ABSTRACT

CHUNMING JIN, Growth and Characterization of ZnO and ZnO-Based Alloys \text{Mg}_{x}\text{Zn}_{1-x}\text{O}
and \text{Mn}_{x}\text{Zn}_{1-x}\text{O}. (Under the direction of Prof. Jagdish Narayan)

The goals of this work were to synthesize ZnO and ZnO-based alloys in the forms of thin films by using pulsed-laser deposition technique and to study the structural, stoichiometric, optical and electrical properties of these thin films for the potential applications in the new optoelectronic devices.

The optimized deposition conditions for growing epitaxial hexagonal MgZnO alloy thin films on sapphire (0001) substrates were determined by a systematic analysis of XRD and TEM. The epitaxial growth mechanism of these films on sapphire (0001) substrates is demonstrated to be domain-matched. The films are of high single-crystalline quality and show bright excitonic luminescence. Based on the RBS results, the maximum Mg concentration in the films with hexagonal wurtzite structure was found to be 34 at. %, which is almost ten times of the value allowed by the phase diagram. The bandgap energy of MgZnO thin films was found to be changed to the higher energy side with increasing Mg concentration. By changing Mg content, the bandgap of MgZnO alloy film can be tuned from 3.40 eV to 4.19 eV, this provides an excellent opportunity for bandgap engineering for optoelectronic applications.

ZnMgO thin films with cubic (NaCl) structure were also synthesized by using PLD. The maximum Zn concentration in these cubic alloy films was 18 at. %. The epitaxial growths of
cubic ZnMgO thin films were realized on both MgO and sapphire (0001) substrates via lattice-matching epitaxy and domain-matching epitaxy, respectively. Cubic phase ZnMgO thin films were successfully grown on the silicon substrate by applying TiN and MgO as buffer layers, which is believed to be of significant importance for integrating ZnO-based alloys to the Si-based electronics. This cubic ZnMgO/MgO/TiN/Si(001) heterostructure was developed via epitaxial layer by layer growths. The epitaxial growth of TiN layer was accomplished by domain-matching epitaxy. The MgO buffer layer was grown epitaxially by lattice-matching epitaxy. The epitaxial mechanism of ZnMgO thin film was also lattice-matching epitaxy.

Towards the practical applications of ZnO-based optoelectronics, the phase stability of MgZnO/ZnO/MgZnO superlattice structures was studied using XRD and HRTEM methods. The MgZnO with maximum Mg content of about 34 at. % was used as the barrier layers in these superlattices. The diffusion of Mg from the MgZnO barrier to the ZnO well was observed by using the HRTEM and optical measurements. The cubic nanoinclusions were also observed with HRTEM.

For the potential applications in spintronic devices, epitaxial MnZnO thin films were also synthesized on sapphire (0001) substrates by using PLD. These MnZnO thin films have hexagonal wurtzite structure and very high single-crystalline quality according to the XRD, TEM and RBS results. The maximum Mn concentration was 35 at. %. The bandgap of these films shifts to the higher energy side with increasing Mn content. Magnetic investigations indicate that these films are paramagnetic.
Single-crystalline ZnO thin films have been grown successfully on Si(111) substrates by using PLD. This integration of ZnO thin films with silicon substrates was realized with two different heterostructures, ZnO/AlN/Si(111) and ZnO/MgO/TiN/Si(111). In ZnO/AlN/Si(111) heterostructure, the ZnO film was grown epitaxially on the AlN buffer which was grown on the Si substrate with domain-matching epitaxy. Two buffer layers were applied for the ZnO/MgO/TiN/Si(111) heterostructure. The excellent epitaxial property of TiN on Si substrate ensures the epitaxial growths of the MgO buffer layer and the ZnO film. These heterostructure thin films have excellent single crystalline quality and extremely bright excitonic emission based on the analysis of XRD, TEM and PL measurements.

ZnO thin films were also grown on the amorphous silica substrates by using PLD for the potential applications of ZnO in the planar displays and random lasers. XRD results show that these films have textured structure with the c-axis of the ZnO thin film perpendicular to the substrate surface. The excitonic absorption peaks were observed in these films at room temperature. PL studies show that the PL characteristics of these films are comparable to that of the films grown on the sapphire substrates.

An ultraviolet illumination-enhanced luminescence effect was observed in the ZnO thin film samples. We found that the PL intensity increased with the UV light exposure time. This new phenomenon is attributed to the oxygen desorption on the ZnO sample surface. A phenomenological model was proposed to explain this new effect. The time dependent
equations derived from this model result in a very good agreement with the experimental data.
Growth and Characterization of ZnO and ZnO-Based Alloys $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mn}_x\text{Zn}_{1-x}\text{O}$

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A dissertation submitted to the Graduate Faculty of North Carolina State University, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

Materials Science and Engineering

Raleigh, Fall 2003

Approved by

Prof. Jagdish Narayan
Chair of Advisory Committee

Prof. Carl C. Koch

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Prof. Robert M. Kolbas
This thesis is dedicated to my wife and my parents
BIOGRAPHY

Chunming Jin was born on February 4th, 1965 in Jilin, China. He graduated from Department of Physics, Jilin University, China in 1986. From 1986 to 1996, he worked in Changchun Institute of Physics, Chinese Academy of Sciences where his research was focused on the linear and nonlinear optical properties of semiconductor and semiconductor nanoparticles. He got his MS in physics, University of Puerto Rico in May 1998. He was accepted into the Ph.D. program by Department of Materials Science and Engineering at North Carolina State University in Spring 1999. He worked under the direction of Prof. Jagdish Narayan for his Ph.D. thesis.
ACKNOWLEDGEMENT

First, I would like to express my sincere appreciation to my advisor Prof. Jagdish Narayan for his wonderful guidance and tremendous support during my Ph.D. study and research. He is a wonderful advisor who helped me go through all the difficulties that I encountered in my study, research, and even life. He is a great materials scientist. It is my great honor to be his student. What I learned from him will benefit my whole life.

I would like to thank Prof. Ronald O. Scattergood, Prof. Carl C. Koch, and Prof. Robert M. Kolbas for serving on my committee and supporting my research. They give me a lot of instructive discussions and helpful suggestions. They also give me the wonderful lectures during my study.

The help provided by Dr. Wayne Holland of Oak Ridge National Labs for RBS and Dr. Kumar in NCA&T for magnetic measurements is greatly appreciated. I would like to appreciate Dr. Muth for his helpful discussions and optical characterizations.

I want give my special thanks to Dr. Alex Kivit, Dr. Ajay Sharma, Dr. Tapan Nath, and Dr. Ashutosh Tiwari for all their wonderful helps and discussions.
I would like to thank all my colleagues: Haiyan Wang, Honghui Zhou, Hugh Porter, Amit Chugh, Abhishek Gupta, Thomas Rawdanowich, and Jason Haverkamp for their supports and helpful discussions.

I would like to express my appreciation to Edna Deas for all her helps on a daily basis.
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Chapter 1. INTRODUCTION

The growth and characterization of II-VI semiconductor ZnO and ZnO-based alloys (including MgZnO, CdZnO, and MnZnO) have been becoming a more and more active research field in recent years. The research works have been encouraged by both scientific significance and the potential of various practical applications such as light-emitting diode (LEDs) and ultraviolet photodetector, \(^1\) UV-blue semiconductor laser, \(^2\) flat panel displays, \(^3\) solar cell, \(^4\) gas sensor, \(^5\) and surface acoustic wave devices, \(^6\) and so on.

The properties and the growth of bulk zinc oxide crystal had been investigated extensively as early as 1950-1960’s. \(^7\) The new research wave for this material started in early 1990’s stimulated by the demand of new opto-electronic devices. Due to its unique characteristics, ZnO is considered to be a very promising alternative of III-nitride for opto-electronic devices in the blue to ultra-violet range. Most of the recent interests on zinc oxide material have been focused on the future potentials of UV-blue light emitting devices (LED) and UV-blue lasers. III-nitrides and ZnSe-based II-VI compounds are well-known materials for blue and ultraviolet light emitters. Both of these materials have been successfully used to fabricate continuous wave laser diodes operating at room temperature. In table 1-1, the properties of the most popular wide band gap semiconductors are compared. \(^8\) The most desirable features of zinc oxide can be listed as follows:

1. Zinc oxide has the largest exciton binding energy of 60 meV, which is 2.4 times the effective thermal energy at room temperature. This is one of the key parameters that enable the UV laser diode and other exciton related light emitting devices to be
operated at room temperature.

2. Zinc oxide has the largest optical gain ever reported.

3. ZnO is one of the “hardest” materials in II-VI compound semiconductors due to the higher melting point and larger cohesive energy. It can be expected that a degradation of the material due to the generation of dislocations during the device operation will be reduced.

4. The constituent elements of zinc oxide are abundant and of low cost. Also the material is nontoxic, which is an important consideration for environment.

5. Interfacial energy between ZnO and sapphire or other oxide substrates is such that two-dimensional growth is favored, which results in high quality films at lower temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>Lattice constants</th>
<th>Bandgap at RT (eV)</th>
<th>Cohesive energy (eV)</th>
<th>Melting point (K)</th>
<th>Exciton binding energy (meV)</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>wurtzite</td>
<td>a (Å) 3.249, c (Å) 5.207</td>
<td>3.37</td>
<td>1.89</td>
<td>2248</td>
<td>60</td>
<td>$\varepsilon(0)=8.75$ $\varepsilon(\infty)=3.75$</td>
</tr>
<tr>
<td>ZnS</td>
<td>wurtzite</td>
<td>a (Å) 3.823, c (Å) 6.261</td>
<td>3.8</td>
<td>1.59</td>
<td>2103</td>
<td>39</td>
<td>$\varepsilon(0)=9.6$ $\varepsilon(\infty)=5.7$</td>
</tr>
<tr>
<td>ZnSe</td>
<td>Zinc blende</td>
<td>a (Å) 5.668, c (Å) — —</td>
<td>2.70</td>
<td>1.29</td>
<td>1793</td>
<td>20</td>
<td>$\varepsilon(0)=9.1$ $\varepsilon(\infty)=6.3$</td>
</tr>
<tr>
<td>GaN</td>
<td>wurtzite</td>
<td>a (Å) 3.189, c (Å) 5.185</td>
<td>3.39</td>
<td>2.24</td>
<td>1973</td>
<td>21</td>
<td>$\varepsilon(0)=8.9$ $\varepsilon(\infty)=5.35$</td>
</tr>
<tr>
<td>6H-SiC</td>
<td>wurtzite</td>
<td>a (Å) 3.081, c (Å) 15.117</td>
<td>2.86 (ind)</td>
<td>3.17</td>
<td>&gt;2100</td>
<td>—</td>
<td>$\varepsilon(0)=9.66$ $\varepsilon(\infty)=6.52$</td>
</tr>
</tbody>
</table>

Many different techniques, such as chemical vapor deposition (CVD), pulsed laser deposition (PLD), rf-magnetron sputtering, spray pyrolysis, ion-beam assisted
deposition, molecular beam epitaxy (MBE), oxidation of metallic zinc, and atomic layer deposition have been used to synthesize ZnO thin films. Most of the ZnO thin films have been grown on α-Al2O3 substrates on which the films grow epitaxially by domain-matching epitaxy. Single crystalline ZnO thin films grown on a lattice-matched substrate have also been reported. Another substrate that has been frequently used is fused quartz (glass). Textured ZnO films can be obtained on such amorphous substrates and have the potential to be used in display devices and random lasers.

Zinc oxide based alloys have also attracted more attention during the past few years. These alloys include MgZnO, CdZnO and MnZnO. The purposes for the first two alloy systems are mainly from the consideration of band gap engineering. Another reason for developing such ZnO-based alloys is to construct the superlattice heterostructures with less lattice-mismatched alternative layers such as ZnO/CdZnO/ZnO, MgZnO/CdZnO/MgZnO, and MgZnO/ZnO/MgZnO. As already demonstrated for III-nitride and GaAs systems, the fabrication of these heterostructures is key to realization of ZnO-based devices.

ZnO is a compound semiconductor of II-VI family with a direct band gap of 3.39 eV at room temperature. The crystalline structure of ZnO is hexagonal wurtzite with lattice constants of a=3.249 Å and c=5.207 Å. MgO has a cubic structure of NaCl type with the lattice constant of 4.216 Å. The bandgap of MgO is 8.2 eV. Although the common stable phases of ZnO and MgO have different crystal structures, these two materials can still be alloyed with each
other to form MgO-ZnO compounds. The crystal structures of such alloys can be either hexagonal wurtzite type or cubic NaCl depending on the relative concentrations of Mg and Zn. The bandgap of wurtzite MgZnO alloys is expected to vary from 3.4 eV (value of the bandgap of pure ZnO) to much higher values. On the other hand, the bandgap of CdO is 2.0 eV. A decreased bandgap can be obtained for CdZnO alloys. So alloy systems of MgZnO and CdZnO are expected to provide a series of optoelectronic materials with wavelength range from red to deep UV. This is similar to III-nitride system, where GaN (3.4 eV) is alloyed with AlN (6.2 eV) to increase the bandgap or with InN (1.8 eV) to decrease the bandgap.

Another interesting ZnO-based alloy is Zn$_{1-x}$Mn$_x$O. This is a diluted magnetic semiconductor (DMS). The exploration for Zn$_{1-x}$Mn$_x$O alloys was motivated by its potential in the field of spintronics. In Spintronics, the spin of charge carriers (electrons and holes) is used to provide new functionality for microelectronic devices. Diluted magnetic semiconductors (DMS) have a great potential to be used as spintronics materials.$^{24}$ One key factor that determines the practical application of DMS in spintronics is that it has to be room-temperature ferromagnetic material. According to the recent results of theoretical investigations provided by Dietl et al.$^{25}$ MnZnO alloys are expected to be ferromagnetic material with Curie temperatures higher than 300 K. As a candidate of new DMS material, the growth and characterization of MnZnO thin films have been becoming an attractive research topic.

Another technical challenge in the field of the future ZnO-based devices is how to integrate
the material to silicon based microelectronics. To do so, epitaxial growth of ZnO thin films on Si substrates is required. Since Si is easily oxidized, the epitaxial growth has to be accomplished by using some suitable buffer layers. Although the integration of ZnO with silicon has been reported where GaN was used as a buffer, alternative systems are still required since the epitaxial growth of GaN itself on silicon substrate is a big challenge.

Despite extensive research on ZnO, there are still so many unanswered questions. The origin of green emission band is one of these unknown questions as pointed in Ref. [26]: “The origin of the luminescence center and the luminescence mechanism of ZnO:Zn phosphors are barely understood.” (see also the discussions in Chapter 2). This green emission band is considered as the fundamental feature for ZnO to be used as a green emission phosphor for planar displays. It is also closely related to the excitonic emission (which is the key for the ZnO uv-blue optoelectronic devices) because of the competition between these two recombination processes.

ZnO and its alloys have a definite advantage over their counterpart-III-nitrides and their alloys, particularly in terms of exciton binding energy and their luminescence properties. The ZnO and its alloys have been grown on sapphire; however, quality of epitaxy is not very good. The focus of my research is to grow ZnO and its alloys by our patented method of domain-matching epitaxy, where integral multiples of lattice planes match across the film-substrate interface. 28 We have discovered a new cubic phase of ZnMgO, which can be grown epitaxially on Si (001) via domain-matching epitaxy. Thus we can integrate optoelectronic devices with silicon microelectronic devices.
Based on these research challenges discussed above, the objectives of this work are as follows:

(1) Growth and characterization of hexagonal wurtzite MgZnO alloys thin films
First effort is to realize the epitaxial growth of MgZnO thin films on sapphire (0001) substrates by using pulsed laser deposition technique. Second effort is to find out the nature of DME and optimized deposition parameters of MgZnO thin films.

(2) Characterization of MgZnO/ZnO/MgZnO heterostructures
The effort is to develop the MgZnO/ZnO/MgZnO heterostructure on sapphire (0001) substrates by applying PLD technique and investigate the interfacial structure and properties by using TEM.

(3) Growth and characterization of cubic phase ZnMgO thin films
The effort is focused on the epitaxial growth of cubic ZnMgO thin films on MgO, Si and sapphire substrates via domain-matching epitaxy.

(4) Growth and Characterization of MnZnO thin films on sapphire (0001) substrates.

(5) Growth and characterization of ZnO on Si (111) substrates
Explore the methods of integrating ZnO thin film with silicon substrates with AlN and TiN as buffer layers.
(6) Growth and characterization of ZnO thin films on amorphous substrates.

(7) Investigation of luminescence behavior of ZnO thin films.
References


Chapter 2. MATERIALS BACKGROUND

2.1 Crystal Structure and Native Defects of ZnO

2.1.1 Crystal Structure of Zinc Oxide

Zinc oxide has a hexagonal wurtzite structure as shown in Figure 2-1-1. Wurtzite structure is one of the most common crystal structures of semiconductors. Other semiconductors that crystallize in wurtzite include nitrides (GaN, AlN, BN), II-VI semiconductors (ZnS, CdS, ZnSe, CdSe, ZnTe, CdTe), SiC, and InAs, etc.

ZnO has a hexagonal close-packed (hcp) Bravais lattice as shown in Figure 2-2-2. The structure of ZnO can be considered to be composed of two interpenetrating hcp sublattices of cation (Zn) and anion (O) displaced by the length of cation-anion bond in the c-direction. The lattice constants of ZnO hexagonal unit cell are a=3.250 Å and c=5.206 Å. Since ZnO is a two-element compound with different ion radii, the c/a ratio for ZnO hcp unit cell is 1.60, which is a little smaller than the ideal value of 1.633 of hcp structure. The number of the nearest neighbors in wurtzite is four. Each O (or Zn) ion is tetrahedrally surrounded by four Zn (or O) ions. Furthermore each ion also has twelve next-nearest neighbors of the same type of ions. The O-Zn distance of the nearest neighbors is 1.992 Å in the direction parallel to the c-axis of the hexagonal unit cell and 1.973 Å in the other three directions of the tetrahedral arrangement. The tetrahedral arrangement of the nearest neighbors indicates the covalent bond between the Zn and O atoms. The covalent radii of Zn and O were reported to
be 1.31 Å and 0.66 Å, respectively.\(^4\)

Figure 2-1-1. Wurtzite structure of ZnO (Large ball — Zn, Small ball — O).

Figure 2-1-2. Hexagonal close-packed (hcp) structure of ZnO.
ZnO is an-isotropic crystal with the symmetry of point group of C_{6v} (or 6mm). Group C_{6v} is the point group of the hexagonal wurtzite structure, which includes rotations by ±60°, ±120°, and ±180° around the hexagonal axis and two sets of three equivalent mirror planes that are parallel to the hexagonal axis.

### 2.1.2 Native Defects in Zinc Oxide

Under the common preparation conditions, excess zinc is always found in ZnO. Due to this zinc excess, ZnO is a non-stoichiometric compound and an n-type semiconductor. The point defects in ZnO can be zinc interstitials or oxygen vacancies. However, it is not clear yet that whether zinc interstitial or oxygen vacancy is the dominant defects. In general, two types of thermally formed point defects can be distinguished in ion crystals, i.e. Schottky defects and Frenkel defects. The dominant defect type can be predicted from the radii of cations and anions. Schottky defects are dominating in the crystals with nearly equal radii of cations and anions. These defects appear as pair-wise vacancies of cations and anions. Frenkel defects are dominating defects if one ion radius is distinctly smaller than the other one. These defects appear as pair-wise interstitials and vacancies of the smaller ions. The ionic radius is 1.32 Å for O^{2-} ion and 0.74 Å for Zn^{2+} ion. If we consider ZnO as an ionic crystal, Frenkel disorder in the zinc sub-lattice seem to be preferred since the radius of Zn^{2+} is much smaller than that of O^{2-}. However, the nearest neighbors in ZnO are tetrahedrally coordinated. This is a characteristic of a covalent bond. The covalent radii of zinc and
oxygen are 1.31 Å and 0.66 Å, respectively. So if ZnO is treated as a covalent compound, Frenkel disorder in the oxygen sublattices is preferred. The ionicity of ZnO was found to be about 50-60%, which corresponds to an effective ionic charge of 1 to 1.2. As a result, the dominating defects in ZnO can not be figured out from the consideration of ionic and covalent radii.

