holes for GaN (c) and (f) shows a concentration of $1.5 \times 10^{17} \text{cm}^{-3}$ with a distribution range all across the gradient region.
To further investigate this, a gradient MgZnO structures were grown after calibration of Mg composition in MgZnO. Careful design of the increasing Mg cell temperature was used to achieve a linearly gradient MgZnO structure. Figure 57 shows the Second Ion Mass Spectroscopy (SIMS) scan of approximately 100 nm thickness of gradient on 100nm ZnO buffer layer. It’s shown that the Mg composition was linearly grading from 0% to 43%. However, no p-type properties were found for these gradient structures by the Hall Effect measurement.
5.4 Summary

Spontaneous polarization and piezoelectric polarization effect on both MgZnO/ZnO structure and gradient MgZnO/ZnO structure were investigated. While the spontaneous polarization of ZnO is large, the piezoelectric polarization induced by the strain cancels the polarization effect, resulting in a weak polarization induced effect. The polarization induced bound charge $\sigma$ for II-oxides is about one order lower than that of III-nitrides. The ZnO PIN structure with a MgZnO gradient layer was also investigated. The optimal doping concentration for holes distribution was
calculated larger than $1 \times 10^{17} \text{cm}^{-3}$ and the depth of the gradient structure should be larger than 100nm. Although the polarization effect for gradient MgZnO cannot be used for enhancing the hole concentration, it would still work for efficient electron blocking layer while not influencing the transport of holes.
6. CHAPTER SIX: SOL GEL OF MGZNO

6.1 Introduction

While MBE is one of the most expensive growth techniques, sol-gel is one of the most cost-effective one. Sol gel has many advantages over high vacuum system (i.e. MBE, MOCVD), such as being cost-effective, highly suitable for oxide materials, and providing excellent control of elemental composition and additives at the molecular level. In some applications, such as transparent conductors and photodetectors, single crystal films are not necessary. Polycrystalline or amorphous ZnO films have the application in these fields and thus sol-gel is the best way to synthesize this kind of film\textsuperscript{108-111}.

Figure 58 shows two synthesis method for this films and powder by the sol-gel. The film preparation can be summarized to three parts\textsuperscript{112}: (1) preparation of the precursor solution in the physical form of a sol; (2) deposition of the gel on substrates by either spin-coating or dip-coating; and (3) heat treatment of the xerogel film, which is the dried gel at the ambient pressure. In the sol, there are several kinds of transformations: hydrolysis, condensation and polymerization. Take zinc acetate 2-hydrate (Zn(CH\textsubscript{3}COO)\textsubscript{2}\cdot2H\textsubscript{2}O) for example.

*Hydrolysis* occurs when a hydroxyl ion becomes attached to the metal atom, as in the following reaction:

\[
\text{Zn(CH}_3\text{COO)}_2 + \text{H}_2\text{O} \rightarrow \text{HO-Zn-(CH}_3\text{COO) + CH}_3\text{COOH};
\]
Or \[ \text{Zn(CH}_3\text{COO)}_2 + 2 \text{H}_2\text{O} \rightarrow \text{HO-Zn-OH} + 2 \text{CH}_3\text{COOH}; \]

Two partially hydrolyzed molecules can link together in a condensation reaction, such as

\[ \text{HO-Zn-(CH}_3\text{COO)} + \text{HO-Zn-(CH}_3\text{COO)} \rightarrow \text{HO-Zn-O- Zn-(CH}_3\text{COO)} + \text{CH}_3\text{COOH}; \]

Or

\[ \text{HO-Zn-OH} + \text{HO-Zn-(CH}_3\text{COO)} \rightarrow \text{HO-Zn-O- Zn-(CH}_3\text{COO)} + \text{H}_2\text{O}; \]
Condensation usually liberates a small molecule, such as water or alcohol. This type of reaction can continue to build larger molecules through the process of polymerization. It may form a dimer, a chain, or even a ring as shown below \(^{112}\):

**Dimer**

\[
\text{HO-Zn-O- Zn-OH}
\]

**Chain**

\[
\text{HO-(Zn-O)}_{n-1} - \text{Zn-OH}
\]

**Ring**

\[
(n+4)(\text{HO-Zn-OH}) \rightarrow (\text{Zn-O})_{n/2} + (n+4) \text{H}_2\text{O} ;
\]

Diethanolamine (HN(CH\_2CH\_2OH)\_2, DEA) is usually added to the solution as the stabilizer, which retards Zn condensation and increases the lifetime of the sol. However, the presence of this amine also increases the pH, which promotes the formation of ZnO. The reaction of DEA and Zn monoacetate generates ZnNH(C\_2H\_4O)\_2 which also results in the formation of ZnO, suggested by Wang et al\(^{113}\). Wang et al. also suggests there are other intermediate zinc copolymers during the reaction of formation ZnO, such as Zn\_4O(CH\_3COO)\_6.
When the solution is ready, films were prepared by spin-coating around 60°C. Usually there are two stages of heating: The first step is pre-heating, which is applied during a short time after each coating for solvent evaporation and some organic compounds removal. The second is post-heating, which is employed to obtain a crystalline films and the final decomposition of organic by-products between 400°C and 900°C.

6.2 Background

As we discussed above, in principle MgₓZn₁₋ₓO has tunable bandgap from 3.3eV for wurtzite ZnO to 7.8 eV for rock salt MgO. However, although the ionic radius of Mg²⁺ (0.57 Å) is close to that of Zn (0.6 Å), the crystal structure difference and large lattice mismatch between ZnO (wurtzite, 3.25 Å) and MgO (rock salt, 4.22 Å) causes phase segregation in MgₓZn₁₋ₓO with Mg compositions between 37%<x<62% ³,¹¹⁴. As a result, development and subsequent application of MgₓZn₁₋ₓO within the 4.27 to 5.4 eV regions has been hindered. This is a critical spectral window on the edge of the solar blind region (250-290 nm) where both detectors and emitters are necessary for many applications. Recently we reported on a new route towards avoiding the current mixed phase issues for MgₓZn₁₋ₓO within this spectral region, thus providing a new possible route towards controllable and reproducible energy gap tuning of optoelectronic devices based on this ternary¹¹⁵.
Both phase segregation and lattice mismatch between substrate and film can be avoided by growing amorphous Mg$_x$Zn$_{1-x}$O ($\alpha$- Mg$_x$Zn$_{1-x}$O) films\textsuperscript{116-118}. Amorphous films are usually very smooth, with few to no grain boundaries, and amenable to low temperature and large area deposition. For preparing amorphous films, sol-gel method is the best due its own advantages. However, existing studies on sol-gel synthesized Mg$_x$Zn$_{1-x}$O\textsuperscript{108,109} are limited to low Mg concentration up to $x =$0.36, corresponding to a bandgap of 3.93 eV. We showed a sol-gel deposition method applied to fabricate $\alpha$- Mg$_x$Zn$_{1-x}$O thin films with full composition tuning ($x=0\sim1$), corresponding to bandgap energies from 3.3eV to more than 6.5 eV, providing a new route towards low-cost optoelectronic devices in the 200 – 300 nm spectral region\textsuperscript{115}.

6.3 Experimental procedure

The Mg$_x$Zn$_{1-x}$O thin films were synthesized on quartz substrates by the sol-gel method\textsuperscript{115}. Commercially available zinc acetate 2-hydrate (Zn(CH$_3$COO)$_2$$\cdot$$2$H$_2$O) and magnesium acetate 2-hydrate (Mg(CH$_3$COO)$_2$$\cdot$$2$H$_2$O) were dissolved in 20 ml 2-methoxethanol. Diethanolamine (HN(CH$_2$CH$_2$OH)$_2$, DEA) was then added to the solution as the stabilizer. The total concentration of metal ions was maintained at 0.2mol/L and the molar ratio of the DEA to the total metal ions was 1:1. The percentage of Mg to total metal ions, $x$, was adjusted from 0 to 1 to realize the full $\alpha$- Mg$_x$Zn$_{1-x}$O compositional range. For each metal ion ratio, the solution was stirred at $60^\circ$C for 30 minutes and spin-coated on quartz substrates at 2000 rpm. The as-coated
films were immediately preheated to 300°C for 10 minutes to evaporate or burn off the solvent and other organic components in the film. To obtain a thickness of more than 300 nm, this cycle was repeated ten times and then the film was post-annealed in air atmosphere at 400°C for 1 h.