Although it is believed that the stoichiometric deviation of excess zinc is reasonable for the n-type conductivity, there was no consistent results of experimental investigations about the type and concentrations of defects. The difficulty of quantitative determination of stoichiometric deviation is to maintain the homogeneity of defect concentration throughout the sample. Equilibrium between the sample and the vapor phase is a faster process compared to the homogenization of the defect concentration that is controlled by a slow bulk diffusion process. The experimental methods and results of quantitative determination of excess zinc were reviewed by G. Neumann in Ref. 6.

In the literature, point defects such as Zn interstitial, Zn and O vacancies in ZnO are referred to the native lattice defects of the material. Based on the numerous studies of electrical and optical properties of ZnO and of diffusion processes, Kroger was able to estimate the location of the energy levels of native defects in ZnO. These energy levels are shown schematically in Figure 2-1-3. In the figure, $V_{Zn}$ and $V_{zn}''$ represent Zn vacancies with effective charges of $-q$ and $-2q$, respectively. The symbols of $Zn_i^*$ and $Zn_i^{*+}$ are the Zn interstitials with effective charges of zero and $+q$, respectively. The O vacancies are indicated by $V_{O}^*$ and $V_{O}^{*+}$ with neutral charge and effective charge $+q$. The locations of these energy levels were given by
referring either to the bottom of the conduction band or to the top of the valence band. The intrinsic bandgap in the figure is given by $E_i=3.2\times10^{-3} T$ (eV). This value is smaller than the value of about 3.4 eV (at RT) indicated by later measurements (see the following section). The activation energy for the two acceptor levels of $V'_{Zn}$ and $V''_{Zn}$ as a function of temperature $T$ are given by $E_{a1}=0.7\times10^{-4} T$ (eV) and $E_{a2}=2.8\times10^{-3} T$ (eV), respectively. The binding energies of the two Zn-interstitial donor levels are $E_{b1}=0.05$ eV and $E_{b2}=0.5-1.5\times10^{-4}$ T (eV). For O vacancy, the binding energies of the two donor levels are given by $E_{c1}=0.05$ eV and $E_{c2}=2.6\times10^{-4}$ T (eV).

Figure 2-1-3. Electronic energy levels of native defects in Zn O. (From Ref. 7).
References

2.2 Energy Band Structure and Optical Properties of ZnO

2.2.1 Band Structure of Zinc Oxide

For semiconductors, the energy of single free carrier is described by the band structure \( E(\mathbf{k}) \), which is the function of quasi-momentum \( \mathbf{k} \) that is determined by the periodic boundary conditions. Naturally, properties of the band structure are determined by the symmetric properties of the semiconductor crystal and the chemical binding of the constituting elements. The symmetric properties of band structure can be qualitatively understood by assuming the lattice periodic parts of the Bloch functions are still related to atomic orbitals of the constituting elements.\(^1\) This assumption is fulfilled for compounds with rather strong ionic contribution to the binding such as the Cu-halides or the II-VI compounds, but only to a minor degree for the III-V compounds with homeopolar binding.\(^1\)\(^-\)\(^2\) However the correct symmetries of the lowest conduction band and the upper valence bands can be determined with this approach for all the three classes of semiconductors. Based on the atomic orbitals, the conduction bands are mainly constituted by the first unoccupied s-levels that are generally from the cations, such as the 4s levels of Zn in ZnO and the 4s levels of Cu and Cl in CuCl. The corresponding valence bands are formed by the highest occupied levels, which are, in the most cases, the p-levels of the anions such as 3p-level of Cl and 2p-levels of O.

ZnO has the wurtzite structure with the symmetry of the point group of \( C_{6v} \) (6mm). \( C_{6v} \) has six nonequivalent irreducible representations that correspond to the six classes of its
elements. These nonequivalent representations are usually labeled as $\Gamma_1 (A_1)$, $\Gamma_2 (A_2)$, $\Gamma_3 (B_1)$, $\Gamma_4 (B_2)$, $\Gamma_5 (E_1)$, and $\Gamma_6 (E_2)$, in which the first four representations have the dimension of one and the last two are two-dimensional. If the spin of electrons is considered, the “double group” must be applied. In case of $C_{6v}$, the double group gives three additional irreducible representations with dimensions of two, labeled as $\Gamma_7$, $\Gamma_8$, and $\Gamma_9$. The character table and basis functions of the point group $C_{6v}$ are shown in the Table 2-2-1 with the additional irreducible representations of the double group.

Table 2-2-1. Character table of the point group $C_{6v}$ (6mm). Below $E_2$ or $\Gamma_6$ are the additional irreducible representations of the double group.

<table>
<thead>
<tr>
<th>$C_{6v}$</th>
<th>$E$</th>
<th>$E'$</th>
<th>$c_2/c_2$</th>
<th>$2C_3$</th>
<th>$2C_3'$</th>
<th>$2C_6$</th>
<th>$2C_6'$</th>
<th>$3\sigma_d/3\sigma_d$</th>
<th>$3\sigma_v/3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$ $\Gamma_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$ $\Gamma_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$ $\Gamma_3$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_2$ $\Gamma_4$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$E_1$ $\Gamma_5$</td>
<td>2</td>
<td>2</td>
<td>-2</td>
<td>-2</td>
<td>-2</td>
<td>-2</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$E_2$ $\Gamma_6$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>-2</td>
<td>-2</td>
<td>-2</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>$\Gamma_7$</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>$3^{1/2}$</td>
<td>$-3^{1/2}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Gamma_8$</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>$-3^{1/2}$</td>
<td>$3^{1/2}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Gamma_9$</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>-2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The band structure of ZnO near the $\Gamma$ point of the Brillouin zone is shown schematically in Figure 2-2-1. The lowest conduction band arising from the 4s levels of the Zn cations has twofold degenerate and $\Gamma_7$-symmetry (see Table 2-2-2). The uppermost valence bands are formed by the 2p-levels of O anions with some admixture of lower-lying d-levels. The six-fold anion level is split by the uniaxial crystal field of the hexagonal wurtzite structure and by the spin-orbit coupling into three degenerate valence bands, labeled A, B and C from higher to lower energies. A, B and C valence bands have symmetries $\Gamma_7$, $\Gamma_9$ and $\Gamma_7$, respectively.
The symmetries of the upper two valence bands of ZnO are reversed compared to those of other II-VI semiconductors (such as CdS) that have symmetries in the order of $\Gamma_9$, $\Gamma_7$ and $\Gamma_7$, respectively. This is from the fact that ZnO has a negative spin-orbit coupling.

![The schematic band structure of ZnO around the $\Gamma$ point of Brillouin zone.](image)

Figure 2-2-1. The schematic band structure of ZnO around the $\Gamma$ point of Brillouin zone.

<table>
<thead>
<tr>
<th>Atomic level</th>
<th>$z$-component of orbital angular momentum $l_z$</th>
<th>Irreducible representation</th>
<th>Degeneracy</th>
<th>$z$-component of the spin $s_z$</th>
<th>Irreducible representation</th>
<th>Degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>0</td>
<td>$\Gamma_1$</td>
<td>1</td>
<td>$\pm 1/2$</td>
<td>$\pm 1/2$</td>
<td>$\Gamma_7$</td>
</tr>
<tr>
<td>p</td>
<td>$\pm 1$</td>
<td>$\Gamma_5$</td>
<td>2</td>
<td>$\pm 1/2$</td>
<td>$\pm 1/2$</td>
<td>$\Gamma_7$</td>
</tr>
<tr>
<td>p</td>
<td>0</td>
<td>$\Gamma_1$</td>
<td>1</td>
<td>$\pm 1/2$</td>
<td>$\pm 1/2$</td>
<td>$\Gamma_7$</td>
</tr>
</tbody>
</table>
The band structure of ZnO had been calculated with the KKR \(^4\) and pseudo-potential method\(^5\). Photoemission measurements\(^6\) and UPS measurements\(^7\) essentially confirmed these results. The results of pseudo-potential band calculation are shown in Figure 2-2-2. The names of the points and lines of high symmetry in the first Brillouin zone for hexagonal wurtzite type structure are indicated in Figure 2-2-3.

![Figure 2-2-2. Calculated energy bands of hexagonal ZnO. The dashed line at 7.8 eV is the vacuum level. (from Powell et al. Phys. Rev. B6, 3056(1972).)](image)

D.M. Kolb reviewed the typical features of the band structure of ZnO:\(^8\) (a) The lowest conduction band is free-electron-like so that no structure is found in the optical measurements immediately above the fundamental absorption edge. (b) The p-like conduction bands is starting at about 14 eV above the top of the valence band. (c) The
valence band is broad with 5 eV width. (d) The d-band is just below the valence band with half width of 1.6 eV. This is considerably broader than the other II-VI semiconductor and is from the mixing of d-band and valence band states.

![Figure 2-2-3. The first Brillouin zone of hexagonal wurtzite structure.](image)

2.2.2 Excitons in Zinc Oxide

An ideal semiconductor is at its ground state at 0 K if there is not any excitation source. In its ground state, the bands below the top of valence band are fully filled with electrons and the conduction band is completely empty. If an electron is excited from the valence band to the conduction band by a photon with energy in the band gap region (or by the other excitation processes), the N electron system of the semiconductor is brought to an excited state from the ground. The quanta of these excitations are called “excitons”.

Although excitons can be described at various levels, the effective mass model is the most useful and simplest one. In this picture, exciton is considered as a pair of electron and hole that interacts each other through Coulomb field. Naturally exciton represents the interaction of a system with N-1 electrons in the valence band and one electron in the conduction band. In the effective-mass approximation, the (N-1) electrons are represented by a hole with its effective mass determined by the valence band structure. The whole problem of exciton in this frame is, therefore to find a solution of a hydrogen-like electron-hole pair in the media of the semiconductor. For the simple parabolic bands of a direct semiconductor, the relative motion of electron and hole can be separated from the motion of the center of mass. The energy dispersion relation of excitons with wavevector can be written as

$$E_{ex}(n_B K) = E_g - R_y^* \frac{1}{n_B^2} + \frac{\hbar^2 K^2}{2M} , \quad (2-2-1)$$

where $E_g$ is the band gap of the semiconductor; $n_B=1, 2, 3...$ is the principle quantum number; $M=m_e+m_h$, $K=k_e+k_h$ are the translational mass and wave vector of the exciton.

$R_y^*$ is the exciton binding energy,

$$R_y^* = 13.6 \cdot \frac{\mu}{m_0} \frac{1}{e^2} (eV) \quad (2-2-2)$$

with

$$\mu = \frac{m_e m_h}{m_e + m_h} m_0 \quad (2-2-3)$$

where $\mu$ is the reduced mass of the electron and hole system; $m_0$ is the mass of free electron; and $\varepsilon$ is the dielectric constant.
In Equation (2-2-1), the first term \((E_g)\) represents the energy of the electron-hole pair without
Coulomb interaction, which is the band gap since we are considering the electrons and holes
near the band edge. The second term is the Coulomb interaction energy of the electron and
hole pair. The third term describes the kinetic energy of the exciton. Exciton states lead to a
series of separated energy levels just below the bottom of the conduction band as shown
schematically in Figure 2-2-4.

Figure 2-2-4. Schematic energy levels of an exciton for direct semiconductor.

Similarly to the case of hydrogen atom, the Bohr radius of an exciton can be defined as
\[
\alpha_{B}^{ex} = \alpha_{B}^{H} \epsilon \frac{m_0}{\mu}
\]  

(2-2-4)

with \(\alpha_{B}^{H}\) being the Bohr radius of hydrogen atom.

Based on the magnitude of the excitonic Bohr radius, two types of excitons can be distinguished. When the binding energy is small, the Bohr radius is larger than the lattice constant of the semiconductor. In this case the excitons are called Wannier excitons.\(^{10}\) The excitons are found to be Wannier type for most of semiconductors. There is another type of excitons. These are so called Frenkel excitons.\(^{11}\) The Bohr radius of Frenkel exciton is smaller than the lattice constant, so that the wavefunctions of the electron-hole pair are confined in the unit cell. Frenkel excitons are usually found in the insulators and organic crystals.

If excitons can move freely in the semiconductor, they are called free excitons. Excitons can also form ion-like or molecule-like complex if they are associated with other particles in the semiconductor. The simplest set of possible excitonic complexes can be described below:\(^{12}\)

a. Exciton ions

\[\begin{array}{c}
\Theta^+ \\
\Theta^- \\
+ + -
\end{array}\]  \(\rightarrow\) \(H_2^+\)

\[\begin{array}{c}
\Theta^- \\
- - -
\end{array}\]  \(\rightarrow\) \(H^-\)

\[+ + -\]  \(\rightarrow\) \(H_2^+\)

b. Exciton molecules
\[+ + - - \quad H_2\]

\[\ominus + - - \quad H_2\]

where \(\ominus\) represents a donor, + represents a hole, and − represents an electron. Two free excitons (or say two free holes and two free electrons \((+ ++ - -)\)) can combine to form a positronium-like molecule. This new type of quasi-particle is called exciton molecule in the most of the literatures. It can move freely in the lattice and has a lower energy than that of the system with two free excitons. A free exciton can be attracted to neutral or ionized point defects as well. As a result, excitonic complexes can be formed in either molecule-like or ion-like forms. Excitons associated with point defects can not move freely and are called bound excitons.

The valence band in ZnO splits into three doubly degenerated subbands (labeled as \(\Gamma_7\), \(\Gamma_9\) and \(\Gamma_7\), respectively) due to the hexagonal crystal field and spin-orbits interactions. Corresponding to these subbands, three types of holes can be distinguished by the different effective masses. In consequence, ZnO has three series of excitons, which are formed due to the Coulomb interaction of electrons in the \(\Gamma_7\)-conduction band with the holes in the three subbands. These excitons are usually called A (\(\Gamma_7\)\(\rightarrow\)\(\Gamma_7\))-B (\(\Gamma_7\)\(\rightarrow\)\(\Gamma_9\))- and C (\(\Gamma_7\)\(\rightarrow\)\(\Gamma_7\))-excitons.\(^{13}\) In terms of the irreducible representations in \(C_{6v}\) point group of the corresponding bands and the electrical field vector of the light beam, the following selection rules can be obtained for the three exciton series:\(^{14}\)

(a) For \(E \perp c\), transitions are allowed for A-, B- and C-bands (excitons);
(b) For $\mathbf{E} \parallel \mathbf{c}$, transitions are forbidden for the B-band (exciton), allowed for A-band (exciton) with small oscillator strength, allowed for C-band (exciton) with large oscillator strength.

Numerous papers about excitonic properties of ZnO can be found in the literature.\textsuperscript{15-20} Thomas first investigated the fundamental exciton spectrum of ZnO crystals by using reflection and absorption measurements in 1960.\textsuperscript{15} The measurements were performed between 300 K and 4.2 K. He had identified three exciton series, which associated with each of three valence bands. The second valence band (B band) was found to be separated from the top valence band (A band) by approximately 6 meV, and the separation between the third valence band (C band) and the second valence band (B band) was about 38 meV. He also reported the exciton binding energy as large as 60 meV. Three well-marked exciton features in the reflection occurred at 77 K. In reflection spectra, A and B excitons were found to be active for light polarized with $\mathbf{E} \perp \mathbf{c}$, and C exciton was active when the light polarization is parallel to the c-axis ($\mathbf{E} \parallel \mathbf{c}$). Park et al.\textsuperscript{18} also performed the low-temperature reflection and absorption measurements for the exciton features in ZnO. Their values of exciton parameters were modified from Thomas’s results.\textsuperscript{15} The comparison of the A exciton parameters obtained from these two investigations is given in Table 2-2-3.

It should be pointed out that Park et al.\textsuperscript{18} also concluded that the band symmetries and valence band ordering in ZnO were same as in other II-VI semiconductors. The conclusion about the valence band ordering was contrary to the conclusions that were reported later by other groups (see for examples in Refs. [1], [3], and [8].). It seems to be widely accepted that
the symmetries of the upper two valence bands of ZnO are reversed compared to other II-VI semiconductors (such as CdS) that have symmetries in the order of $\Gamma_9$, $\Gamma_7$ and $\Gamma_7$, respectively. However, the normal valence band ordering: $(\Gamma_9 - \Gamma_7 - \Gamma_7)$ for ZnO are supported by the new evidences that have been reported recently.\textsuperscript{21-24} In a theoretical study, Gil has shown that the reversal of valence band ordering $(\Gamma_9 - \Gamma_7 - \Gamma_7)$ needs high biaxial tension for ZnO films.\textsuperscript{23}

Table 2-2-3. Comparison of exciton and energy band parameters of ZnO

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Thomas\textsuperscript{a}</th>
<th>Park et al.\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$</td>
<td>3.436 eV</td>
<td>3.435 eV</td>
</tr>
<tr>
<td>A exciton ground state energy</td>
<td>3.3768 eV</td>
<td>3.3931 eV</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>0.059 eV</td>
<td>0.042 eV</td>
</tr>
<tr>
<td>$E_{AB}$</td>
<td>0.006 eV</td>
<td>0.040 eV</td>
</tr>
<tr>
<td>$E_{BC}$</td>
<td>0.038 eV</td>
<td>0.037 eV</td>
</tr>
<tr>
<td>Exciton effective mass</td>
<td>0.31 $M_0$</td>
<td>0.20 $M_0$</td>
</tr>
<tr>
<td>Exciton Bohr radius</td>
<td>14 Å</td>
<td>22 Å</td>
</tr>
</tbody>
</table>


A set of relatively complete exciton parameters of ZnO were reported by Muth et al.\textsuperscript{24} They had measured the absorption spectra of single-crystal ZnO thin films deposited by pulsed laser deposition technique at room temperature and 77 K. The transitions from all the three excitons (A, B, and C excitons) were observed at 77 K. By modeling the experimental data, they were able to extract the parameters for all three exciton series. Their results are presented in Table 2-2-4.
Table 2-2-4. Excitonic properties of single-crystal ZnO on α-Al₂O₃ (0001).

<table>
<thead>
<tr>
<th></th>
<th>Exciton A Annealed/unannealed</th>
<th>Exciton B Annealed/unannealed</th>
<th>Exciton C Annealed/unannealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy gap (eV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>295 K</td>
<td>3.40 eV</td>
<td>3.45</td>
<td>3.55</td>
</tr>
<tr>
<td>77 K</td>
<td>3.445 eV</td>
<td>3.516</td>
<td>3.60</td>
</tr>
<tr>
<td>Binding energy (meV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>63.1</td>
<td>50.4</td>
<td>48.9</td>
</tr>
<tr>
<td>Γ_{ex,0} (meV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>295 K</td>
<td>1.3/1.5</td>
<td>4.4/4.8</td>
<td>7.5/8.0</td>
</tr>
<tr>
<td>77 K</td>
<td>0.33/0.4</td>
<td>2.3/2.9</td>
<td>3.4/4.2</td>
</tr>
<tr>
<td>Oscillator strength</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>295K</td>
<td>5.66/4.84</td>
<td>5.63/5.63</td>
<td>1.0</td>
</tr>
<tr>
<td>77 K</td>
<td>7.21/5.66</td>
<td>4.85/5.00</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*This table is copied from the report given by Muth et al.24

2.2.3 Luminescence

ZnO has been known to be a luminescent material for one century. Tremendous works about the luminescent properties of ZnO can be found in the literature. These works had been encouraged either by the fundamental research interests or by the industrial demands of optoelectronic devices. Room temperature PL spectrum of ZnO is usually composed of a near UV-emission band (375 nm) and a green emission band (510 nm)24-26 although a yellow-orange band (610 nm) can also be observed in some situations27-28.

The near UV-band is closely related to the excitonic nature of the material and may be superposed with the free exciton emission, its phonon replica, bound exciton emission, as well as biexciton emission.29-32 This band is split into many emission lines at low
temperature, especially at the temperature as low as a few degree of absolute temperature (K). Exciton emissions are often explained by using the concept so called exciton polariton. Polaritons are the quanta of the mixed state of photon and polarization wave in solid. The polarization waves are related to different elementary excitations (or quasi-particles such as phonon and exciton), and in case of excitons, the exciton polarization waves are considered. The behavior of exciton polariton in ZnO was well reviewed in Ref. [3].

The observation of luminescence from exciton polaritons is usually difficult even at low temperatures. This comes from a lot of factors. First, the efficiency of radiative emission is low even for direct gap semiconductors, which is often found to be $10^{-1}$ to $10^{-3}$. A large part of the radiative emission comes from bound-exciton complexes and defect centers. Second, exciton emission is limited by the internal reflection of the exciton polariton and the small escape length. As a quasi-particle, exciton polariton moves with their group velocity through the semiconductor. During its movement, exciton polariton can be trapped or scattered by impurities and phonons. When it eventually reaches the surface of the semiconductor, in most cases, it will be reflected back into the semiconductor. Except the internal reflection, the radiative combination yield from free-exciton polaritons is also limited by the small escape length, which is defined as the depth from which polaritons can reach the surface. Only the free-exciton polaritons inside the escape length can have the contribution to the luminescence. Although it is difficult to measure the emission from the free exciton polariton, the free exciton luminescence of ZnO was still observed. Compared to the small luminescence yield of the free-exciton polaritons, the value of their phonon replicas are usually higher. The lineshape of the emission of the m-th LO-phonon replica is given by:
\[ I_m(h\omega) \propto E_{kin}^{1/2} \exp(E_{kin}/k_B T) W_m(E_{kin}) \quad (2-2-5) \]

with \( h\omega = \varepsilon_0 m h \omega_{LO} + E_{kin} \) and \( E_{kin} = h^2 k^2/2M \) the kinetic energy of the exciton. \( W_m \) is the transition probability and can be written as,

\[ W_m(E_{kin}) \propto E_{kin}^{-\nu} \quad (2-2-6) \]

The ratio of the integrated intensities can be deduced, which is proportional to the temperature \( T \),

\[ R_{1,2} = \frac{\int I_1(\omega) d\omega}{\int I_2(\omega) d\omega} \propto T \quad (2-2-7) \]

The examples for the luminescence of LO-phonon replica in ZnO and the plot of \( R_{1,2} \) as a function of temperature can be found in Ref. [36].

Compared to that from free excitons, the luminescence from bound excitons is much stronger. The experimental observations of bound exciton emissions in ZnO have been reported extensively.\(^4,13,30,31\). The positions of emission lines from both free exciton and bound exciton in ZnO and their identifications can be found in the work provided by Tomzig and Helbig.\(^31\) In their paper, more than 40 emission lines related to the near UV-band were listed and some of them were identified.

The research interest for the green band emission in ZnO can be traced back to the early stage of last century.\(^37\) Due to this green emission, ZnO is considered as an important luminescent material for the planar display and short-decay cathodoluminescence screens. Unfortunately, the mechanisms behind this emission band are still unclear even though the
researches on this topic have been lasted for many years. At this point, an impressive statement can be found in the Phosphor Handbook (1999 edition):38 “The origin of the luminescence center and the luminescence mechanism of ZnO:Zn phosphors are barely understood.” Although the mechanism of the green band emission was first attributed to an excess of zinc39, various different models were proposed in the later reports. Almost all the proposed mechanisms about the green emission are attributed to the native lattice defects except the one that is based on the divalent Cu impurities. In the order of time evolution, these models can be listed as follows:

a. Zn-excess related transitions (Zn$^+$ to Zn$^{2+}$);39-40
b. Oxygen vacancies (V$_0$);41
c. Transitions at Cu$^{2+}$;42
d. Zn interstitial to Zn vacancy (Zni to Vzn);43
e. Singly ionized oxygen vacancies (transitions from VO$^+$ to VB);44-45
f. Transitions from shallow traps to doubly-ionized oxygen vacancies (VO$^{++}$);46-48
g. DA pair (VO$^+$ to Vzn$^-$);49

Among these explanations, model c (Cu$^{2+}$ related transitions) is the one that has been widely demonstrated by the other individual groups.42, 50-53 The luminescence spectrum at 1.6 K from Cu$^{2+}$ is characterized by a no-phonon doublet line at 2.8590 eV and a broad multiphonon side band.42 These features can be clearly observed only at very low temperature. It should be pointed out that the green emission from Cu$^{2+}$ is not only observed in Cu-doped ZnO samples, but also observed in the ZnO samples that were not deliberately doped.50, 53 In the later reports about the mechanisms of green emission, the exclusion of
Cu$^{2+}$ mechanism were mostly provided by the comments that the ZnO sample were undoped. In the report given by Vanheusden et al (model e), the effect of surface depletion layer on the green emission was considered. They found that the green emission intensity was strongly influenced by the free-carrier depletion at the surface.

Although numerous works have already been performed on the green emission, a unique model is still lack. The situation here is very complicated. We may ask that whether the green emission only has one origin. Since the observed green emission band covers a large energy range, multi-contributions are quite possible.

**References**

p161.


14. Ref. 9, p244.


26. A. van Dijken, E.A. Meulenkamp, D. Vanmaekelbergh, and A. Meijerink, J. Lumin. 87-
29. N. Ohashi, T. Sekiguchi, K. Aoyama, T. Ohgaki, Y. Terada, I. Tsurumi, and H. Haneda,
33. Ref. 9, p 61.
34. See Ref. 9, p 203.
37. Ref. 8, p 254 and the references therein.


2.3 Properties of MgO and ZnMgO materials

2.3.1 Magnesium Oxide

Magnesium oxide (MgO) is a widely used material for the applications of catalysis, microelectronics and electrochemistry. It is also widely used as substrate and buffer material for thin film growth in the field of materials science and engineering. Although MgO is usually considered as a wide bandgap semiconductor, it is close to an ideal insulating ionic solid since its valence band is determined by the strong potential of ionic core.\(^1\)

The physical and chemical properties of MgO are summarized in Table 2-3-1. MgO has a sodium chloride (NaCl) structure with the lattice constant of 4.216 Å as shown in Figure 2-3-1. The structure of MgO can be described as a fcc lattice of O\(^{2-}\) ions with Mg\(^{2+}\) ions occupying all the octahedral holes, or vice versa. Since the interaction between O and Mg is characterized by the ionic nature, the material has a very large bandgap about 8 eV and is transparent in a wide spectral range from 300 nm to 6000 nm. As an ionic solid, MgO has a very high melting point of 2800 °C. With these features, MgO has been widely used as the substrate material for the thin films growth processes in the present micro-electronic and opto-electronic devices. Numerous materials can be grown epitaxially on MgO substrates. These materials include metal,\(^2\) metal-composite nanoparticles\(^3\), phosphors\(^4\), ferromagnetic materials (nitrides\(^5\), oxides\(^6\)), electro-optic (or ferroelectric) materials (SBN\(^7\), SBT\(^8\), BTO\(^9\)), semiconductor oxides\(^10-11\), optical storage materials\(^12\), superconductive materials\(^13\), etc. MgO is also a good gate-dielectric for GaN-based MOS diodes\(^14-15\).
Table 2-3-1. The general properties of magnesium oxide.

<table>
<thead>
<tr>
<th>Structural properties</th>
<th>Physical and chemical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure:</td>
<td>Density:^a</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.576 g/cm^3</td>
</tr>
<tr>
<td>Lattice constant:</td>
<td>Melting point (K):^a</td>
</tr>
<tr>
<td>4.216 Å</td>
<td>3073</td>
</tr>
<tr>
<td>Space group:</td>
<td>Elastic Moduli (dyn cm^-2):^a</td>
</tr>
<tr>
<td>O_h^5</td>
<td>c_11=29.71</td>
</tr>
<tr>
<td></td>
<td>c_12=9.65</td>
</tr>
<tr>
<td></td>
<td>C_{44}=15.57</td>
</tr>
<tr>
<td>Dielectric constants:^a</td>
<td>ϵ(0)=9.83, ϵ(∞)=2.94</td>
</tr>
<tr>
<td>Phonon frequency (s^-1):^a</td>
<td>υ_{LO}=21.73, υ_{TO}=12.02</td>
</tr>
<tr>
<td>Bandgap (eV):^a</td>
<td>Eg_{th}=7.9, Eg_{dir}=7.833 (at 85 K)</td>
</tr>
<tr>
<td>Exciton binding energy (meV):^a</td>
<td>E_b= 161</td>
</tr>
<tr>
<td>Thermal Conductivity:^b</td>
<td>42 Wm^-1K^-1 (at 273K)</td>
</tr>
<tr>
<td>Hardness:^b</td>
<td>Knoop 692 with 600g</td>
</tr>
<tr>
<td>Youngs Modulus (E):^b</td>
<td>249 GPa</td>
</tr>
<tr>
<td>Shear Modulus (G):^b</td>
<td>155 GPa</td>
</tr>
<tr>
<td>Bulk Modulus (K):^b</td>
<td>155 GPa</td>
</tr>
<tr>
<td>Molecular Weight:^c</td>
<td>40.32</td>
</tr>
<tr>
<td>Solubility:^c</td>
<td>0.00062g/100g</td>
</tr>
</tbody>
</table>

^b from the data sheet of Crystran Ltd at www.crystran.co.uk/.

MgO has also been used as a buffer layer for developing heterostructures. Most of research works in this field are based on the fact that there is a good epitaxial compatibility between TiN and MgO, since both the epitaxial growths of TiN thin films on MgO substrates^16 and MgO thin films on TiN substrates^17 had been realized. It is well known that TiN is a very important metallic material in the Si-based electronics due to its unique diffusion and mechanical properties. One of most attractive aspects of TiN is that TiN thin films can be epitaxially developed on Si substrates with high quality. This paves a road to integrate other interesting oxide materials to Si substrate with TiN and MgO as buffer layers. Such
heterostructures have been realized for different systems. One of the most successful examples is the synthesis of PZT/YBCO/STO/MgO/TiN/Si(100) heterostructures by combining domain and lattice matching epitaxial growths, in which five epitaxial layers had been grown on Si (001) substrates by using TiN and MgO as the first two buffer layers. Other heterostructures developed by integrating oxides on Si substrates with TiN and MgO as buffer layers include NdNiO$_3$/STO/MgO/Tin/Si(001)$^{21}$, LCMO/STO/MgO/TiN/Si(001)$^{22}$, and PMN–PT/MgO/TiN/Si(001)$^{23}$ etc.

Figure 2-3-1. Schematic diagram of NaCl-type crystal structure for MgO.
2.3.2 ZnMgO Alloy

The research interests on ZnO have been encouraged by the industrial and technological demands for the new generation of opto-electronic devices. One of the key-steps towards the realization of these devices is to construct heterojunctions that are composed of ZnO and another wide-gap compounds. For this purpose, the compound should have the lattice constants similar to ZnO and adjustable energy gaps so that the interfacial defects can be minimized and the carriers in the radiative ZnO layer can be confined. Similarly to what has been done for the other systems such as GaN/AlGaN, a ZnO-based ternary alloy, Mg_xZn_{1-x}O is expected to fulfil the requirements. As more and more attentions have been focused on ZnO, Mg_xZn_{1-x}O has also become the subject of intense scientific researches.\(^{24-27}\)

MgZnO alloy has to be of a wurtzite structure for keeping the lattice similarity with ZnO and large solubility of Mg for band gap engineering. Compared to ZnO, the reports of the bulk MgZnO alloys are relatively less in the literature. Although the wide range solubility of Mg in the zinc blend structure was expected due to the similar tetrahedral ionic radii of Mg\(^{2+}\) (0.57 Å) and Zn\(^{2+}\) (0.60 Å), the small solubility of Mg in wurtzite structure ZnO was reported.\(^{28-29}\) Figure 2-3-2 shows the phase diagram of MgO-ZnO system reported by Segnit and Holland.\(^{29}\) Although the solid solution limit of ZnO in periclase MgO was extended to approximately 56 wt. % of ZnO (40 at.%) at 1600 °C, the solubility of MgO in wurtzite ZnO was less than 4%. For increasing the bandgap of MgZnO alloy, large content of MgO that exceeds the limit of thermal dynamic equilibrium is necessary. Pulsed laser deposition method is an ideal technique for this purpose because the nonequilibrium nature of PLD
processes makes it possible to fabricate solid-solution films well above the thermodynamic solubility limit. Up to now several groups have already reported the growth of MgZnO thin films with the Mg content as high as 34 mol.%.\textsuperscript{24-25} These films were deposited epitaxially on sapphire (0001) substrates with high crystalline quality. The bandgap of the MgZnO thin films can be as large as 4.15 eV with the maximum Mg content of 34% in the system. In this case, the bandgap offset of 0.85 eV can be provided for the ZnO-based heterostructure devices. Besides being used as the barrier material for ZnO-based heterojunctions, MgZnO thin films themselves are also considered to be the promising candidates for the short-wavelength light emitting devices (LED) with adjustable bandgaps that enable the devices to be operated at different wavelengths. PL spectra from these films are featured with significant enhancement of the excitonic emissions. The PL peak position was found to be blue-shifted as the bandgap of the film increases.\textsuperscript{25} The ZnO/Mg\textsubscript{0.2}Zn\textsubscript{0.8}O superlattice structures had been reported with the band-gap offset of 0.5 eV.\textsuperscript{27} The heterostructures were grown epitaxially by applying PLD process on sapphire (0001) substrates with 100-nm-thick ZnO buffer layer in between. The thickness of the well (ZnO layer) varied from 1.7 nm to 12 nm with the constant barrier (MgZnO layer) thickness of 6.2 nm. The quantum-confine effects were observed from the PL and PLE spectra. This work demonstrates that MgZnO ternary thin films with significant amount of Mg can be used as the wide-gap compounds for ZnO-based heterojunctions that will be used for the potential opto-electron devices. The even larger enhancement for excitonic binding energy of ZnO can be obtained if the Mg content in the barrier MgZnO layer is further increased. It was reported that the exciton binding energy of ZnO layer could be as large as about 120 meV in a ZnO/Mg\textsubscript{x}Zn\textsubscript{1-x}O multiquantum wells, which is two times as large as the value of bulk ZnO.\textsuperscript{30}
The Mg content in MgZnO thin films grown by using PLD technique can be as large as 34 mol. %, which is far beyond the thermodynamic limit of about 4 mol. %%. This means that these films are in the metastable phases. The thermal stability of the supersaturated MgZnO thin films had been investigated by Ohtomo et al.\textsuperscript{31} The MgZnO thin films were first deposited on sapphire (0001) substrate at 550 °C by using laser molecular-beam epitaxy (LMBE). The films of different Mg concentrations were then annealed at different temperatures from 700 °C to 1000 °C. They found that the segregation of MgO started at 850 °C for the films with Mg content larger than 15 mol. % (x>0.15). After annealed at 1000 °C, the bandgaps of the films were reduced to the value of the film with x=0.15. No segregation of MgO was found for the films with Mg content less than 15 mol. % even after the films were annealed at 1000 °C. They concluded that the thermodynamic limit of MgO
in Mg$_{x}$Zn$_{1-x}$O epitaxial film is about $x=0.15$. The thermal diffusion of Mg across the Mg$_{x}$Zn$_{1-x}$O/ZnO interface was observed only after the film was annealed at the temperature above 700 °C. This temperature is higher than that observed in other II-VI semiconductor systems. The temperature at which annealing induced considerable inter-diffusion occurs is less than 600 °C for CdZnSe/ZnSe$^{32}$ and 650 °C for ZnSe/ZnSSe$^{33}$ systems. Since the temperature for the epitaxial growth of ZnO and MgZnO thin films are usually in the range from 550 to 650 °C, thermodynamically stable heterostructures of ZnO/MgZnO with high crystalline quality can be fabricated by using PLD processes.

Although the solubility of MgO in wurtzite ZnO is low, phase diagram (see Figure 2-3-1) shows that about 40 mol.% ZnO can be incorporated into periclase MgO. Since MgO has a large bandgap of 8 eV, cubic Zn$_{x}$Mg$_{1-x}$O alloy is expected to be of much larger bandgap than that of hexagonal Mg$_{x}$Zn$_{1-x}$O thin film so that devices based on such cubic Zn$_{x}$Mg$_{1-x}$O thin films can be operated in the deep UV range of spectrum. Narayan et al.$^{34}$ first reported the epitaxial growth of cubic Mg$_{x}$Zn$_{1-x}$O thin films with maximum Zn content of 18 mol. %. The bandgap of Zn$_{0.18}$Mg$_{0.82}$O thin films was 6.7 eV. Cubic ZnMgO thin films can be grown epitaxially on sapphire (0001), MgO (001) and Si (001) (with buffer) substrates. So far, the maximum Zn concentration in Mg$_{x}$Zn$_{1-x}$O thin films was reported to be 38 mol. %.$^{35}$ The bandgap of the $x=0.38$ film was about 7.4 eV.

ZnMgO photodetector operated in deep UV region was also reported.$^{35}$ The detector was fabricated by using cubic ZnMgO/STO/Si multilayers with metal-semiconductor-metal
The advantage of such cubic ZnMgO-based detectors over other wide bandgap materials, such as AlGaN, SiC, and diamond is the possibility of detection of a wide range of UV spectrum from 157 nm to 230 nm, depending on the Zn concentrations varying from 0 mol. % to 32 mol. %.