6.4 Results and discussions

The MgₓZn₁₋ₓO films were characterized by X-ray diffraction (XRD) (Rigaku D/MAX x-ray diffractometer) using Cu-Kα radiation (λ = 1.54056 Å), as shown in Figure 59. MgₓZn₁₋ₓO films with x=0.2~1 had no observable peaks at 2θ diffraction angles between 10° to 90°, indicating an amorphous structure. In contrast, the pure ZnO film had peaks (FWHM=0.65~0.7) at 2θ diffraction angles around 31.8º, 34.41º and 36.25º, attributed to the (100), (002), and (101) planes of wurtzite ZnO, respectively. We subsequently found that the crystalline structure of ZnO could be suppressed and circumvented by lowering the post-annealing temperature to 300°C, resulting in a completely amorphous ZnO thin film. The amorphous nature and morphology of the α - MgₓZn₁₋ₓO films was further investigated using atomic force microscopy (AFM, Veeco Dimension 3100), as shown in Figure 60. The root-mean-square of the surface roughness of these films ranged from 0.3 to 1 nm, showing no recognizable crystalline features for films annealed up to 400°C and indicating significantly smooth surfaces. For films annealed at higher temperature, crystalline surface features were present, indicating that higher temperatures resulted in polycrystalline films.
Figure 59. X-ray diffraction patterns for the films with different Mg concentrations, x, for Mg$_x$Zn$_{1-x}$O films after annealing at (a) 300°C and (b) 400°C.
Figure 60. AFM images (5µm×5µm) of the films (a) Mg$_{0.2}$Zn$_{0.8}$O; (b) Mg$_{0.5}$Zn$_{0.5}$O and (c) Mg$_{0.7}$Zn$_{0.3}$O. AFM images (1µm×1µm) for Mg$_{0.7}$Zn$_{0.3}$O annealed for 1 hour at (d) 400°C, (e) 600°C and (f) 800°C.
X-ray photoelectron spectroscopy (XPS, Physical Electronics 5400 ESCA) was carried out using an Al-K$_\alpha$ X-ray source to analyze the composition. The position of the C1s peak was taken as a standard with a binding energy of 285.0 eV. Figure 61 shows the XPS spectra of an $\alpha$-Mg$_{0.7}$Zn$_{0.3}$O film. Signatures of both Zn and Mg atoms are clearly observed in the XPS spectra of the film. The ratio of Zn/Mg was determined to be 30.3:69.7 using AugerScan3 software. This is in good agreement with the initial ratio (30:70) in the precursor solution, indicating the ratio of Zn/Mg in the solutions is maintained in the amorphous films after deposition and
annealing at low temperature. Figure 61 (c) shows the XPS spectra of O1s and its two Gaussian-resolved components centered at 530.04 eV and 532.11 eV, respectively. The lower binding energy component centered at 530.04 eV is attributed to $O^{2-}$ ions in the Zn-O and Mg-O bonds, while the other component located at 532.11 eV shows the presence of loosely bound oxygen chemisorbed on the surface, e.g., –OH, –CO$_3$ or absorbed $O_2$\textsuperscript{119,120}. No peaks were detected around a binding energy of 398 eV (N1s), indicating that N related chemicals are burnt out or evaporated, and no longer present in the amorphous films.