References


24. A. Ohtomo, M. Kawasaki, T. Koida, K. Masubuchi, H. Koinuma, Y. Sakurai, Y.
27. A. Ohtomo, M. Kawasaki I. Ohkubo, H. Koinuma, T. Yasuda and Y. Segawa, Appl.
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31. A. Ohtomo, R. Shiroki, I. Ohkubo, H. Koinuma, and M. Kawasaki, Appl. Phys. Lett. 75,
35. W. Yang, S.S. Hullavarad, B. Nagraj, I. Takeuchi, R.P. Sharma, and T. Venkatesan,
2.4 Properties of MnO and MnZnO materials

Stimulated by the demands of future electronic devices, a new branch of electronics, so-called spintronics (spin electronics), has been under rapid development in the past years.\textsuperscript{1-3} In spintronics, the spin of charge carriers (electrons and holes) is used to provide new functionality for microelectronic devices. Diluted magnetic semiconductors (DMS) have great potentials to be used as spintronics materials.\textsuperscript{4} DMS are semiconductors that contain some magnetic impurities such as Mn, Co, and Cr etc. In 1999, two successive papers were published in Nature (London) by Flederling et al.\textsuperscript{5} and Ohno et al.\textsuperscript{6}, in which they reported the controlling of the polarization of light in p-(i)-n junctions by using DMS as polarizer. In their works, the polarization of light can be systematically controlled by the spin direction in the DSM. The DSM material used by Flederling et al. was II-VI semiconductor alloy, BeMnZnSe, while III-V magnetic semiconductor GaMnAs was used by Ohno et al. However, these spintronic devices only worked at low temperatures because the Curie temperatures (\(T_c\)) of those DMS are too low. For achieving practical applications of such spintronic devices, the Curie temperature of the DMS has to be increased above room temperature. Extensive research efforts have already been focused on the exploitation of high \(T_c\) ferromagnetic semiconductor materials. Some successful works had been reviewed very recently by Pearton et al.\textsuperscript{4} The DSM materials with \(T_c\) higher than room temperature are summarized in Table 2-4-1.
Table 2-4-1. Semiconductors and oxides showing room temperature ferromagnetism. (from Ref. 4)

<table>
<thead>
<tr>
<th>Material</th>
<th>Bandgap (eV)</th>
<th>Comments</th>
<th>Ordering temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd_{1-x}MnxGeP_2</td>
<td>1.72</td>
<td>Solid-phase reaction of evaporated Mn</td>
<td>&gt;300\textsuperscript{a}</td>
</tr>
<tr>
<td>(Ga,Mn)N</td>
<td>3.4</td>
<td>Mn incorporated by diffusion</td>
<td>228-370\textsuperscript{b}</td>
</tr>
<tr>
<td>(Ga,Mn)N</td>
<td>3.4</td>
<td>Mn incorporated during MBE, n-type</td>
<td>&gt;300\textsuperscript{c}</td>
</tr>
<tr>
<td>(Ga,Mn)N</td>
<td>3.4</td>
<td>Mn incorporated during MBE</td>
<td>&gt;940\textsuperscript{d}</td>
</tr>
<tr>
<td>(Ga,Cr)N</td>
<td>3.4</td>
<td>Cr incorporated during MBE</td>
<td>&gt;400\textsuperscript{e}</td>
</tr>
<tr>
<td>(ZnO):Co</td>
<td>3.1-3.6</td>
<td>Co incorporated during PLD, ~15% Co</td>
<td>&gt;300\textsuperscript{f}</td>
</tr>
<tr>
<td>(TiO\textsubscript{2}):Co</td>
<td>3.1</td>
<td>Anatase; ~7% Co; PLD or O\textsubscript{2} MBE</td>
<td>&gt;380\textsuperscript{g}</td>
</tr>
<tr>
<td>(Ga, Mn):P:C</td>
<td>2.2</td>
<td>Mn incorporated by implant or MBE; p~10\textsuperscript{20} cm\textsuperscript{-2}</td>
<td>&gt;330\textsuperscript{h}</td>
</tr>
<tr>
<td>(Zn\textsubscript{1-x}Mnx)GeP\textsubscript{2}</td>
<td>1.83-2.8</td>
<td>Sealed ampule growth; insulating; ~5.6 % Mn</td>
<td>312\textsuperscript{i}</td>
</tr>
<tr>
<td>(Zn\textsubscript{1-x}Mnx)GeP\textsubscript{2}</td>
<td>&lt;2.8</td>
<td>Mn incorporated by diffusion</td>
<td>350\textsuperscript{j}</td>
</tr>
<tr>
<td>ZnSeAs\textsubscript{2}</td>
<td>0.65</td>
<td>Bulk growth</td>
<td>329\textsuperscript{k}</td>
</tr>
<tr>
<td>ZnSiGeN\textsubscript{2}</td>
<td>3.52</td>
<td>Mn-implanted epi</td>
<td>~300\textsuperscript{l}</td>
</tr>
</tbody>
</table>

\textsuperscript{k} S. Choi et al, Solid State Commun. 122, 165(2002).

Recently, Dietl et al.\textsuperscript{7} had calculated the Curie temperatures of various semiconductors that contain Mn magnetic elements by applying the original Zener model\textsuperscript{8} of ferromagnetism. A plot of the predicted Curie temperatures as a function of the bandgap is shown in Figure 2-4-1. Among these materials, ZnO and GaN are the wide-gap semiconductors with highest T\textsubscript{c} values. It has to be pointed out that the ferromagnetic phase transformation of MnZnO thin films occurs only in case of p-type semiconductors. ZnO is naturally an n-type.

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semiconductor, and the realization of p-type ZnO is still a challenge. Motivated by the theoretical prediction, more research works have been focused on the growth and characterization of MnZnO-alloy thin films aimed to develop a new type of room temperature ferromagnetic semiconductor.

Figure 2-4-1. Predicted Curie temperatures as a function of the bandgap (from Ref. 4).

The general properties of MnO were described in Ref. 9. MnO has a crystal structure of NaCl type with lattice constant of 4.445 Å at temperatures above 120 K. At temperatures below 120 K, MnO undergoes a 0.8% rhombohedral distortion. The melting point of MnO is 2058 K. Its density is 5.18 g/cm³. Pure MnO is an insulator at low temperature and has its conductivity of \(10^9 - 10^{15}\) ohm cm at room temperature. MnO is an anti-ferromagnetic material with Neel temperature of 122 K. The forbidden energy gap of MnO is 2.7 eV.
Phase diagram of ZnO-MnO system is shown in Figure 2-4-2, which was reported by Bates et al.\textsuperscript{10} During their measurements, metallic manganese was used as starting material to keep the manganese in a divalent state. The phase diagram shows that significant amount of Mn\textsuperscript{2+} can be incorporated into hexagonal ZnO lattice even at relatively low temperatures. The solubility of Mn\textsuperscript{2+} in ZnO is 13 per cent at 600 °C. At 800 °C, the solubility of Mn\textsuperscript{2+} increases to a value of 25 per cent. It was found that the lattice constants of ZnO change considerably with increasing Mn content. There is also a good agreement between the solubility determined by the change in lattice constant and that measured by the electron probe. However, the solubility of Zn\textsuperscript{2+} in cubic MnO is relatively low at lower temperatures. At temperature below 500 °C, Zn ions can not be incorporated into MnO. The solubility of Zn\textsuperscript{2+} in MnO is about 10 per cent at 800 °C.
Several groups have reported the growth of MnZnO alloy thin films.\textsuperscript{11-14} Epitaxial growth of MnZnO thin films can be realized at temperatures from 600 to 750 °C on sapphire (0001) substrates. The maximum Mn contents in MnZnO alloy films are about 35 per cent, which is much higher than the solubility limit for the bulk material. The bandgap of MnZnO thin films shifts to the higher energy side as the Mn contents increase. However, none of MnZnO thin films that had been reported so far showed the ferromagnetic behavior. This is consistent with the theoretical prediction that the ferromagnetic transition occurs only in p-type ZnO.

References


2.5 Properties of substrate buffer materials

In this section, we will discuss the general properties of the materials used as substrates or buffer layers for the thin film growth processes in this project. These materials include silicon, $\alpha$-Al$_2$O$_3$, MgO, fused silica, TiN and AlN. The crystalline structures and melting points of these materials are listed in Table 2-5-1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal structure and lattice constant</th>
<th>Melting point (K)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>Diamond, $a$=5.431 Å (at 295.7 K)</td>
<td>1685</td>
<td>2.329 (RT)</td>
</tr>
<tr>
<td>MgO</td>
<td>NaCl, $a$=4.216 Å</td>
<td>3073</td>
<td>3.576</td>
</tr>
<tr>
<td>$\alpha$-Al$_2$O$_3$</td>
<td>hcp, $a$=4.75 Å, $c$=13 Å</td>
<td>2320</td>
<td>3.99</td>
</tr>
<tr>
<td>AlN$^a$</td>
<td>Wurtzite, $a$=3.11 Å, $c$=4.98 Å (RT)</td>
<td>3273</td>
<td>3.255</td>
</tr>
<tr>
<td>TiN</td>
<td>NaCl, $a$=4.24 Å</td>
<td>2390</td>
<td>5.22</td>
</tr>
<tr>
<td>Silica (fussed)</td>
<td>amorphous</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.5.1 Silicon

Silicon is a group VI element semiconductor. At present, most of the commercial electronic devices are based on silicon. The development of modern semiconductor industry leads to very matured techniques for producing and processing high-quality silicon wafers. Besides being used extensively in semiconductor industries, silicon is also widely used in the scientific researches, either as subjects aimed to the generation of new silicon-based devices or as substrate materials for developing other new functional materials. Silicon is widely used as substrates in thin-film growth processes for several reasons:

a. The material is much cheaper compared to other single-crystalline materials (i.e. MgO, sapphire, STO etc.).

b. Large size silicon wafers can be obtained commercially with low cost and can be cut to any size to fit the requirements of deposition processes.

c. It is highly desired to integrate semiconductor thin films with silicon substrates. In this case, most of the advantages of modern semiconductor industries can be used in the later device development.

d. Modern semiconductor industry can provide low-cost silicon wafers with various properties required by customers.

Silicon has a diamond-crystal structure (see Figure 2-5-1) with lattice constant of 5.431 Å. The temperature dependence of lattice constant for high-purity silicon can be approximated as
\[ \alpha(T) = 5.4304 + 1.8138 \times 10^{-5} (T - 298.15 K) + 1.542 \times 10^{-9} (T - 298.15 K)^2. \]

Silicon is an indirect semiconductor. The indirect band gap is 1.1242 eV at room temperature and is 1.17 eV at 0K. The temperature dependence of the bandgap is given by

\[ E_{g, \text{int}} = A + BT + CT^2, \]

with \( A = 1.170 \text{ eV}, B = 1.059 \times 10^{-5} \text{ eV/K}, \) and \( C = -6.05 \times 10^{-7} \text{ eV/K}. \)

![Figure 2-5-1. Schematic diagram of crystal structure of Si.](image)

The linear thermal expansion coefficient of silicon is \( \alpha = 2.59 \times 10^{-6} \text{K}^{-1}. \) Its temperature dependence in the range of 120 to 1500 K, \( \alpha(T) \) (with T in K) can be approximated as

\[ \alpha(T) = [3.725[1 - \exp(-5.88 \times 10^{-3} (T - 124))] + 5.548 \times 10^{-4}] \times 10^{-6} \text{K}^{-1}. \]

The thermal resistivity of silicon as a function of temperature is given by

\[ K_L^{-1}(\text{cmKW}^{-1}) = 0.1598 + 1.532 \times 10^{-3} T + 1.583 \times 10^{-6} T^2. \]
The diffusion coefficients for the elements that are mostly concerned in this work are listed in Table 2-5-2. These elements include Al, N, O, Ti, Mg, and Zn. Other properties of silicon (such as bandgap structure, phonon frequencies) can be found in Ref. [1].

Table 2-5-2. Diffusion coefficients of impurities in Si. Parameters in the table occur in the equation $D = D_0 \exp\left[\frac{Q}{k_BT}\right]$.

<table>
<thead>
<tr>
<th>Element</th>
<th>$D_0$ [cm$^2$s$^{-1}$]</th>
<th>$Q$ [eV]</th>
<th>Temperature range [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$^a$</td>
<td>8.69</td>
<td>3.39</td>
<td>1060 — 1240</td>
</tr>
<tr>
<td>N$^b$</td>
<td>0.87</td>
<td>3.29</td>
<td>1100 — 1200</td>
</tr>
<tr>
<td>O$^c$</td>
<td>0.13</td>
<td>2.53</td>
<td>500 — 1400</td>
</tr>
<tr>
<td>Ti$^d$</td>
<td>0.015</td>
<td>1.8</td>
<td>950 — 1200</td>
</tr>
<tr>
<td>Zn$^e$</td>
<td>$3 \times 10^{-6}$</td>
<td>0.40</td>
<td>1100 — 1300</td>
</tr>
</tbody>
</table>

---


### 2.5.2 Sapphire ($\alpha$-Al$_2$O$_3$)$^7$

Aluminum oxide has several different modifications. The most stable one is $\alpha$- Al$_2$O$_3$ (sapphire). Sapphire has a corundum structure as shown in Figure 2-5-2. The Bravais lattice of sapphire is hexagonal close-packed (hcp) structure with lattice constants of $a=4.75$ Å and $c=13$ Å.$^7$ In the corundum structure of sapphire, Al atoms occupy two thirds of the octahedral interstitial voids of each successive hcp packed layer of oxygen atoms. Sapphire has large bandgap of 9.7 eV, which enables the material to transmit light over a broad wavelength range from 150 nm to 5000 nm. Sapphire has a melting point of is 2040 °C, and
it has extremely high chemical stability even at high temperatures. Sapphire is also one of the strongest and hardest materials available. The hardness of sapphire on the Mohs scale is 9, compared to 10 for diamond. It also has excellent abrasion resistance and exceptional thermal shock properties.

![Figure 2-5-2. The corundum structure of sapphire (α- Al2O3).](image)

With these unique properties, sapphire has various applications in the areas of optics, laser, semiconductors, optoelectronics, industry and military. Sapphire is also widely used as substrate material in thin film growth processes. The hexagonal structure of sapphire makes the material to be the top one choice of substrates for the other hcp materials such as GaN, AlN and ZnO, etc. The large bandgap of sapphire makes optical characterization of the thin films developed on it to be carried out without disturbing. The high chemical stability can effectively reduce the interface reaction between the thin film and sapphire substrate so that thin films can be grown with high crystalline quality. Up to now, many different materials have been grown in form of thin films on sapphire, such as ZnO\textsuperscript{8}, MgZnO\textsuperscript{9}, GaN\textsuperscript{10}, AlN\textsuperscript{11},
CuInS$_2^{12}$, YBCO$^{13}$, and LiNb$_{1-x}$Ta$_x$O$_3^{14}$, etc. The physical and mechanical properties of sapphire are listed in Table 2-5-3.

Table 2-5-3. Physical and mechanical properties of sapphire.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Hexagonal system (rhombohedral)</th>
<th>Thermal conductivity (60° to c-axis) at 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters</td>
<td>$a = 4.758$ Å, $c = 12.991$ Å</td>
<td>Thermal expansion coefficient 8.40 × 10$^{-6}$ °C$^{-1}$</td>
</tr>
<tr>
<td>Density</td>
<td>3.98 g cm$^{-3}$</td>
<td>Specific heat at 25 °C 0.10 cal g$^{-1}$</td>
</tr>
<tr>
<td>Melting point</td>
<td>2040 °C</td>
<td>Heat capacity at 25 °C 18.6 cal °C$^{-1}$ mol$^{-1}$</td>
</tr>
<tr>
<td>Boiling point</td>
<td>2980 °C</td>
<td>Dielectric strength 480,000 V cm$^{-1}$</td>
</tr>
<tr>
<td>Hardness</td>
<td>9 mohs</td>
<td>Dielectric constant 9.4 (E$_c$); 11.5(E$_c$)</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>$50 \times 10^6$ psi</td>
<td>Compressive modulus $55 \times 10^6$ psi</td>
</tr>
<tr>
<td>Poisson's ratio</td>
<td>0.29</td>
<td>Volumetric modulus of $35 \times 10^6$ psi</td>
</tr>
</tbody>
</table>

Data are taken from http://www.crystalsystems.com/

2.5.3 Aluminum Nitride

Aluminum nitride (AlN) is a covalent-bond material. The structure of the stable-phase AlN is hexagonal wurtzite structure belonging to the space group $C_6v^{\text{4-P6_3mc}}$ (see Figure 2-5-3). The lattice constants of the hexagonal unit cell are $a=b=3.11$ Å and $c=4.98$ Å, respectively.$^{15}$ AlN transits into a metastable phase with NaCl structure at 21 GPa pressure. The corresponding physical properties of wurtzite AlN are listed in Table 2-5-4.
Figure 2-5-3. Hexagonal wurtzite structure of AlN. (large ball-Al, small ball-N).

Table 2-5-4. Properties of wurtzite AlN.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>49.99</td>
</tr>
<tr>
<td>Structure and lattice constants</td>
<td>Wurtzite,  a=3.11 Å, c=4.98 Å</td>
</tr>
<tr>
<td>Bandgap</td>
<td>6.20 eV (at 300K)</td>
</tr>
<tr>
<td></td>
<td>6.23 eV (at 77K)</td>
</tr>
<tr>
<td>Melting Point</td>
<td>3273 K</td>
</tr>
<tr>
<td>Density</td>
<td>3.255 g/cm³</td>
</tr>
<tr>
<td>Conductivity (Ω⁻¹cm⁻¹)</td>
<td>10⁻¹¹—10⁻¹³ (intrinsic)</td>
</tr>
<tr>
<td>Linear thermal expansion coeff.</td>
<td>α₁=7.27×10⁻⁶K⁻¹</td>
</tr>
<tr>
<td></td>
<td>α‖=4.15×10⁻⁶K⁻¹</td>
</tr>
<tr>
<td>Hole mobility</td>
<td>14 cm²/Vs</td>
</tr>
<tr>
<td>Dielectric constants</td>
<td>ε(0)=9.14</td>
</tr>
<tr>
<td></td>
<td>ε(∞)=4.84</td>
</tr>
<tr>
<td>Micro Hardness</td>
<td>15.3 Gpa</td>
</tr>
</tbody>
</table>

Data are taken from Ref. 1.

AlN is stable at very high temperatures in inert atmospheres. Surface oxidation of AlN occurs above 700°C in air. A layer of aluminum oxide can protect the material up to 1370°C. Above this temperature bulk oxidation occurs. AlN has high thermal conductivity, high resistivity and low thermal expansion coefficient that closely match silicon. It has the
potential for the applications in high performance electronic industry as integrated circuit packages and heat sinks. AlN is a wide bandgap III-V semiconductor with direct bandgap of 6.2 eV at room temperature. Due to its large bandgap, AlN is transparent from infrared to near UV wavelengths (3 to 0.3 µm), and can be used as window material for near UV, infrared and radar.

Various thin film growth techniques have been used to grow AlN thin films such as pulsed laser deposition (PLD), plasma assisted CVD, MOCVD, MBE, and reactive dc-magnetron sputtering, etc. Several different substrates have been used for growing epitaxial AlN thin films including sapphire (0001), 6H SiC, and Si (111) etc. Developing epitaxial AlN thin films on silicon is highly concerned for scientific and technological reasons. The integration of III-nitride-based LEDs with silicon electronics requires III-nitride thin films grown locally on processed Si chip. AlN are usually used as the buffer layer between the terminal GaN layer and the Si substrate. The epitaxial growth of AlN thin films on Si (111) had been reported by Vispute et al. The epitaxial mechanism between AlN film and Si (111) substrate was found to be domain-matched epitaxy with 4/5 ratio of the interplanar distances of Si (011) and AlN (2110).

2.5.4 Titanium Nitride (TiN)

Titanium Nitride (TiN) is a metallic transition-metal nitride with high hardness, good corrosion and erosion resistance, and high sublimation temperature. This material has
various applications ranging from corrosion and erosion resistance coatings, to diffusion barriers in advanced integrated circuit devices, and to the wavelength-selective films.\textsuperscript{24-26} TiN has a NaCl-type crystal structure with lattice constant of 4.24 Å. TiN also has a relatively high melting point of 2390 K and high microhardness of 19.9 GPa.

Epitaxial growth of TiN thin films on Si substrates has been reported extensively since the material has the great potentials for applications of ohmic contacts and contact metallurgy in integrated circuits and diffusion barriers.\textsuperscript{24, 27-28} The epitaxial mechanism of TiN thin films on Si (001) substrate was found to be cube-on-cube domain-matching epitaxy of less than 4% misfits with 4-TiN unit cells matching 3-Si unit cells.\textsuperscript{24} TiN is also widely used as buffer layer to integrate oxide thin films to Si substrate.\textsuperscript{29-32}

References


3.1 Pulsed Laser Deposition Technique

3.1.1 A General Description of Pulsed Laser Deposition Technique

Pulsed laser deposition (PLD) is a relatively simple and versatile technique for growing a variety of materials in thin film form. In principle, PLD is a method by which thin films are deposited from the materials that are vaporized by an intense laser beam. As reviewed by J.T. Cheung, the idea was proposed in the early 1960’s, soon after the first high power ruby laser became available, and was first demonstrated by Smith and Turner in 1965. Although PLD technique has been developed and improved since its first stage, it became more and more popular in 1980’s. Several advantages are responsible for the current popularity of the technique. The most attractive one among these features is its nonequilibrium process, which results in stoichiometric nature of multi-component system. The start-up cost for PLD is low. A PLD system can produce the thin films with quality comparable to that from molecular beam epitaxy (MBE) system with the 1/10 cost of the later one. Another feature of PLD technique that attracts materials scientists is its versatility. With PLD technique tremendous materials have been developed in their thin film forms. K.L. Saenger had listed out more than two hundreds thin film materials deposited with PLD technique, all were inorganic materials including metals, semiconductors, superconductors etc. In addition, organic polymer thin films and biocompatible thin films are also the topics of PLD technique. Principally any material can be developed into its thin film form by PLD as long as it has
large enough absorption coefficient for the laser light used in the PLD system. Another advantage of PLD is the capability of generating films that match the stoichiometry of the target. This is of particular importance in the deposition of multi-component materials. A qualitative explanation for this “congruence” is that the heating rate provided by pulsed laser irradiation is so fast that material removal occurs before the individual components of the target material can segregate out into low and high vapor pressure components.\(^6\) Compared to other deposition techniques, multi-layer-heterostructures with different materials can be developed much easily by using PLD. For example, the epitaxial growth of the heterostructure of PZT/YBCO/STO/MgO/TiN/Si(100) was reported,\(^7\) in which all the layers between Si(100) substrate and the top-layer of PZT were used to be the buffer layers to integrate epitaxial PZT thin film on silicon substrate.