The transmission spectra for Mg$_{0.7}$Zn$_{0.3}$O films annealed at different temperatures, shown in Figure 62 (a), were generated using a Cary 500 UV-VIS spectrophotometer. The absorption edge of the film becomes sharper when annealed at 400°C as compared to as-deposited film. This was also observed for $\alpha$-Mg$_x$Zn$_{1-x}$O films of other compositions, and is most likely attributed to the burning off of organic chemicals in the film. However, at annealing temperatures higher than 450°C, all samples exhibited obvious transmission tails, indicating that phase segregation begins to occur in the films at annealing temperatures above 400°C. The phase segregation becomes rather pronounced at temperatures higher than 500°C and two absorption edges at around 360 nm and 210 nm were observed in all cases, representing Zn-rich and Mg-rich phases, respectively. When annealing at a temperature higher than 800°C, the transmission curves changes little, implying that a stable crystalline Mg$_{0.7}$Zn$_{0.3}$O alloy with phase segregation has been obtained.
We observed similar phase segregation signatures for $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ with $x = 0.5$ and 0.75 when annealing at temperature higher than 450°C. These observations indicate that the optimal post-annealing temperature for $\alpha$-$\text{Mg}_x\text{Zn}_{1-x}\text{O}$ is 400°C in order to avoid crystalline films with phase segregation. As expected, for Mg concentration lower than 38% or higher than 75%, the phase segregation does not happen, even when annealing at 800°C. It is noteworthy that the phase segregation range of sol-gel synthesized $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ with $38%<x<75%$ is different from that grown by PLD ($38%<x<62%$).
The presence of phase segregation was further confirmed by XRD, as shown in Figure 62 (b). No obvious XRD peaks were observed for annealing up to 400°C. For annealing at temperatures ≥450°C, the film begins to exhibit multiple peaks associated with both wurtzite and rock salt MgZnO, similar to the work by M. Wang et al.\textsuperscript{121} This is consistent with the transmission data in Figure 62 (a), where phase segregation signatures were observed for annealing temperatures of 450°C and higher.

Figure 63 (a) illustrates the optical transmission spectra of α-\textsubscript{Mg_xZn_{1-x}}O (x=0~1) in the wavelength range of 190-800nm. It is observed that the films are highly transparent (greater than 90%) in the visible and near infrared region of 400-800nm. This is attributed to low surface roughness of amorphous film since the scattering between the air and film interface increases when surface roughness increases. The absorption coefficient, \( \alpha \), can be derived from the transmission \( T \) by Beer’s law \( T = I/I_0 = e^{-\alpha d} \), where \( I \) is the transmitted intensity, \( I_0 \) is the incident intensity, and \( d \) is the thickness of the film, as measured by standard profilometry, varying from 170nm to 650nm. We generated a plot of \( (\alpha h\nu)^2 \) versus photon energy, \( h\nu \), as shown in the inset in Figure 63 (a), and used this to estimate the bandgap by linearly extrapolating to the energy \( (h\nu) \) axis as shown in the inset. The determined bandgap, \( E_g \), as function of Mg concentration, \( x \), is shown in Figure 63 (b). It can be seen that the bandgap value increases linearly for Mg content up to \( x=0.7 \). For Mg content greater than 0.7, a departure to another linear behavior is observed. These two linear fits are described by the following two equations:
\[ E_g(x) = 1.36x + 3.28 \quad \text{when } 0 \leq x \leq 0.7 \]
\[ E_g(x) = 8.4x - 2.064 \quad \text{when } 0.75 \leq x \leq 0.95 \]

Figure 63. (a) Transmission spectra of $\alpha$-Mg$_x$Zn$_{1-x}$O films with different Mg concentration, $x$, from 0 to 1; The inset shows the curve of $(\alpha h\nu)^2$ versus photon energy $h\nu$. (b) The resultant bandgap of $\alpha$-Mg$_x$Zn$_{1-x}$O as a function of Mg concentration, including data from other works.
It should be noted that the bandgap of high Mg content (x>0.95) films could not be well
determined since the absorption edge begins near the detection limit of the spectrometer at
~190nm, limiting the number of data points available. Using the limited data, we observe that the
bandgap for pure $\alpha$-MgO is larger than 6.5 eV [open square in Figure 63 (b)], indicating that the
optical bandgap of $\alpha$- $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ is continuously tunable from 3.3 eV to more than 6.5 eV. The
values of bandgap determined in this work are in good agreement with those for crystalline films
reported in other sol-gel publications\textsuperscript{110,122} as shown in Figure 63 (b). The slight difference in
observed bandgap is mainly associated with a shift of absorption edge due to different post-
annealing temperature of the films\textsuperscript{123} and resultant variations in crystallinity.

6.5 Summary

Amorphous $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films across the full compositional range were obtained using a sol-gel
deposition method on quartz substrates, overcoming the known mixed phase region for the
ternary and offering band gap tunability within the critical UV-C spectral region. Post-annealing
temperature was optimized to 400°C to obtain a sharp absorption edge and to eliminate phase
segregation issues intrinsic to crystalline $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films. The ratio of Zn/Mg in the precursor
was found to remain in the amorphous films after annealing, simplifying band gap tuning, and $\alpha$-
$\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films with high smoothness (< 1nm RMS) and high transmissivity (>90%) in the
visible and near infrared regions were obtained. The bandgap of the films could be engineered
continuously from 3.3 eV to more than 6.5 eV as the Mg concentration increases from x=0 to
x=1, showing controllable tunability in the UV-C spectral region. Thus, sol-gel synthesized amorphous Mg$_x$Zn$_{1-x}$O films are a promising candidate for simple and low-cost fabrication of amorphous-based optoelectronic devices as solar-blind detectors.
7. CHAPTER SIX: ULTRAVIOLET PHOTODETECTORS

7.1 Introduction

Wide bandgap semiconductor based photodetectors are not yet considered a mature technology compared to silicon, but their development has attracted considerable attention in a wide range of civil and military applications, such as flame detection, optical communications, and biological analysis. In semiconductor photodetectors, photons are absorbed by the semiconductor material and electron-hole pairs are created and separated by an electric field if there is any bias or built-in potential. There are various types of semiconductor photodetectors, the most common are: photoconductors, metal-semiconductor-metal (MSM) photodetectors, Schottky diodes, p-n and p-i-n photodiodes, and field-effect phototransistors. Several parameters are considered crucial for high performance photodetectors: responsivity, response time (or bandwidth), and dark current (or Noise Equivalent Power). Responsivity and response time are in general two contradictory factors: high responsivity detectors may have high gain and thus slow response. The dark current for high responsivity detectors is also large due to the large leakage current. Fast response photodetectors could be used in communications.

High responsivity photodetectors can work without any pre-amplifying equipment and have applications in faint light detection, which is especially useful for monitoring weak signal such as weak flame or combustion detection. However, there are some general rules of photodetector design to improve these factors. For MSM devices, to achieve low dark current one has to: (1) to
make a Schottky contact or grow a Schottky barrier enhancement layer; and (2) grow high quality films with low donor concentration (for n type semiconductor), which means low impurities, vacancies, phase boundaries, and other defects. To absorb more light: (1) the film thickness should be close to the inverse of the absorption coefficient, (2) the area should be as large as possible to maximize light absorption, and (3) finger width should be small and spacing should be large. For fast response photodetector, however, the above principle could be opposite, since large area and thickness reduces the bandwidth. The spacing should also be optimized since responsivity is both RC time limited and transit time limited\textsuperscript{129}.