A PLD system basically consists of three main components: Laser, deposition system, and the optics between the former two. Figure 3-1-1 shows the schematic of the PLD system that is used in this work. Usually any type of laser can be used in a PLD system if the power of out-put laser beam is high enough. The lasers that had already been used in the PLD technique included ruby laser,\(^8-12\) CO\(_2\) gas laser,\(^13-15\) Nd-YAG laser,\(^16-19\) Nd-glass laser,\(^20-22\) and excimer lasers\(^23-30\), etc. However, due to its unique characteristics, excimer laser has become the number one choice in the PLD system. Excimer laser is a gas laser operated in the UV range.\(^31\) It is also a pulsed laser with the repetition rate up to several hundreds hertz and a common pulse width of 25 nanoseconds. Depending on the gas used, the operating wavelength of excimer laser can be changed from 157 nm for F\(_2\) to 351 nm for XeF. Table 3-1-1 lists the wavelengths for the commercial excimer laser systems. Compared to other
commercial lasers excimer laser also has an output energy as high as 1J/pulse. The higher output energy and the short operating wavelength make excimer laser the ideal one for PLD systems since most of the materials used for the deposition have strong absorption in range of 200 nm to 400 nm.

Figure 3-1-1. Schematic diagram of the PLD system used in this work.

Table 3-1-1 Operating wavelengths of excimer laser for different gases.

<table>
<thead>
<tr>
<th>Excimer</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>157</td>
</tr>
<tr>
<td>ArF</td>
<td>193</td>
</tr>
<tr>
<td>KrCl</td>
<td>222</td>
</tr>
<tr>
<td>KrF</td>
<td>248</td>
</tr>
<tr>
<td>XeCl</td>
<td>308</td>
</tr>
<tr>
<td>XeF</td>
<td>351</td>
</tr>
</tbody>
</table>
In a PLD system, thin films are grown in a high vacuum chamber. The vacuum may vary from $10^{-6}$ Torr for the general purpose to $10^{-11}$ Torr for the laser MBE systems. One of the advantages of PLD is that it requires very simple and relatively economical pump and gas-flow systems. The basic elements inside the vacuum chamber include substrate holder, targets holder, vacuum gauges, etc. Compared to other thin film growth methods, films are usually grown at mediate temperature in PLD systems. The multiple-target mounting assembly is usually adopted for the PLD system. In the system used for this work, four targets can be loaded into the vacuum chamber at the same time. The multiple-target assembly gives another advantage of PLD technique, by which in situ multilayer structures can be easily developed.

For all the PLD system, the optical elements are needed to achieve the optimized focused beam for ablating the target material. These optical elements, such as mirror, aperture, beam splitter, and lens are placed between the output port of the laser and the laser window of the vacuum chamber.
3.1.2 Interaction between Laser Beam and Matters: Mechanisms and Plume Properties

In PLD technique, the target materials are first sputtered (or say ablated) into a plasma plume by a focused intense laser beam. The materials ablated then flow (or fly) onto the substrate surface, on which the desired thin films are developed. Therefore, the interaction of intense laser with matters plays an important role in PLD process. As reviewed by R. Kelly and A. Miotello\(^{32}\), several sputtering mechanisms are responsible for the PLD processes. These can be classified as primary sputtering mechanisms and secondary sputtering mechanisms. The primary sputtering includes collision sputtering, thermal sputtering, electronic sputtering, exfoliation sputtering, and hydrodynamic sputtering. The secondary sputtering can be distinguished as outflow with reflection, outflow with recondensation, effusion with reflection, and effusion with recondensation.

**PRIMARY SPUTTERING**

Primary sputtering results in particle emission. It occurs when solid materials are bombarded with ions, electrons, single photon, or pulsed phonons as the case in PLD process.

**Collision Sputtering**

In collision sputtering, the target material is removed as particles from the target surface through momentum transformation from the incident particles to the particles that are removed. Obviously the direct collision effect can not happen in PLD process because of the
small momentum of photons. However, indirect collision effect does exist in PLD process, in which the particles of target material are removed through the collision effect between laser-induced plasma and the target material.

**Thermal Sputtering**

Thermal sputtering refers to the evaporation of the target material due to the transiently heating effect as a result of intense laser absorption. The evaporation rate can be written as

\[
Vaporation - flux = condensation - flux = p(2\pi mk_{\text{B}}T)^{-1/2} = p_0\{\exp(-\frac{\Delta H_v}{k_{\text{B}}T})\} \times (2\pi mk_{\text{B}}T)^{-1/2} \text{ atoms/m}^2\text{s}
\]

where \(p\) is the pressure, \(p_0\) is constant, \(\Delta H_v\) is the heat of evaporation. Then the total loss from the target is

\[
Depth/\text{pulse} = \frac{p_0}{n_c} (2\pi mk_{\text{B}})^{-1/2} \times \int_0^\infty \exp(-\frac{\Delta H_v}{k_{\text{B}}T})T^{-1/2} dt
\]

where \(n_c\) is the number of density of the condensed phase.

**Electronic Sputtering**

Electronic sputtering is a group of processes that have the common feature of excitation. For high laser-pulse energy, high density of electrons is excited, \(n_c \approx 10^{22}\ \text{cm}^{-3}\). These dense electrons will increase the total energy by an amount of \(\sim n_c E_{\text{gap}}/n_c\) (\(E_{\text{gap}}\) is energy gap), and thus increase the vapor pressure by orders of magnitude or break the lattice bound. The
resultant effect for this high-energy excitation is that the system makes a transition from a tightly bound solid to a densely packed, repulsive gas, and particles are expelled energetically. This model is referred to the rapid energy deposition model. When laser-pulse energy is low, the defects formed near the target surface can lead to the energetic expulsion of individual atom. The details of the electronic processes are not straightforward, but the effect are characterized by the following features:

i. Existence of a threshold energy density for particle emission,

ii. The kinetic energies of order of a few eV,

iii. High degree of directionality,

iv. Non-thermodynamic yields of molecules and ions.

**Exfoliation Sputtering**

When target is subjected to repeated thermal shocks, the flakes of the target materials detach from the target. This is referred to the exfoliation sputtering. This effect is expected to occur when the target has a high linear thermal expansion ($\Delta L/L_0$, where $L_0$ is the thickness heated and $\Delta L$ is the change in thickness), or a high Youn’s modulus ($E$), or a high melting point ($T_m$) where the laser-induced excursions approach but do not exceed $T_m$.

**Hydrodynamic Sputtering**

Hydrodynamic sputtering is referred to the processes in which droplets of the target material are formed and expelled due to the transient melting in PLD processes. Such effects are
mostly observed on metals.

SECONDARY MECHANISMS

Primary mechanisms describe the interactions between the target material and the incident laser beam. As results of these interactions, particles of the target materials are emitted out. The secondary mechanisms describe the development of the resultant pulse of particles.

When the density of the emitted particles is small enough, the particles escape without interaction. These particles go into free flight with velocity distribution that is appropriate to the primary sputtering mechanisms. As the density becomes large enough, the emitted particles exhibit prominent gas-dynamic effects due to the gas-phase collisions. First of all, an unsteady adiabatic expansion (UAE) may occur, which is similar to the case where wall is removed from a gas reservoir (as indicated in Figure 3-1-2. (a)). This was termed as outflow model.\textsuperscript{36-37} Whether the particles backscattered toward the target surface are reflected or absorbed (re-condensed) leads to two types of outflow — outflow with reflection or outflow with recondensation. If collisions among the emitted particles are sufficient, equilibrium can be achieved within a few mean free paths in a thin region that is called Knudsen layer (KL). A UAE process coupled with Knudsen layer leads to another possible expansion model, which is called effusion\textsuperscript{36-37}. Effusion may occur when the wall for UAE is porous (Figure 3-1-2 (b) and (c)). This process has two phases. The first one constitutes a UAE with a KL as the surface boundary condition for $0 \leq t \leq \tau_r$ ($\tau_r$ is the length of release process). The second
phase begins when the release process ceases abruptly at $t=\tau_r$, as when the wall is resealed. The backscattering of the particles toward to the target surface leads two types of effusion, the one with reflection and the one recondensation.

R. K. Singh and J. Narayan had reported the detailed study of the physical phenomena involved in the interaction of high-powered nanosecond excimer-laser pulses with bulk

Figure 3-1-2. The different types of unsteady adiabatic expansion (UAE). (a) Outflow with either reflection or re-condensation. Gas in a finite reservoir escapes into vacuum when the wall is released at $t=0$. (b) Effusion with reflection. Gas in a semi-infinite reservoir effuses into vacuum at $t=0$ (when the wall is porous) to $t=\tau_r$ (when the wall is resealed). Particles backscattered toward the wall are reflected. (c) Effusion with re-condensation. Situation is like that of (b). But for $t>\tau_r$, particles backscattered toward the wall are absorbed (re-condensed). (replotted from Ref. [32])
targets, which results in evaporation, plasma formation, and thin film deposition.\textsuperscript{38} According to their theory, the PLE process can be classified into three separated regimes (as shown schematically in Figure 3-1-3): (i) interaction of the laser beam with the target material resulting in evaporation of the surface layer; (ii) interaction of the evaporated material with the incident laser beam resulting in an isothermal plasma formation and expansion; (iii) anisotropic adiabatic expansion of the plasma leading to the characteristic nature of the laser-deposition process.

Figure 3-1-3. Schematic diagram showing the different phases present during laser irradiation of a target: (A) uneffected target, (B) evaporated terget material, (C) dense plasma absorbing laser radiation, (D) expanding plasma outer edge transparent to the laser beam. (replotted from Ref. 38)

By using the simple energy balance considerations, the evaporated thickness per pulse can be obtained from the heat balance equation,
\[ \Delta x_i = \frac{(1-R)(E - E_{th})}{\Delta H + C_v \Delta T} \]

where \( \Delta x_i \), \( \Delta H \), \( C_v \), and \( \Delta T \) are the evaporated thickness, volume latent heat, volume heat capacity and the maximum temperature rise, respectively. \( E \) is the energy of the laser pulse and \( E_{th} \) is the threshold energy that describes the energy losses.

The plasma that is absorbing the laser energy (region C in Figure 3-1-3) can be stimulated as a high-temperature, high-pressure gas, which is initially confined in small volume and is suddenly allowed to expand in vacuum. The plasma density \( n \) can be expressed as a Gaussian function,

\[
n(x, y, z, t) = \frac{N_T t/\tau}{2^{0.5} \pi^{1.5} X(i) Y(i) Z(i)} \exp \left( -\frac{x^2}{2X(i)^2} + \frac{y^2}{2Y(i)^2} + \frac{z^2}{2Z(i)^2} \right), \quad \text{for } (t<\tau)
\]

where \( N_T \) is total number of evaporated particles at the end of the laser pulse \((t=\tau)\). By assuming that the plasma behaves as an ideal gas, the pressure \( P \) can be obtained by \( P = n k T_0 \) with \( T_0 \) is the isothermal temperature. The velocity can be expressed as

\[
\vec{v}(x, y, z, t) = \frac{x}{2X(t)} \frac{dX(t)}{dt} \hat{i} + \frac{y}{2Y(t)} \frac{dy(t)}{dt} \hat{j} + \frac{z}{2Z(t)} \frac{dZ(t)}{dt} \hat{k}
\]

where \( dX/dt \), \( dY/dt \), and \( dZ/dt \) refer to the expansion velocity of the plasma edges \( X \), \( Y \), and \( Z \), respectively. Figure 3-1-4 shows schematically the density, pressure, and velocity profiles in the plasma. At the inner edge of the plasma, the density is maximum, while the velocity is minimum.

After the laser pulse terminates, the plasma expands adiabatically. This adiabatic expansion gives rise to the characteristic nature of the laser-deposition process. The temperature of
this expansion process is given by the adiabatic thermodynamic equation

\[ T \left[ X(t)Y(t)z(T) \right]^{-1} = \text{const} \]

where \( \gamma \) is the ratio of the specific heat capacity at constant pressure and volume. By assuming that there are no spatial variations in the plasma temperature, the equation that controls the expansion of plasma can be obtained as

\[
X(t) \left[ \frac{d^2X}{dt^2} \right] = Y(t) \left[ \frac{d^2Y}{dt^2} \right] = Z(t) \left[ \frac{d^2Z}{dt^2} \right] = \frac{kT_0}{M} \left[ \frac{X_0Y_0Z_0}{X(t)Y(t)Z(t)} \right]^{-\gamma^{-1}}
\]

where \( X_0, Y_0, \) and \( Z_0 \) are the initial orthogonal edges of the plasma after the termination of the laser pulse (\( t=\tau \)). This equation shows that the acceleration of the plasma species depends upon the mass of the species, the temperature, and the dimensions of the plasma. As the velocities are dictated by the dimensions, the highest velocities are in the direction of the small dimensions. This gives rise to the characteristic plasma shape elongated outward from the surface. If initially the plasma is longer in the \( y \) than in the \( z \) direction, it will be accelerated more rapidly in the \( z \) direction. As the plasma expands, most of the thermal energy is converted into kinetic energy, and there is no more energy left for the expansion process. Thus the plasma becomes elongated in the shorter dimensions and retains its profile during the deposition process. This effect is shown schematically in Figure 3-1-5.

Based on the theoretical work discussed above, R. K. Singh and J. Narayan\textsuperscript{38} had calculated the thickness profile of film. The results clearly show that most of the evaporated materials deposits preferentially in the region perpendicular to the irradiated target spot and the thickness profile is roughly Gaussian in shape. The effect of substrate-target distance can also be obtained from this theoretical work. The two authors have found that the maximum
thickness of film could be expressed in the form of $d^p$, where $p$ is the expansion coefficient describing the nature of the expansion. They also found that the expansion of the plasma tends to the one-dimensional value for larger laser-spot sizes. As the spot size is decreased, the expansion becomes more spherical. The theory also predicts the compositional variations in multi-element films, which are attributed to the different atomic velocities of the species in the plasma.

Figure 3-1-4. Schematic profile showing the plasma density ($n$), pressure ($P$), and velocity ($v$) gradients in the $x$ direction that is perpendicular to the target surface. The density and plasma gradients are monotonically decreasing from the target surface with linear increase in the velocity. (replotted from Ref. 38)
Figure 3-1-5. Schematic diagram showing the initial elliptical plasma shape after termination of the laser pulse and the final shape of the plasma before it strikes the substrate. The major axis of these diagrams is perpendicular to each other. (replotted from Ref. 38)
References


32. Ref. 1, chapter 3, p55.
35. Ref. 1, p66.
3.2 Thin Film Growth in Pulsed Laser Deposition Process

3.2.1 Basic Nucleation Modes

The growth of thin films usually involves three stages: (a) the transfer of the desired materials (usually in molecular, ionic or atomic forms) onto the substrate, (b) the nucleation of these incident species, (c) the growth of the initial nuclei. Among these, the nucleation processes play an important role since the whole films are developed from these nuclei. Unlike bulk single-crystal that is usually grown from single nucleus, thin films are developed from many different nuclei. The properties of these nuclei, the correlation among them, as well as the relationships of these nuclei with the substrate are the key factors for the structure of the resultant films. Three different nucleation modes had been distinguished during the growth processes\(^1\) (as shown in Figure 3-2-1): (1) Volmer-Weber nucleation and growth mode (three dimensional island growth); (2) Frank van Merwe nucleation and growth mode (two dimensional full-mono-layer growth); (3) Stranski-Krastanov nucleation and growth mode (two dimensional full-mono-layer growth followed by island growth mode).

After incident particles arrived on a substrate, these film atoms can move on the substrate, nucleate on the substrate, re-evaporate from the substrate to the environment, incorporate to a pre-existing nuclei leading to the growth of the nuclei, re-evaporate from a pre-existing nuclei as shown in Figure 3-2-2. The change of free energy for the formation of a nucleus can be written as

\[
\Delta G = \alpha_v r^3 \Delta G_v + \alpha_m r^2 \Gamma_{sv} + \alpha_m r^2 \Gamma_{ss} - \alpha_s r^2 \Gamma_{sv} \tag{3-2-1}
\]
where \( r \) is the radius of the nucleus, \( \Gamma \)'s are the interfacial energies, \( \Delta G_V \) is the change in volume free energy of the nucleus, and \( \alpha \)'s are the constants that depend on the shape of the nucleus. The subscript \( n, s, \) and \( v \) refer to nucleus, substrate, and vacuum. The critical size \( r^* \) for which the nucleus is stable can be obtained by setting \( (\partial \Delta G / \partial r) = 0 \), leading to critical radius,

\[
r^* = \frac{-2(\alpha_{sn} \Gamma_{sn} + \alpha_{vn} \Gamma_{vn} - \alpha_{sv} \Gamma_{sv})}{3\alpha \Delta G_V}
\] (3-2-2)

and the free energy for nucleation,

\[
\Delta G^* = \frac{4(\alpha_{sn} \Gamma_{sn} + \alpha_{vn} \Gamma_{vn} - \alpha_{sv} \Gamma_{sv})^3}{27\alpha \Delta G_V^2}. \] (3-2-3)

For keeping the mechanical equilibrium among the interfacial tensions, we have

\[
\Gamma_{sv} = \Gamma_{sn} + \Gamma_{vn} \cos \theta
\] (3-2-4)

For island growth, \( \theta > 0 \), and therefore

\[
\Gamma_{sv} < \Gamma_{sn} + \Gamma_{vn}.
\] (3-2-5)

For layer growth, the film “wets” the substrate and \( \theta = 0 \), one has

\[
\Gamma_{sv} < \Gamma_{sn} + \Gamma_{vn}.
\] (3-2-6)

For Stranski-Krastanov growth,

\[
\Gamma_{sv} > \Gamma_{sn} + \Gamma_{vn}.
\] (3-2-7)

In this case, the strain energy per unit area of film overgrowth is large with respect to \( \Gamma_{vn} \) so that nuclei form above the layers.
Figure 3-2-1. Basic nucleation modes. (a) three dimensional island growth; (b) two dimensional full-mono-layer growth; (c) two dimensional full-mono-layer growth followed by island growth mode.