An attractive application of wide bandgap semiconductor detectors is that they can be made “visible blind” and “solar blind”, with cut-off wavelength of 400nm and 290nm, respectively\textsuperscript{130}. A solar blind photodetector is only responsive to UV radiation below 290nm, which is out of the spectrum range of solar radiation on the Earth due to the absorption of ozone. In other words, no photocurrent will be generated when exposed to normal outdoor lighting. UV detection has been most commonly achieved by UV enhanced silicon detectors which suffer from low sensitivity, degradation under UV illumination, and reduction of quantum efficiency for the deep-UV (because of a passivation layer, SiO\textsubscript{2}). Furthermore, to make a solar blind detector based on Si, one has to apply a filter which further reduces the UV light coming to the device. An additional benefit of wide bandgap semiconductor DUV detectors is radiation hardness\textsuperscript{131,132}, which is crucial for harsh environments, i.e. space application.
Among the wide bandgap materials, ZnO is a promising candidate due to its strong radiation hardness and low cost. By alloying ZnO with MgO, the bandgap can be tuned across the UV region, and detectors can be fabricated with different cut-off wavelengths, resulting in visible blind and solar blind photodetectors\textsuperscript{133-138}. As mentioned earlier, single phase wurtzite MgZnO with high Mg composition is difficult to be obtained due to the well-known phase segregation issue. Some researchers have realized cubic MgZnO in the solar blind region on MgO substrates\textsuperscript{111,136,137}, with maximum responsivity of 396 mA/W at 10V bias. Wurtzite ZnO has been reported with a responsivity of 26000 A/W at 8 V bias, which is the highest value reported for ultraviolet photodetector\textsuperscript{139}. MgZnO has been demonstrated with very high responsivity of 1200 A/W, but the peak of 308 nm is out of solar blind region \textsuperscript{140}. All these results provide insight that photodetectors based on wurtzite MgZnO could demonstrate very high responsivity in the solar blind region if the single phase wurtzite MgZnO can be achieved with high Mg composition. Some literature has been reported on wurtzite MgZnO growth and detectors\textsuperscript{141,142}, but the maximum responsivity was reported to be 304 mA/W at 260nm with 10V bias and is far below the a few A/W as expected for wurtzite MgZnO.

7.2 Experimental procedure

MSM interdigital electrode geometry (Figure 64) with Schottky and Ohmic electrodes with interdigital finger spacing ranging from 2 to 15 μm were fabricated from epitaxial layers mentioned in Chapter 4. A Ni/Au contact (20nm/130nm) was chosen for Schottky contact and Ti/Au (20nm/130nm) was chosen for ohmic contact. To characterize the photoresponse
properties of the photodetectors, a 300W Xe lamp was used as the excitation source and a monochromometer was used for scanning the spectrum.

### 7.3 Results and Discussions

Figure 65 shows the response spectrum of ZnO MSM photodetector at 5 V bias. The peak Responsivity is around $2 \times 10^4$ A/W below 380nm. This is comparable to the highest reported responsivity for ZnO photodetector\textsuperscript{139}. But in our case, we have smaller bias, which means our responsivity could be slightly higher. The quantum efficiency ($\eta$) and gain ($g$) can be expressed in the following formula:

$$\eta g = \frac{Rh\nu}{q} \quad (24)$$

where $R$ is the responsivity depending on voltage, $q$ is the electron charge and $\nu$ is the light frequency. The $\eta g$ for the ZnO photodetector was estimated to be $6.6 \times 10^4$ at 5 V bias.
Figure 65 shows the responsivity of ZnO MSM photodetector at 5 V bias (the inset is the log scale).

Figure 66 shows the photo response of Mg_{0.46}Zn_{0.54}O MSM photodetector at 0V bias and 5V bias. The log scale was shown in Figure 67. The main optical cutoff is in the 280-300 nm range that corresponds to the fundamental optical absorption band in the MgZnO alloy. The small shoulder that appears near 310 - 375 nm is due to the photocurrent contribution from the thin ZnO buffer layer. Schottky photovoltaic devices show responsivity at 265nm of 0.01A/W with dark current of 23pA, and rejection ratio R_{265nm}/R_{400nm}=180 and R_{265nm}/R_{500nm}=505. Photoconductive devices show responsivity at 260nm of 200A/W, resulting in photoconductive gain of $1 \times 10^3$ with dark current at 5V of 2.7 µA, and rejection ratio R_{265nm}/R_{400nm} =140 and R_{265nm}/R_{500nm} =392.
Figure 66. Responsivity of MSM Schottky photodetector at 0 V bias (viewgraph on the Top) and MSM photoconductive detector with 5 V bias (viewgraph on the Bottom) and measured on single crystal Mg$_{0.46}$Zn$_{0.54}$O.
Figure 67. Log scale plot of the responsivity of a MSM MgZnO photodetector with 10 µm pitch interdigitated electrodes at biases of 0, 1 and 5 V.