Figure 3-2-2. Schematic diagram of nucleation on substrate surface.
Nucleation Rate

The nucleation rate can be written as

\[ \frac{dN}{dT} = N^* A^* \omega (\text{nuclei/cm}^2 - \text{sec}) \]  \hspace{1cm} (3-2-8)

where \( N^* \) is the equilibrium concentration (per cm\(^2\)) of nuclei with critical size, and \( \omega \) is the rate at which atoms impinge onto the critical area \( A^* \). The equilibrium number of critical nuclei per unit substrate area is given by

\[ N^* = n_s \exp(-\Delta G^*/kT), \]  \hspace{1cm} (3-2-9)

where \( n_s \) is the total nucleation site density. The surface density, \( n_a \) of adatoms is given by the product of the vapor impingement rate \( R_i \) and the adatom lifetime \( \tau_s \),

\[ n_a = \tau_s R_i. \]

The adatom lifetime is given by \( \tau_s = v^{-1} \exp(E_{\text{des}}/kT) \), where \( v \) is the vibrational frequency of the adatom on the surface and \( E_{\text{des}} \) is the activation energy of desorption. So, \( n_a \) can be written as

\[ n_a = v^{-1} R_i \exp(E_{\text{des}}/kT) \]  \hspace{1cm} (3-2-10)

The total impingement flux \( \omega \) is the product of \( n_a \) and the jump frequency given by \( v \times \exp(-E_s/kT) \) (where \( E_s \) is the activation energy for surface diffusion). So we have

\[ \omega = R_i \exp[(E_{\text{des}} - E_s)/kT]. \]  \hspace{1cm} (3-2-11)

Finally the nucleation rate can be expressed as

\[ \frac{dN}{dT} = n_a A^* R_i \exp[E_{\text{des}} - E_s - \Delta G^*/kT]. \]  \hspace{1cm} (3-2-12)
The nucleation rate depends strongly on the nucleation energies that are largely contained in the term of $\Delta G^*$. A high nucleation rate leads to a fine-grained thin film, or even amorphous structure. At low deposition rate, a coarse-grained film would be expected. The free energy change per unit volume can be written as\(^1\)

$$\Delta G_v = -\frac{kT}{V} \ln \frac{R}{R_e},$$

(3-2-13)

where $R$ is deposition rate, $R_e$ is the equilibrium evaporation rate from the nucleus, and $V$ is the atomic volume. By using the typical values for the surface and volume free energies, as well as their temperature dependence, some useful inequalities can be deduced.\(^1\) First, we have

$$\left(\frac{\partial r^*}{\partial T}\right)_R > 0.$$  

(3-2-14)

This inequality implies that higher substrate temperature leads to a larger critical size. So for an island structure growth, we can expect a higher coverage at higher substrate temperature. For $\Delta G^*$, we have

$$\left(\frac{\partial \Delta G^*}{\partial T}\right)_R > 0.$$  

(3-2-15)

This inequality means that the nucleation barrier increases as the substrate temperature increases. So the nucleation rate or the number of supercritical nuclei decreases rapidly as increasing substrate temperature. The development for a continuous film will take longer time at higher temperature. For the critical radius, we also have

$$\left(\frac{\partial r^*}{\partial R}\right)_T < 0.$$  

(3-2-16)

This means that a higher deposition rate leads to a smaller nucleus or island. It should be
noticed that $\Delta G^*$ is also reduced as increasing the deposition rate so that nucleation rate is increased. So a continuous film with lower film thickness can be expected at higher deposition rate. A large $r^*$ and $\Delta G^*$ can be associated with large crystallites or even monocystal formation, this is equivalent to high substrate temperature and low deposition rate. So low substrate temperature and high deposition rate correspond to polycrystalline or even amorphous formations.

The discussion above is based on the so-called capillary theory, which can only provide the qualitative description for the nucleation process. Walton et al.\textsuperscript{2} proposed an atomistic theory to interpret nucleation processes, in which the nuclei are treated as macromolecules. In this theory, the critical concentration $N_i$ of nuclei per unit area of size $i$ is given by

$$
\frac{N_i}{n_0} = \left(\frac{N_0}{n_0}\right)^i \exp\left(\frac{E_i}{kT}\right), \quad (3-2-17)
$$

where $E_i$ is the critical dissociation energy that is defined to be the energy required to disintegrate a critical nucleus containing $i$ atoms into $i$ separate adatoms, and $N_0$ is the monomer density that is given by $N_0 = \tau_s R$. The adatom has the average rest time $\tau_s$ (before they desorb from the substrate) and the diffusion distance $X = (2D_s \tau_s)^{1/2}$. $D_s$ is the diffusion coefficient that is given by

$$
D_s = \frac{1}{2} \alpha^2 \nu \exp(-E_s / kT), \quad (3-2-18)
$$

where $\alpha$ is an atomic dimension. All the adatoms within the diffusion distance $X$ during the rest time $\tau_s$ can be captured by the critical nuclei. Number of these adatoms are given by the product of $X^2$ (area) and deposition rate,
\[ RX^2 = 2RD_t \tau_e = R \alpha^2 \exp\left(\frac{E_{\text{des}} - E_s}{kT}\right). \] 

So the critical nucleation rate is given by

\[ \frac{dN}{dt} = \alpha^2 n_0 R \left( \frac{R}{\nu n_0} \right)^i \exp\left(\frac{(i+1)E_{\text{des}} - E_s + E_i}{kT}\right). \] 

The nucleation rate in the atomistic theory is expressed in terms of measurable parameters rather than macroscopic quantities such as \( \Delta G^* \), \( \gamma \), and \( \theta \) that are used in the capillarity theory. The dependence of nucleation rate on deposition rate can be used to extract \( i \) (the critical size of nuclei). At low temperature and high supersaturation, \( \frac{dN}{dt} \sim R^2 \) could be found, implying that \( i=1 \). This means that the critical nucleus contains only one adatoms. At higher temperature, the critical size of 2 or 3 could be realized. Epitaxial films would then evolve over macroscopic dimensions if the original nucleus orientation were preserved with subsequent deposition and cluster impingement. This theory also suggests that there are critical temperatures where the nucleus size and orientation undergo change. The transition temperature for 1-atom nucleus to \( n \)-atom nucleus is given by

\[ T_{i \rightarrow n} = \frac{(n-1)E_{\text{des}} + E_n - E_i}{(1-n) \ln(R / nN)}. \] 

This temperature represents the transition temperature for epitaxial growth.

### 3.2.2 Thin Film Processes in Pulsed Laser Deposition

The nucleation and thin film growth processes in PLD are characterized by the plasma properties of the laser-induced plume. As long as the incident laser beam interacts with the
target, the plasma flux is induced. The plasma flux is characterized by a high density (high deposition rate), high ionization degree (up to 70%), and a high particle energy (from several eV to 2000 eV). Two main thermodynamic parameters determine the growth mechanism and the properties of thin films. First one is the substrate temperature $T$. Second parameter is the supersaturation $\Delta m$, which is defined as

$$\Delta m = kT \ln\left(\frac{R}{R_e}\right),$$

where $k$ is the Boltzmann constant, $R$ is the actual deposition rate, and $R_e$ is the equilibrium deposition rate at temperature $T$. The plasma-flux supersaturation in PLD processes can be as high as $10^5$ J/mol. This high degree of the supersaturation or high deposition rate can lead to the two-dimensional nucleation with monoatomic height, which is favorable for the layer growth mode.

The plasma parameters also play an important role on the film properties grown by PLD. As discussed by S. Metev, the influence of the plasma parameters can be reviewed as follows:

1. The effects of thermal energy of the evaporated particles

When the thermal energy of the particles of plume is much less than the dissociation energy of the molecules of the target material, the resultant thin films can keep the stoichiometry of the poly-component target materials. However, if a composite target is used, the expected films may not be obtained. If the thermal energy of the particles of plume is of the order of the dissociation energy, the target material may be partially or completely dissociated and stoichiometric poly-component film with perfect structure and smooth surface can be obtained.
2. The effect of the kinetic energy of the evaporated particles

When the kinetic energy of the particles is comparable to the defect-formation energy, radiative defects (vacancies) can be induced in the single-crystalline substrate. These defects act as additional crystallization centers. As a result, the epitaxial growth can be realized at lower temperature compared to other techniques. When laser intensity is high ($10^8$-$10^9$ W/cm$^2$), large amount of high-energy particles exist in the plasma plume. These particles (ions) result in individual vacancies in a thin layer (~30 Å) on the substrate surface. These vacancies diffuse deep into the substrate and recombine in a time ~ $10^{-8}$ s. This procedure increases the diffusion coefficient and leads to a radiation-stimulated diffusion process that provides excellent adhesion of the films even at low temperature. Another advantage from this radiation-stimulated diffusion process is that it can be used to obtain semiconductors with a sharp active-dopant distribution in submicron layers.

3.2.3 Mechanisms of Epitaxial Growth

Depending on the specific growth parameters, the resultant thin films may be amorphous, polycrystalline, or monocrystalline. Although all these thin films have their applications associated with their crystallographic characteristics, single-crystalline thin films are mostly expected for the optimized device operations. An extended formation of single-crystalline thin films on a single-crystalline substrate is referred to epitaxy.$^{6-9}$ In terms of the substrate
and the film material, two types of epitaxy can be distinguished. The first type of epitaxy is called homoepitaxy, which is referred to the case where the substrate and film are composed of same material. If the film and substrate are different materials, we have met the second type of epitaxy, which is called heteroepitaxy.

It is not surprising to ask why another single-crystalline epitaxial layer has to be extended in case of homoepitaxy. We have several reasons to be engaged in this task although it seems nonsense in some sense. At first, the epilayer is usually freer of defects than the substrate. It can be purer than the substrate too. The epilayer can also be doped independently compared to the underlying substrate so that a multiple device design can be achieved.

Heteroepitaxy can be used to obtain a single-crystalline film for the material that is difficult or impossible to be grown in crystalline form. Heteroepitaxy also plays an important role in obtaining heterostructures such as superlattice and multiple quantum-well structures (i.e. GaN/AlGaN, GaAs/AlGaAs). These heterostructures are widely used in the opto-electronic devices.

The difference between the two types of epitaxy originates from the interfaces between the substrates and thin films. In case of homoepitaxy, the epilayer and the substrate are identical and there are no interfacial bonds. For heteroepitaxy, however, the epilayer and the substrate are different materials. The properties of heteroepitaxial films are influenced by the lattice mismatch, the difference in film and substrate chemistry, and the difference in film and substrate thermal expansion coefficients.
When the lattice parameters of the thin film and the substrate are different, a quantity that is called lattice misfit can be introduced to characterize heteroepitaxy. The lattice misfit $f$ is defined as:

$$f = \frac{\alpha_0(f) - \alpha_0(s)}{\alpha_0(s)}$$

where $\alpha_0(s)$ and $\alpha_0(f)$ are the lattice parameters of film and substrate, respectively.

Depending on the value of the lattice misfit, two types of epitaxy mechanisms can be distinguished. When lattice misfit is small (less than 7-8%), the epitaxial growth is referred to the lattice-matching epitaxy (LME). During the LME growth, heteroepitaxial film first grows pseudo-morphically, which means the epilayer is elastically strained to have the same interatomic spacing as the substrate. At this point, the interface would be coherent with atoms on either side. This pseudo-morphical growth is energy favorable when film thickness is small. As the film thickness increases, the total elastic strain energy stored in the film increases, which in turn increases the total energy of the system. So the pseudo-morphism exist only up to some critical film thickness $d_c$. Beyond the critical thickness the initially strained film becomes energetically favorable to contain dislocations. Figure 3-2-3 shows schematic diagram of the strained and relaxed growth processes. Most of dislocations are generated on the surface and then the dislocations glide to the interface as half loops. The glide process leads to the formation of detrimental threading dislocations throughout the electrically active regions of the film.
When lattice misfit between the film and the substrate is larger than 7%-8%, the heteroepitaxial growth of film can be realized by domain-matching epitaxy (DME).\(^{10, 14-15}\) The idea for DME is that when film has a large misfit relative to the substrate, it grows epitaxially by domain-matching epitaxy, where integral multiples of lattice constants match across film-substrate interfaces. This is schematically illustrated in Figure 3-2-4. The important feature of domain-matching epitaxy concept is that most of the strain in the film is relieved quickly within a couple of monolayers, so that the misfit strain can be engineered and confined near the interface. This enables the rest of the film to be grown free of defects and lattice strain. On the other hand, the idea of DME has also paved a way to grow epitaxial films on the substrates that have large misfit with the film material.
Figure 3-2-4. Schematic illustration of domain-matching epitaxy growth, in which 4 lattice planes of film match 5 lattice planes of substrate.

In the recent work reported by J. Narayan and B.C. Larson\textsuperscript{10}, the original concept of DME has been generalized such that integral multiples of lattice planes (rather than the lattice constant) match across the film-substrate interface and the size of the domain equals integral multiples of planar spacing. If the film and the substrate have similar crystal structures, then the matching of planes becomes equivalent to the matching of lattice constant. Another important feature of this generalized DME theory is that for small lattice misfit, this generalized DME is equivalent to the conventional LME. This unifies the concept of LME and DME to the universal one. The idea of planar-spacing matching in this generalized DME theory provides the more choices of substrates for hetero-epitaxial growth of thin films since only the planar symmetries of the film and substrate are considered rather than that of the unit cells.

In DME growth, the initial misfit strain of $\varepsilon = d_f/d_s - 1$ could be very large and can be relaxed by matching $m$ planes of the film with $n$ planes of the substrate. The residual strain $\varepsilon_r$ is
given by\(^{10}\)

\[
\varepsilon_r = \frac{m d_f - n d_s}{n d_s} .
\]

This residual strain is zero in case of a perfect matching (\(m d_f = n d_s\)). If the residual strain for the m/n matching is finite, a perfect matching can be reached by alternating two domains with a certain frequency according to the following relationship\(^ {10}\)

\[
(m + \alpha) d_f = (n + \alpha) d_s ,
\]

where \(\alpha\) is the frequency factor. The basic assumption of this multi-domain matching is that there is a complete relaxation of the strain without any dislocation nucleation barrier. Figure 3-2-5 shows a unified framework of lattice matching and domain matching epitaxy. If the domain matching is not perfect, epitaxy occurs by accommodating the additional misfit by changing the domain size, controlled by the parameter \(\alpha\).

Since the concept of DME was first proposed\(^ {14-15}\), DME growth has been playing more and more important role for growing heterostructures on which thin films have been grown epitaxially on the foreign substrates with large lattice misfit. The typical examples for the DME growth can be found for TiN/Si(100) system,\(^ {16}\) III-nitride epitaxy on Si(111),\(^ {17}\) and ZnO and III-nitrides on sapphire(0001),\(^ {18-19}\) etc. DME provides a great opportunity for realizing the epitaxial heterostructure thin films for the electronic devices. One of the purposes of this work is to synthesize the high quality epitaxial ZnO and ZnO-based alloy thin films on sapphire and silicon substrates by using domain-matching epitaxy.
Figure 3-2-5. Unified plot of strain vs film-substrate planar spacing ratio. The LME region is above about 12/13 ratio or below 7.7% strain. (from Ref. 10)

References

1993.


3.3 Characterization Methods of Thin Films

Thin films are usually characterized by their structural, stoichiometric, optical, electrical and mechanical properties. In this section, the characterization methods used in this work are reviewed briefly. These techniques include x-ray diffraction (XRD) and transmission electron microscope for structural characterization, absorption spectra, and photoluminescence spectra for the optical characterization.

3.3.1 X-ray Diffraction Technique

X-ray diffraction is one of the widely used experimental techniques for determining lattice parameters, preferred orientation of the crystal, phase composition (qualitatively and quantitatively), grain sizes, lattice strain, residual stress etc. XRD is a nondestructive technique and can provide the information from a relative larger area of the specimen compared to TEM.

The mechanism of XRD is simple. When a monochromatic x-ray beam incident onto a crystal sample, the constructive diffractions (or interference) from parallel planes of atoms with inter-planar spacing d occur if Bragg’s law is satisfied (see Figure 3-3-1),

\[ 2d \sin \theta = n\lambda, \]

(3-3-1)

where \( n \) is integer that indicates the order of the reflection, \( \theta \) is Bragg angle, and \( \lambda \) is the wave length of the x-ray beam. By measuring the Bragg angle \( \theta \), the interplanar distant \( d \)
The relative intensity of the diffracted beam can be written as

\[ I = |F_{klm}|^2 \left( p \frac{1 - \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right). \quad (3-3-2) \]

In this equation, the whole term in the brackets is called Lorentz polarization factor. Factor \( p \) is the so-called multiplicity factor and it represents the relative proportion of the planes contributing for the same reflection. \( F \) is called the structure factor of the crystal, which represents the complex amplitude of the electromagnetic field scattered by one unit cell of the crystal. Structure factor has the general expression of the form

\[ F_{klm} = \sum_{n=1}^{N} f_n \exp(2\pi i(hx_n + ky_n + lz_n)), \quad (3-3-3) \]

with \( r_n \) is the coordinate of nth atom in the unit cell, and \( f_n \) is the atomic scattering factor. Structure factor \( F \) is related to the symmetric properties of the unit cell and can be
calculated for any specific crystal lattice.

The common experimental methods of XRD include X-ray diffractometer, Laue method, rotating-crystal method, moving-film method, and powder method. X-ray diffractometer is widely used for the characterization of thin films, which is also used in this work. There are three kinds of measurement strategies for detecting the intensity of diffracted x-ray beam in diffractometer method:²

1. Fixed crystal and fixed detector.
2. Moving crystal and fixed detector, in which the crystal is rotated slowly through its reflecting range about the detector axis (ω scan), while the detector is stationary at the appropriate 2θ angle.
3. Moving crystal and moving detector, in which the crystal and detector are suitably coupled for each reflection, and both rotate through the diffractometer axis (ω, 2θ scan).

Figure 3-3-2 shows the schematic diagram of X-ray 2θ scan.

Figure 3-3-2. Schematic diagram of X-ray 2θ scan.
Transmission electron microscopy (TEM) is a technique that is widely used in materials science for the characterization and observation of the structure and the microstructure of materials. The first reason for which TEM is used for materials scientists is its high resolution. Table 3-3-1 lists the spatial resolution limits of materials-characterization techniques. Among these techniques, TEM has highest resolution of about a few Å. From the view of modern quantum theory, electrons have both the particle and wave characteristics. Form de Broglie’s ideas of the wave-particle duality, the wavelength $\lambda$ of a particle has the following relationship with its momentum $p$

$$\lambda = \frac{h}{p},$$

where $h$ is the Planck’s constant. So $\lambda$ can be expressed in terms of the accelerating voltage $V$ of the electron microscope as

$$\lambda = \frac{h}{\sqrt{2m_0eV}},$$

where $m_0$ is the rest mass of electron and $e$ is the electron charge. For 100 kV accelerating voltage, the wavelength can be as small as 0.039 Å. If the classical Raleigh criterion for image resolution $\delta$

$$\delta = \frac{0.61\lambda}{\beta}$$

is used, the resolution of TEM is extremely small. In fact, the resolution of TEM is limited by the equipment defects. The main defects are the spherical aberration, chromatic aberration, and stigmatism.
A TEM has two essential components. One is the illumination system, which takes the electrons from the electron gun and transfers them to the specimen with either a broad beam or a focused beam. The other one is the image system composed of apertures, magnetic lens and screen. Image system takes the electrons that are scattered from the specimen and forms the final image or diffraction patterns.
**Diffraction Mode and SAD**

TEM has two essential operation modes: diffraction mode and image mode as shown in Figure 3-3-3. The information obtained in diffraction mode is derived mainly from elastic scattering of the incident beam by the specimen. If the scattering centers in the specimen are arrayed in an orderly, regular manner (as in crystal), the scattering is coherent and results in spot patterns. If the specimen is poly-crystalline, ring patterns are expected. The diffraction pattern in TEM is usually obtained from a selected area of the specimen by inserting a selecting aperture. In this case, the operation is called selected-area diffraction (SAD).

**Image Mode**

No matter what kind of specimen is used, SAD pattern contains a bright central spot that contains directly transmitted electrons and some scattered electrons. The image in TEM can be formed by using the central spot or by using some or all of the scattered electrons. If the central spot is used to form the image, the resultant image is called a bright-filed (BF) image. If the scattered electrons are selected to form the image, the image is called dark-field (DF) image. The ray diagrams of BF and DF images are shown in Figure 3-3-4.
Figure 3-3-3. The two basic operations of TEM imaging system. A. Projecting the diffraction pattern on the viewing screen. B. Projecting the image onto the screen. (from Ref. [3])

Figure 3-3-4. Ray diagrams for (A) a BF image formed from the direct beam, and (B) a DF image formed with a specific off-axis scattered beam. (from Ref.[3])
Contrast and HRTEM

Image contrast is defined in terms of the difference in intensity ($\Delta I$) between the two adjacent areas. TEM image contrast comes from the scattering of the incident electron beam by the specimen. Since the change of the electron wave can be either in amplitude or in phase, two types of contrasts can be distinguished: amplitude contrast and phase contrast. In most cases, both types of the contrast can contribute to an image. There are two principal amplitude contrasts, one is mass-thickness contrast and the other one is diffraction contrast. Mass-thickness contrast occurs due to the incoherent elastic scattering of electrons. This type of contrast is important if non-crystalline sample is observed. Diffraction contrast occurs due to the coherent elastic scattering at Bragg angles. BF and DF imaging are the two basic ways to form amplitude-contrast images.$^3$

Phase contrast is very sensitive to many factors such as small change in thickness, orientation, scattering factor of specimen and variations in the focus of the objective lens. This sensitivity is also the reason that phase contrast can be used to image the atomic structure of thin specimens.$^5$ To form phase-contrast image, one needs to select more than one beam. Generally, the higher the resolution of image is required, the more beams need to be collected.
3.3.3 Optical Characterization of Thin Films

To study the properties of solids, we need a variety of experimental probes, among which techniques using electromagnetic radiation are the most fruitful ones. The widely used methods of optical characterization include absorption (from infrared to ultraviolet range), photoluminescence, and Raman spectroscopy. Semiconductor properties that can be characterized by these methods are listed in Table 3-3-2.

Table 3-3-2. Semiconductor properties which can be characterized by the optical methods. (from Ref[6])

<table>
<thead>
<tr>
<th>Semiconductor property</th>
<th>Optical method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PL</td>
</tr>
<tr>
<td>Band</td>
<td></td>
</tr>
<tr>
<td>Gap</td>
<td>●</td>
</tr>
<tr>
<td>Effective mass</td>
<td>●</td>
</tr>
<tr>
<td>Band offset</td>
<td>●</td>
</tr>
<tr>
<td>Free carrier</td>
<td></td>
</tr>
<tr>
<td>Concentration</td>
<td>●</td>
</tr>
<tr>
<td>Mobility</td>
<td>●</td>
</tr>
<tr>
<td>Scattering time</td>
<td>●</td>
</tr>
<tr>
<td>Resistivity</td>
<td>●</td>
</tr>
<tr>
<td>Lattice</td>
<td></td>
</tr>
<tr>
<td>Alloy composition</td>
<td>●</td>
</tr>
<tr>
<td>Orientation</td>
<td>●</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>●</td>
</tr>
<tr>
<td>Stress</td>
<td>●</td>
</tr>
<tr>
<td>Impurity and defect</td>
<td></td>
</tr>
<tr>
<td>Presence and type</td>
<td>●</td>
</tr>
<tr>
<td>Concentration</td>
<td>●</td>
</tr>
<tr>
<td>Microstructure</td>
<td></td>
</tr>
<tr>
<td>Layer thickness</td>
<td>●</td>
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<tr>
<td>Surface behavior</td>
<td>●</td>
</tr>
<tr>
<td>Interface behavior</td>
<td>●</td>
</tr>
<tr>
<td>Layer-by-layer behavior</td>
<td>●</td>
</tr>
<tr>
<td>Other</td>
<td></td>
</tr>
<tr>
<td>Homogeneity mapping</td>
<td>●</td>
</tr>
</tbody>
</table>
Absorption and Absorption Spectrum

When an incident light beam reaches a medium, part of the beam will be reflected by the medium, part of the beam will be transmitted through the medium, and the rest of the beam will be absorbed. Absorption of photons arises due to the transition of the electrons from lower energy levels to the higher energy levels. The absorption ability of a mater is measured by its absorption coefficient. Absorption coefficient $\alpha$ for a uniform medium can be defined in terms of the intensity change of a monochromatic light beam in unit distance that the beam traveled in the medium (see Figure 3-3-5),

$$\frac{dI(\lambda)}{dx} = -\alpha(\lambda)I(\lambda). \quad (3-3-7)$$

So the beam intensity as a function of the distance $x$ can be written as

$$I(\lambda) = I_0(\lambda)e^{-\alpha(\lambda)x}. \quad (3-3-8)$$

In classical electromagnetic theory, absorption coefficient is related to the imaginary part of the complex index of refraction $n_c = n - ik$ with

$$\alpha = \frac{4\pi\nu}{c} \quad (3-3-9)$$

where $\nu$ is the frequency of the light. The imaginary part of the complex index of refraction, $k$ is also called the extinction coefficient. In fact equation (3-3-9) is often used as the definition of absorption coefficient.\(^7^8\) From equation (3-3-8), an important quantity called penetration depth can be defined as $\delta = 1/\alpha$. $\delta$ is the distance over which the intensity of the light beam falls to $1/e$ of the initial value. Penetration depth is useful to estimate how far the light beam penetrates into a medium.
Absorption coefficient is a function of frequency (or wavelength). The variation of absorption coefficient with wavelength is called the absorption spectrum of the medium. The absorption spectrum can be obtained by measuring the transmission spectrum or by measuring the reflectance spectrum. Which method to be used depends on the sample to be measured. For transmission measurement, the sample should have a regular shape and suitable value of $\alpha d$ so that the transmitted light is strong enough for the detector. Reflectance measurements are usually performed for powder samples or for the samples with large value of $\alpha d$ (d is thickness).

If the reflection is negligible, the transmittivity $T(\lambda)$ is equal to the ratio of the intensity of the transmission beam to that of the incident beam,

$$T(\lambda) = \frac{I(\lambda)}{I_0(\lambda)},$$  \hspace{1cm} (3-3-10) 

From equation (3-3-8), we have
\[
\ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = \ln(T(\lambda)) = -\alpha d
\]  

(3-3-11)

where \(d\) is the thickness of the sample. If \(d\) is known, the absorption coefficient can be obtained.

Figure 3-3-6. Optical system arrange of Hitachi A3031 visible-uv spectrometer.

An absorption spectrometer (or transmission spectrometer) is generally composed of one (or two) monochromator, a continuous light source, and a photomultiplier. Figure (3-3-6) shows the optical system arrangement of the absorption spectrometer used in this work. The spectrometer is equipped with two continuous light sources — a W lamp for measuring transmittivity in the visible range (from 1000 nm to 320 nm) and a deuterium lamp for the
measurement in ultraviolet range (from 320 nm to 200 nm). Light beam is first split into a monochromatic one by the pre-monochromator, then is incident onto the sample. A main monochromater is also installed in order to increase the measurement resolution. After the transmitted beam passes through the main monochromater, its intensity is measured by the photomultiplier and recorded by the computer. It should be noticed that reflectivity is not always negligible and the contribution from reflection is also added into the final data. The data obtained from absorption spectrometer is not the absorption coefficient, but its product with the sample thickness \(d\). To obtain the value of absorption coefficient, \(d\) must be known.

### Photoluminescence and Photoluminescence—Excitation Spectroscopy

Luminescence refers to all types of light emission appearing as a consequence of some external excitation, except incandescent emission.\(^8\) Depending on the way by which sample is excited, luminescence is classified as photoluminescence (PL) with light excitation, cathodoluminescence with electron-beam excitation, electroluminescence with electric field as excitation source, and chemoluminescence etc. Luminescence (or photon emission) of semiconductors is the direct results of electron transition from upper energy levels to lower energy levels. The information about the electronic structure of semiconductor could be obtained from the analysis of luminescence spectra.

Two types of spectra can be distinguished upon PL measurements — photoluminescence spectrum and photoluminescence-excitation (PLE) spectrum. Photoluminescence spectrum
refers to the variation of luminescence intensity as a function of wavelength (or photon energy), while photoluminescence-excitation spectrum is measured by monitoring the variation of luminescence intensity at fixed wavelength (or photon energy) as a function of the wavelength (or photon energy) of the excitation source. PL spectrum provides us the information about the structure of energy levels in the sample. PLE spectrum tells the information about the energy transformation among the energy levels in the sample. PLE spectrum is “somehow” related to the absorption spectrum, but the relationship between them is not one-to-one correspondence. From absorption spectrum, we can obtain the information about which kind of energy levels are excited by the incident light beam. PLE spectrum tells if these excitations can induce the photon emission at the desired wavelength.

To measure photoluminescence spectrum, two essential equipments are necessary. One is spectrometer with photo-electro-transfer device; the other one is light-excitation source. Various light sources can be used as excitation source in PL measurement from lasers to lamps. For PLE measurement, a wavelength-adjustable excitation source is necessary. Figure (3-3-7) shows the optical system arrangement of Hitachi F2500 fluorescence spectrophotometer. Xe lamp is used as the excitation source in this spectrometer. The excitation grating (acts as a monochromator) is used to select the desired wavelength for the excitation beam. The excitation wavelength can be varied from 220 nm to 800 nm. Light emission from the sample is first diffracted by the diffraction grating. The diffracted emission beam is then sent to the photomultiplier through the exit slit and finally recorded by the computer. PLE spectrum can be also measured with this spectrometer. To do so, the emission-diffraction grating has to be fixed at the desired position. The variation of
excitation wavelength is achieved by rotating the excitation-diffraction grating.

Figure 3-3-7. Optical system arrangement of Hitachi F2500 fluorescence spectrophotometer.
References

5. Ref. 3, chapter 27, p441.
Chapter 4  THE GROWTH AND CHARACTERIZATION OF HEXAGONAL WURTZITE-STRUCTURE Mg\textsubscript{x}Zn\textsubscript{1-x}O THIN FILMS

4.1 Introduction

In recent years, the intense interest in blue and ultraviolet light emitters and detectors has promoted large research efforts into the wide band gap semiconductors. Up to now, blue lasers, light-emitting-diodes (LEDs), and ultraviolet photodetectors based on GaN and its alloys have already been commercialized.\textsuperscript{1} While there are still major improvements that need to be made in these devices, it now appears that the visible portion of the spectrum can be covered by semiconductor diodes. With these successes there has been an increased interest in the development of ultraviolet light emitters, and truly solar blind photodetectors,\textsuperscript{2-4} which are transparent to the visible and near-UV portion of the spectrum. Compact ultraviolet sources and detectors could be tailored to monitor or catalyze specific chemical reactions or to excite fluorescence in various proteins. Recently several near ultraviolet diode sources on the GaN material system have been reported.\textsuperscript{5-7} ZnO-based alloys are considered as an alternative to the GaN material system. Alloying ZnO films with MgO or CdO potentially permits the band gap to be controlled between 2.8 and 4 eV and higher, which facilitates band gap engineering. This also suggests the possibility of hybrid optoelectronic devices comprised of lattice-matched MgZnO/AlGaN heterojunctions.\textsuperscript{8}

Zinc oxide or zincite (ZnO) has a hexagonal wurtzite structure, whereas magnesium oxide or periclase (MgO) is cubic. However, the similarity in ionic radii between Mg$^{++}$ (1.36 Å) and
Zn\(^{++}\)(1.25 Å) allows some replacement in either structure. According to the phase diagram,\(^9\) MgO allows a maximum of 40 atom.% ZnO at 1600 °C and maintains its NaCl structure with the lattice constant staying close to that of pure MgO (4.208 Å). In the case of ZnO, the solid solubility of Mg is limited to only 4 atom. % maximum, and the unit cell retains its hexagonal structure. The excitonic binding energy of ZnO is ~60 meV which leads to extremely efficient excitonic emission. Based on the excitonic emission, room temperature lasing have been reported in thin films\(^{10}\) and microcrystallites.\(^{11,12}\) Recently, Mg\(_x\)Zn\(_{1-x}\)O films have been grown, which demonstrated the control of the band gap between 3.36 and 3.87 eV and ultraviolet photoluminescence at 4.2 K.\(^{13}\)

In this chapter, we report the results of the growth and characterization of Mg\(_x\)Zn\(_{1-x}\)O thin films. We have achieved nonequilibrium phase space corresponding to 34 at. % Mg in ZnO while maintaining the ZnO hexagonal structure with a lattice constant close to that of ZnO. XRD and TEM results indicate that the epitaxial MgZnO films with single-crystalline quality were obtained on sapphire (0001) substrates. The bandgap of these films can be controlled from 3.36 to 4.12 eV by changing the Mg content. The excitonic nature of the films at room temperature was observed in the absorption spectra. These films also maintained favorable optical characteristics of wide band gap materials, including transparency in the visible range and high excitonic binding energy. The extremely bright excitonic photoluminescence was also observed in these films at room temperature (295 K). The refractive indices were measured by prism-coupled waveguide measurements. By fitting the absorption spectra, the exciton bandgap, binding energies, and broadening parameters of Mg\(_x\)Zn\(_{1-x}\)O alloys were also obtained. These are the encouraging steps in the development of MgZnO based structures for
optoelectronic devices.

4.2 Experimental Procedure

Thin Film Growth

Mg_xZn_{1-x}O thin films were synthesized by pulsed laser deposition system using a KrF excimer laser. Thin films were grown in a high vacuum chamber with background pressure of ~ 5×10^-7 Torr. The KrF laser was operated at the wavelength of 248 nm with the repetition rate of 10 Hz and pulse duration of 25 ns.

MgO-ZnO composite targets with MgO contents from 0 mol. % to 30 mol. % were used during the deposition. The composite targets were obtained by the standard pressing and sintering method. MgO and ZnO powders were first weighted and mixed with corresponding concentrations in methanol by magnetic blender for 1 hour. After the liquid was dry out, the mixed powder was blended mechanically again so that the mixture is uniformly distributed. The mixture was then calcined at 400 °C in flowing oxygen for 6 hours. The resultant powder was ground again and was pressed into round pellets with two-inch diameter. The targets were finally obtained after the pellets were sintered in oxygen at 1000 °C for 12 hours.

Sapphire (α-Al_{2}O_{3}) wafer was used as substrates for growing these Mg_xZn_{1-x}O thin films. The substrates have the thickness of 1 mm and are c-axis oriented. Before loaded into the
vacuum chamber, substrates were cleaned with standard chemical method, by which the substrate was first cleaned in acetone and then cleaned in methanol for 10 min in ultrasonic bath.

Thin films were grown in oxygen environment with O₂ partial pressure of $2 \times 10^{-5}$ Torr at substrate temperature of 700-750 °C. Laser energy density focused on the target was about 2.5-3.5 J/cm². The deposition time was typically 20 min. After the deposition, thin films were cooled down to room temperature at a rate of ~ 20 °C/min in ~ 760 Torr of oxygen pressure.

**Characterization of Crystalline Structure and Composition**

The crystalline structures of the resultant MgₓZn₁₋ₓO thin films were characterized by using X-ray diffraction (XRD) ω-2θ scan and transmission electron microscope (TEM). XRD measurements were performed with Rigaku X-ray diffractometer with CuKα radiation and Ni filter. A JEOL –2010F analytical electron microscope was used for TEM measurements. The composition of the thin films was determined by measuring Rutherford backscattering (RBS) ion channeling spectra. The RBS analysis was performed using a probe beam of 2.75 MeV He⁺-ions and a standard, surface barrier detector positioned at 160°.

**Optical Characterization**

The absorption spectra of MgₓZn₁₋ₓO thin films were measured at room temperature by
recording the transmission using a Cary 5E UV-VIS-NIR spectrophotometer. The photoluminescence spectra were measured with a 0.64 m spectrometer equipped with an S-20 photocathode. A large frame Ar$^+$ ion laser operating with deep UV optics (270–305 nm) was used as excitation source. The refractive indices of Mg$_x$Zn$_{1-x}$O films were measured with a prism-coupling technique. A rutile TiO$_2$ prism was used to couple light into the air/MgZnO/sapphire waveguide. In this geometry, waveguide coupling only occurs at discrete mode angles when the photon tunnels through the air gap with the proper propagation constant to travel in the waveguide.
4.3 Results and Discussion

XRD results showed that the thin films with Mg content of \( x < 0.34 \) had hexagonal wurtzite structure. Only \((0001)\) reflections were observed in the XRD pattern for these films, which indicate that the films were textured with c-axis perpendicular to the substrate surface. The position of \((000l)\) reflection was found to have a shift from the ZnO peak position in proportion to the Mg content. The XRD pattern of the \( \text{Mg}_{0.34}\text{Zn}_{0.66}\text{O} \) film is shown in Figure 4-3-1. The lattice constant of \( \text{Mg}_{0.34}\text{Zn}_{0.66}\text{O} \) film was found to change by about 1\% with respect to that of ZnO. Lattice constants, \( a \) was increased by 1\% and \( c \) was decreased by 0.9\%, corresponding to the values of \( a = 3.28 \text{ Å} \) and \( c = 5.15 \text{ Å} \). By XRD results, the optimum deposition temperature was found between 700-750 °C.

![Figure 4-3-1. XRD pattern of a single crystalline MgZnO thin film on (0001) \( \alpha\)-Al\(_2\)O\(_3\).](image-url)
Figure 4-3-2 shows the Rutherford back-scattering ion-channeling spectrum of MgZnO thin film deposited at 700 °C. The purpose of RBS measurement is to find the Mg content in the film. The Mg content could be obtained by simulating the random yielding using a range of compositions to find the best fit to the actual data. The Mg content of the film is about 34 atomic percent. This concentration is almost an order of magnitude than the value (4 atom. %) allowed by the phase diagram. The MgZnO thin films with high Mg concentration are believed to be in the metastable phase. The formation of metastable materials is possible because of the non-equilibrium nature of pulsed laser deposition processes. As discussed in Chapter 3, the species in the laser-ablated plasma plume have energies in the range of 100-1000 kT compared to the equilibrium value of kT. The mobility of atoms on the substrate
can be largely enhanced by this excess kinetic energy. As a consequence, the nonequilibrium phase can be obtained in PLD processes. The Mg content obtained with RBS is about 4\% higher than the value that expected from the target. This may be due the loss of Zn during the high temperature sintering or due to the difference of vapor pressures between ZnO and MgO. From Figure 4-3-2, we can also see that the minimum yield for aligned scan is only about 5.4\%. This indicates that Mg atoms are mainly located in the lattice sites rather than interstitial sites. The small value of aligned minimum yield also demonstrates that the film has a high single-crystalline quality.

Figure 4-3-3. Cross-sectional TEM micrograph of a Mg_{0.34}Zn_{0.66}O film annealed in oxygen depicting high dislocation density near the MgZnO/sapphire interface. Note that the density of defects decreases substantially towards the surface of the film.
Figure 4-3-3 shows the cross-section, bright-field TEM image taken from a Mg_{0.34}Zn_{0.66}O thin film grown on the α-Al_2O_3 (0001) substrate with α-Al_2O_3 [2110] zone axis. The corresponding selected-area TEM diffraction patterns for the image are shown in Figure 4-3-4. The micrograph and diffraction patterns clearly show that MgZnO thin films are single-phase with hexagonal wurtzite structure without any evidence of phase separation. The number density of threading dislocations is about 10^{10} cm^{-2} in the area close to the film–substrate interface, but decreases significantly as the film grows. The variation of dislocation density as a function of distance from the interface is consistent with ion-channeling results (as shown in Figure 3-4-2), which shows that χ_{min} is higher near the interface.