To explain the high responsivity of the MSM photodetectors, I-V curves is shown in Figure 68 for MSM photodetectors with highest Mg composition with 10 µm spacing measured in dark and under light illumination. Liu. et. al attribute the high gain to the carrier trapping process which was identified by the asymmetric barrier height at the interdigital electrodes\textsuperscript{139}. In Figure 68, the dark I-V curve shows obvious asymmetric Schottky behavior in the positive and negative region, implying the carrier trapping at the metal semiconductor interface.
Figure 68. (top) I-V characteristics of MSM Photodetectors with 10 µm spacing taken in the dark (black curve, viewgraph on the right) and under light illumination with λ = 300nm, 22 µW optical power (red curve, viewgraph on the right). (Bottom) Magnified dark I-V curve.
7.4 Conclusions

MSM structured UV photodetectors have been fabricated for MgZnO with different Mg compositions. At a 5 V bias, high responsivity of $2 \times 10^4$ A/W was reported for ZnO and 200 A/W for solar blind MgZnO photodetectors. The rejection ratios were discussed which is generally above two orders higher. Due to the carrier trapping process on the interface of metal and semiconductor, the photodetector exhibits high gain and thus high responsivity. To further increase the responsivity, a careful design of MSM devices is needed, such as narrower interdigital electrodes and larger spacing. For fast response applications, higher work function metal or even Schottky barrier enhancement layers are necessary, but will result in a loss of responsivity. The results reported in this chapter provide a route to fabricate solar blind photodetectors based on wurtzite MgZnO, leading to potential applications for detection of weak solar blind signals.
8. CHAPTER SEVEN: CONCLUSIONS

Zinc oxide (ZnO) is a wide bandgap semiconductor with a room-temperature (RT) direct bandgap of 3.37 eV which can be tuned up to 7.8 eV by alloying it with MgO and high exciton binding energy of 60 meV. In this dissertation, high quality ZnO thin films grown heteroepitaxially on sapphire and homoepitaxially on ZnO substrates by plasma-assisted molecular beam epitaxy were achieved and the structural, optical, electrical, and morphological properties of the epitaxial films were investigated.

Although there are large lattice mismatch and thermal expansion coefficient mismatch between ZnO heteroepitaxial films and the sapphire substrates, most ZnO epitaxial growth have been carried out on c- and a- plane sapphire substrates due to the large availability of sapphire substrates. We first started with growth on c-plane sapphire. Unlike other works published which used MgO buffer or other new oxidation sources to obtain good quality of thin films, we simply grew a ZnO low temperature nucleation homo-layer before high temperature growth. After careful optimization of growth conditions, we are able to achieve ZnO and MgZnO thin films on sapphire which have been shown with the highest demonstrated quality as compared to known published results. The growth temperature, sequence of Zn and O source shutter, and Zn/O ratio for both ZnO nucleation and high temperature layer growth was optimized on sapphire, resulting in RMS roughness values down to 0.373 nm for 1 μm². Several characterization methods have been applied to reveal the quality of the epitaxial films. The FWHM for (0002) peaks were measured to be 13 arc sec and 17.8 arc sec for ZnO and MgZnO (with low Mg composition)
respectively, indicating good ordering in the growth direction. The RSM provides some evidence of deterioration of crystal structure while doping with Mg. Ga doping was also demonstrated with carrier concentration up to $4 \times 10^{19}$ cm$^{-3}$ while maintaining high mobilities above 60 cm$^2$/V$s$. At higher Mg composition, the crystal quality deteriorates but a thick ZnO buffer helps to improve the surface morphology. We successfully tuned the Mg composition for wurtzite MgZnO from 0% to 46% without phase segregation, with sharp absorption edges and cut-off wavelengths from 378nm to 277nm (which is just at the solar blind region). By fabricating MSM photodetectors on these thin films, we were able to achieve the responsivity of 200 A/W at 5 V bias for a solar blind MgZnO photodetector, which is the highest value reported ever for wide bandgap semiconductor detectors in the deep UV region.

ZnO homoepitaxial growth was also demonstrated which has the potential to achieve very low dislocation densities. ZnO films were grown by PA-MBE on Zn-polar ZnO substrates with 0.5° miscut angle toward the [1100] direction. By growing at a low temperature growth (610°C), we have demonstrated films with very good surface morphology with one or two monolayer step height along the [0001] direction. Such low growth temperature is beneficial for p-type doping of ZnO and increase the lifetime of maintenance of MBE system components in the oxygen growth environment. We have investigated several parameters which are rarely discussed, from processing the substrates to the optimization of growth parameters. Surface treatment such as wet etching was found crucial to achieve a higher PL lifetime. EIT of the oxygen source was found necessary to reduce oxygen flux etching at high oxygen flow rates, resulting in a higher growth
rate and less defects in the films. Use of higher purity 6N oxygen was found to reduce impurities in the films, eliminating the satellite XRD peak (Zn(CN)_2) induced by impurities in the gas tank and improving the PL lifetime to 217 ps. The influence of growth temperature was also investigated and growth rate was increased from 0.02μm/h to 0.246 μm/h by decreasing the growth temperature from 660°C to 580°C, and PL lifetime as high as 0.35 ns was achieved. By fitting growth rate and PL lifetime with a linear curve, we concluded that high growth rate is required for a high PL lifetime since the films will contain lower concentrations of point defects. This provides other researchers the idea to improve the PL lifetime. With all these optimized growth conditions, we were able to grow ZnO thin films on Zn-polar non-miscut ZnO substrates with excellent morphology, without any surface defects like reported in other literatures. When doping the film with Ga, we found Ga act as a surfactant which improves the surface morphology a lot. The carrier concentration was calculated to be \(2.1 \times 10^{18}\) cm\(^{-3}\) from SIMS scan. This indicates an efficient LED or LD structure with perfect interfaces between active layer and n-type doping layer can be obtained.

By expanding the sheet layer of two dimensional hole gases (2DHG) caused by polarization effect to three dimension hole distribution, we investigated the possibility of increasing the hole carrier concentration by growing the gradient layer. The polarization effect was simulated and was proved to be not as strong as that for III-nitrides. This is because the difference of spontaneous polarization between ZnO and MgO is large and the piezoelectric polarization effect even cancels the polarization induced effect. However, even though the polarization cannot be
used to induce p type doping, it could still help to act as an electron blocking layer without blocking any holes. To prove this, we have grown a linearly gradient structure with Mg composition grading from 0% to 43%. The resultant film showed no p type behavior.

While high quality ZnO-based materials were investigated by MBE, we also contribute our effort to search for low-cost method of growing ZnO thin films, by sol-gel process. Amorphous Mg$_x$Zn$_{1-x}$O films were obtained on quartz substrates, with a continuous shifting of absorption edge by tuning Mg composition across the full compositional range. This overcomes the known phase segregation for the ternary and offering band gap tunability within the critical UV-C spectral region. The obtained α-Mg$_x$Zn$_{1-x}$O films showed high smoothness (<1nm RMS) and high transmissivity (>90%) in the visible and near infrared regions. The bandgap could be continuously engineered from 3.3 eV to more than 6.5 eV, with the Mg concentration increasing from x=0 to x=1, showing controllable tunability in the UV-C spectral region.
REFERENCES

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