The selected-area diffraction pattern taken from the interface between MgZnO thin films and α-Al_2O_3 (0001) substrate with α-Al_2O_3 [2110] zone axis is given in Figure 4-3-4 (a). The SAD pattern of MgZnO thin film arises from the diffraction of [0110]-zone planes. The sharp spotted-TEM-SAD pattern and the XRD results clearly demonstrate the epitaxial nature of MgZnO thin film with high crystalline quality. Figure 4-3-4 (b) shows the SAD pattern taken from the MgZnO film alone, which indicates the single crystalline nature of the film. From the analysis of the diffraction patterns, the epitaxial relationship of the MgZnO film was determined to be MgZnO [0001] || α-Al_2O_3 [0001] and MgZnO [2110] || α-Al_2O_3 [0110]. The in-plane epitaxial orientation relationship, similar to that for pure ZnO thin film on α-Al_2O_3 substrate, corresponds to 30° or 90° rotation of the film with respect to the
Figure 4-3-4. Cross-section TEM SAD patterns taken from (a) MgZnO/sapphire interface and (b) MgZnO film.
substrate in the basal plane as shown in Figure 4-3-5. The basal-plane lattice constants of MgZnO and $\alpha$-Al$_2$O$_3$ are 3.28 and 4.75, respectively. This large difference in lattice constant corresponds to a misfit of $-37\%$, which means that the epitaxial mechanism has to be domain-matched. As shown in Figure 4-3-4 and 4-3-5, the actual misfit between the film and the substrate should be determined by the planar spacing of MgZnO $\{01\overline{1}0\}$ planes and $\alpha$-Al$_2$O$_3$ $\{2\overline{1}\overline{1}0\}$ planes, not by the lattice constants. In this situation, the misfit between the two sets of planes is about 17\%, which leads to 5/6 or 6/7 domain- (plane-) matching. The
residual strain for this domain matching is about 0.24%, which means the misfit strain in the film is almost completely relaxed. It should be noted that the prevalent defects in MgZnO films are threading dislocations compared to stacking faults in pure ZnO epitaxial films on sapphire.14

Transmission measurements were made using a Cary 5E UV-VIS-NIR spectrophotometer at room temperature. All films were less than 500 nm thick, specular, and deposited on double side polished sapphire substrates such that transmission measurements could be made from 200 to 3300 nm. Figure 4-3-6 shows the absorbance of the thin films with three different Mg concentrations (x=0.19, 0.27, and 0.34). The spectra were scaled according to the film thickness. The excitonic nature of the films is clearly apparent in the spectra. In the ZnO film (x=0), even at room temperature, A, and B, excitons are clearly distinguished. In the MgZnO alloys, the exciton peaks are broadened due to alloying, and the details of the individual excitons can not be distinguished. However, the excitonic feature in the absorption spectra is still extremely significant. This is a consequence of the high binding energy (~60 meV) of the exciton in MgZnO alloys and the high single-crystalline quality of the films. As a point of comparison, in AlGaN alloys which have an excitonic binding energy similar to that of the MgZnO films, the excitonic structure has not been observed in thin films of comparable thickness.15 In the previous report on MgZnO alloys,13 the exciton peak was only visible in the unalloyed ZnO. In the alloy films, the absorption edge was broad and the exciton structure was not apparent. In the present work, as shown in Figure 4-3-6, the exciton peak remains present for all alloy compositions even though alloy broadening softens the slope of the absorption edge with increasing Mg concentration.
This indicates that for very thin films, transmission spectroscopy provides a sensitive indicator of material quality.

ZnO has three series of excitons, which are formed due to the Coulomb interaction of electrons in the $\Gamma_7$-conduction band with the holes in the three subbands. These excitons are usually called A ($\Gamma_7\rightarrow\Gamma_7$)-, B ($\Gamma_7\rightarrow\Gamma_9$)- and C ($\Gamma_7\rightarrow\Gamma_7$)-excitons. As discussed in Chapter 2, the optical transitions are allowed for A-, B- and C- excitons if the electric field $E$ of the electromagnetic wave is perpendicular to the c-axis ($E \perp c$). When electric field is parallel to the c-axis ($E \parallel c$), the transitions are forbidden for the B-exciton, allowed for A exciton with small oscillator strength and for C exciton with large oscillator strength. In our transmission measurements, the incident beam was normal to the sample surface and $E$ is perpendicular to
the c-axis of the film. So all three exciton series contributed to the absorption spectra with large oscillator strength of A- and B-excitons and small oscillator strength of C-exciton. The absorption spectra with exciton contributions can be modeled as

$$
\alpha(E) = \text{Im} \left\{ \sum_{n=A,B,C} \sum_{m=1}^{\infty} \frac{A_{0n}^{ex}}{m^3 \left( E_{0n} - \frac{R_n}{m^2} - E - i\Gamma_{ex,m} \right)} \right\},
$$

where \( n \) is the index of the valence bands, \( E_{0n} \) is the bandgap energy, \( R_n \) is the exciton binding energy, \( \Gamma_{ex,m} \) is a broadening parameter of the \( m \)th excited exciton state, and \( A_{0n}^{ex} \) is an adjustable fitting parameter. For the continuum absorption above the bandgap, the spectrum can be summed as

$$
\alpha(E) = \sum_{n=A,B,C} \frac{(E - E_{0n})^{1/2}}{E^2 \sinh \left( \frac{R_n}{E - E_{0n}} \right)} \times \frac{1}{1 + \exp \left( \frac{E - E_{0n}}{\Gamma_n} \right)}.
$$

The last term in the brackets is broadening function, in which \( \Gamma_n \) is an additional parameter used to smooth the discontinuity at the band gap. The exciton energy gap, binding energy, and broadening parameter were obtained by fitting the equation above. The results are given in Table 4-3-1. The bandgap of the MgZnO thin films shift to the higher energy side as the Mg content increases. Compared to the bandgap, the exciton binding energies did not change with the Mg content significantly. However, the broadening parameters, \( \Gamma_{ex,m} \) increase significantly with Mg content due to the alloy broadening. The plots of bandgap energy and the broadening parameter as a function of the Mg concentration are given in Figure 4-3-7.
Table 4-3-1. The bandgap energies, binding energies, and broadening parameters of the excitons in Mg$_x$Zn$_{1-x}$O thin films.

<table>
<thead>
<tr>
<th>Energy gap (eV)</th>
<th>Mg$<em>x$Zn$</em>{1-x}$O thin film sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x=0 (Ref. 22)</td>
</tr>
<tr>
<td>A-exciton</td>
<td>3.40</td>
</tr>
<tr>
<td>B-exciton</td>
<td>3.45</td>
</tr>
<tr>
<td>C-exciton</td>
<td>3.55</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Binding energy (meV)</th>
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</thead>
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<tr>
<td>A-exciton</td>
<td>63.1</td>
</tr>
<tr>
<td>B-exciton</td>
<td>50.4</td>
</tr>
<tr>
<td>C-exciton</td>
<td>48.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\Gamma_{ex}$ (meV)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A-exciton</td>
<td>1.5</td>
</tr>
<tr>
<td>B-exciton</td>
<td>4.8</td>
</tr>
<tr>
<td>C-exciton</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Figure 4-3-8 shows the photoluminescence spectra of the MgZnO thin films with different Mg content (x=0 to 0.34). In the figure, the spectra have been normalized for clarity in discussion. These spectra were measured by using a large frame Ar$^+$ ion laser operating with deep UV optics (270–305 nm) as excitation source. The emission was collected and focused on a 0.64 m spectrometer equipped with an S-20 photocathode. The photoluminescence from the alloyed samples was surprisingly bright and of comparable or brighter intensity than the unalloyed ZnO single crystal thin films or single crystal ZnO grown hydrothermally. The excitonic emissions were observed in all the MgZnO thin film samples. The peak position of the emission band increases to the higher energy side as Mg concentration in the film increases. The value of full width of half maximum (FWHM) also increases with the Mg content. The HFWM value for x=0.34 film is almost two times of the value for pure ZnO (x=0) thin film. Figure 4-3-9 shows the plots of peak position and FWHM of the excitonic emission as a function of Mg concentration in the films. From Figure 4-3-8, we can also see that the green band emission decreases with increasing Mg concentration.
Figure 4-3-7. (a) Variations of the exciton bandgap with Mg concentration in the films (solid lines are the results of second order polynomial fitting). (b) Variation of broadening parameters, $\Gamma$ of A-exciton with Mg concentration.
Three MgZnO thin-film samples with Mg concentration of $x = 0.00$, 0.24, and 0.34 were used for the refractive index measurement. The thickness of these films ranges from 0.7 µm to 1 µm in the prism coupling measurements in order to support at least two waveguide modes. During the measurements, six laser wavelengths, 457.9, 488, 514.5, 632.8, 676.2, and 968.3 nm were used. Very little scattering was observed, indicating that the film morphology and crystallinity were good. The measured ordinary ($n_o$) and extraordinary ($n_e$) refractive indices of these Mg$_x$Zn$_{1-x}$O films are given in Table 4-3-2. These data are also plotted in Figure 4-3-10, together with the index of refraction of cubic MgO crystal measured by Stephens and Malitson. The data at each Mg concentration were fitted by least-square method to the first-order Sellmeier dispersion relationship.
Figure 4-3-9. The variation of peak position (a) and FWHM (b) of the excitonic emission of MgZnO thin films with Mg concentration.
Table 4-3-2. Measured refractive index of MgZnO thin films.

<table>
<thead>
<tr>
<th>Mg\textsubscript{x}Zn\textsubscript{1-x}O Thin Film Sample</th>
<th>x=0</th>
<th>x=0.24</th>
<th>x=0.34</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
<td>Extraordinary index</td>
<td>Ordinary index</td>
<td>Extraordinary index</td>
</tr>
<tr>
<td>457.9</td>
<td>2.108</td>
<td>2.080</td>
<td>1.974</td>
</tr>
<tr>
<td>488</td>
<td>2.067</td>
<td>2.048</td>
<td>1.954</td>
</tr>
<tr>
<td>514.5</td>
<td>2.049</td>
<td>2.025</td>
<td>1.943</td>
</tr>
<tr>
<td>632.8</td>
<td>1.998</td>
<td>1.979</td>
<td>1.912</td>
</tr>
<tr>
<td>676.2</td>
<td>1.989</td>
<td>1.969</td>
<td>1.903</td>
</tr>
<tr>
<td>968.3</td>
<td>1.955</td>
<td>1.9345</td>
<td>1.878</td>
</tr>
</tbody>
</table>

\[ n(\lambda)^2 = 1 + \frac{A\lambda^2}{\lambda^2 - \lambda_0^2} \]

where A and \( \lambda_0 \) are the fitting parameters. The fitting results are shown in Figure 4-3-10 with solid lines. The values of fitting parameters are listed in Table 4-3-3. The refractive index of a thin film below the band gap can also be determined by analyzing the interference fringes of optical transmission spectra. The technique has been outlined by Swanepoel for amorphous silicon films\textsuperscript{19} and applied to III-nitride and other films\textsuperscript{20,21}

Table 4-4-3. Values of fitting parameters in first-order Sellmeier dispersion formula.

<table>
<thead>
<tr>
<th>Mg Concentration</th>
<th>Extraordinary index</th>
<th>Ordinary index</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0</td>
<td>x=0.24</td>
<td>x=0.34</td>
</tr>
<tr>
<td>λ₀ (nm)</td>
<td>A</td>
<td>λ₀ (nm)</td>
</tr>
<tr>
<td>157.2±4.45</td>
<td>1.6790±0.0044</td>
<td>154.7±3.51</td>
</tr>
<tr>
<td>130.5±1.41</td>
<td>1.6443±0.0011</td>
<td>129.1±3.14</td>
</tr>
<tr>
<td>131.3±1.42</td>
<td>1.6248±0.0011</td>
<td>121.1±0.39</td>
</tr>
</tbody>
</table>
Figure 4-3-10. The extraordinary and ordinary refractive indices of MgZnO thin films. The solid lines are the results of least-square fit to the first order Sellmeier dispersion relationships.
4.4 Conclusion

In this work, high quality single-crystalline MgZnO films had been grown epitaxially on sapphire substrates by using pulsed laser deposition. Mg content achieved by our nonequilibrium growth method is almost an order of magnitude than that predicted by the phase diagram. The results of photoluminescence investigation indicate that these films have very bright photoluminescence at room temperature. Exciton energy gaps, and binding energies were determined from transmission measurements. The spectral position of the photoluminescence and optical band gap were successfully tuned from 3.4 to 4.19 eV by adjusting the Mg content. Throughout this tuning range the crystal quality was sufficiently preserved to maintain the excitonic nature of the material, resulting in very efficient ultraviolet emission. The effect of increasing Mg content in the ZnO films was found to reduce the defect photoluminescence. The ability to grow high quality MgZnO alloy films opens up numerous possibilities for the construction of ultraviolet optoelectronic devices. Since Mg content achieved by our nonequilibrium growth method is almost an order of magnitude than that predicted by the phase diagram, further investigations are being conducted on segregation and its influence on device operation at high temperatures. We also have investigated the room-temperature refractive indices of these Mg$_x$Zn$_{1-x}$O epitaxial thin films. The indices of refraction below the band gap were obtained by a prism coupling waveguide method. These results provide important information for the design and modeling of ZnO/MgZnO-heterostructure optoelectronic devices.
References


In this chapter, we present the results of synthesis and characterization of new cubic-phase Zn$_x$Mg$_{1-x}$O alloy thin films. These films had been grown epitaxially on MgO (100) by lattice-matching epitaxy, and on Si (100) substrate by domain-matching epitaxy with TiN as buffer layer. Cubic Zn$_x$Mg$_{1-x}$O films on MgO (100) and Si (100) substrates were grown using a rotating target in a single chamber “in-situ” pulsed-laser deposition system. Integration of Zn$_x$Mg$_{1-x}$O films with silicon was accomplished via titanium nitride (TiN) buffer layers where four lattice constants of TiN match with three of the silicon during epitaxial growth via domain epitaxy. Rutherford backscattering ion channeling techniques were used to determine chemical composition and crystalline quality of the films for $x = 0.0$-0.18. Detailed X-ray diffraction and transmission electron microscopy studies confirmed the epitaxial nature of ZnMgO/MgO (100) and ZnMgO/TiN/Si (100) heterostructures, and showed the formation of the Mg$_{2-x}$Zn$_x$TiO$_4$ spinel at the interface with TiN. Using optical transmission measurements, the band gap of cubic Zn$_{0.18}$Mg$_{0.82}$O film was estimated to be approximately 6.7 eV. The potential use of these alloys for optical devices in the ultraviolet range is discussed.
5.1 Introduction

The light-emitting diodes (LEDs) with high brightness and durability have the applications in display devices. Similarly, laser diodes (LDs) have been fabricated for applications ranging from optical communication systems to compact disk (CD) players.\textsuperscript{1-4} For the actual applications, the operating wavelength of these optoelectronic devices must cover the range from red to deep ultraviolet. Under the intense research efforts, the devices working in the range from red to yellow have already been commercialized. At present, ultraviolet and blue optoelectronic devices have attracted a lot of scientific interests. In this regard, III-compounds such as InN, GaN, and AlN and their alloys are being studied extensively with a promise for emerging technologies such as UV-blue laser diodes, LEDs, UV detectors and so on.\textsuperscript{5-6} The hexagonal wurtzite polytypes of III-nitrides (InN, GaN, and AlN) can form continuous solid solutions with direct band gaps ranging from 1.9 eV (InN) to 3.4 eV (GaN) to 6.2 eV (AlN). Since the stable phase of III-nitrides and their alloys is hexagonal wurtzite, these materials can be grown via lattice-matching epitaxy only on 6H-SiC (0001) and ZnO (0001). On sapphire (\(\alpha\)-Al\(_2\)O\(_3\)) and Si (111), which are more practical substrates, epitaxial growth can occur only via domain matching epitaxy, where integral multiples of lattice constants of the film and substrate match across the interface. For example, the domain matching epitaxy on the basal plane after 30\(^\circ\) or 90\(^\circ\) rotation \([\bar{1}2\bar{1}0]\)\textsubscript{nitride} \([01\bar{1}0]\)\textsubscript{sap} involves matching of seven planes of the III-nitride films with six planes of sapphire.\textsuperscript{7-8} The epitaxial films on sapphire contain a high density of growth and misfit related dislocations, which adversely affect the lifetimes of optical devices, particularly lasers.\textsuperscript{2} In addition, the
synthesis of III-nitrides is complicated due to the stability of the N\textsubscript{2} molecule.

As an alternative to III-nitrides, ZnO, which has a hexagonal wurtzite structure and a band gap similar to that of GaN, and its alloys with MgO have been investigated. The lasing action in the epitaxial\textsuperscript{9} and polycrystalline\textsuperscript{10} ZnO films has been demonstrated. ZnO has very bright luminescence in UV range and grows two-dimensionally on c-plane sapphires with low density of extended defects.\textsuperscript{11-12} Recently, high quality, single crystalline MgZnO alloy films has been achieved with Mg content up to 34 at. \% while retaining the hexagonal ZnO lattice (see also Chapter 4).\textsuperscript{13-14} The bandgap of this alloy was found to be variable with Mg content with upper limit around 4.19 eV. This alloy produced a bright UV luminescence at room temperature, which was found to be excitonic in nature.\textsuperscript{13} These recent developments open up enormous interest in this material system (MgO-ZnO) with the possibility of fabricating novel optoelectronic devices in the UV range of the spectrum.

We found that a maximum Mg content of about 34 at. \% in ZnO lattice could be achieved and beyond that, a phase separation into MgO and ZnO took place. Zinc oxide or zincite (ZnO) is hexagonal, whereas MgO is cubic with sodium chloride structure (a=4.213 Å). The similarity in ionic radii between Mg\textsuperscript{++} (1.36 Å) and Zn\textsuperscript{++} (1.25 Å) allows significant replacement in either structure. According to the phase diagram, MgO allows a maximum of 40 at.\% ZnO at 1600°C and maintains NaCl structure with lattice constant increasing only slightly less than 1\%.\textsuperscript{15} This alloy can be integrated with (001) silicon (a=5.43 Å) via domain matching epitaxy where four lattice constants of the film match with three lattice constants of the substrate. In this chapter, we present our first results on the synthesis of
cubic Zn$_x$Mg$_{1-x}$O phase with $x$ varying up to a maximum of 18 at.%. The epitaxial cubic Zn$_x$Mg$_{1-x}$O films on MgO (100) and $\alpha$-Al$_2$O$_3$ (0001) substrates and on TiN/Si (100) epilayer heterostructure were synthesized by using PLD. This opens the way to integrate ZnO-MgO alloys with silicon substrates and may result in the new applications of the optoelectronic devices in the deep UV range since the large bandgap of MgO makes it possible to vary the bandgap of ZnMgO alloys in much higher energy range.

5.2 The Description of Experimental Procedures for the Growth and Characterization of Cubic ZnMgO thin films

Pulsed laser deposition (PLD) was employed to synthesize the cubic Zn$_x$Mg$_{1-x}$O films by ablating the composite targets of ZnO-MgO mixed in various proportions. These targets were made by using standard sintering method described in Chapter 4 with ZnO content varying between 8-20 at.%. Pulsed excimer (KrF) laser ($\lambda$=248 nm, pulse width=25 ns, repetition rate=10 Hz) beam was focused on the composite targets to achieve a fluence of 2.5-3.5 J/cm$^2$. The laser beam is incident on the target at an angle close to 45°. The substrates were mounted on a heater plate parallel to the target with a distance between the two around 5 cm. A high vacuum environment ($\sim$10$^{-7}$ Torr) is routinely obtained in this PLD chamber. The depositions for ZnMgO thin films in this work were carried out in an oxygen partial pressure $\sim$1-5X10$^{-5}$ Torr while the substrates were maintained at the temperatures 650-750°C. Freshly cleaved MgO (100) surfaces and c-plane sapphire were used as substrates for depositions. The depositions were also carried out on Si (100) substrate
with TiN interlayer deposited in-situ using a rotating target holder with four slots. This was aimed to integrate this material with Si for novel optoelectronic device applications. Before the deposition, the silicon substrates were cleaned first with standard chemical method and then etched in 10% HF solution. TiN buffer layers were deposited in the background pressure about 1X10⁻⁶ Torr at 650 °C. A commercial stoichiometric hot-pressed TiN target was used to develop this buffer layer. After the deposition of TiN buffer, ZnMgO thin films were grown immediately at the same temperature.

The structural characterizations of the thin films were carried out using X-ray diffraction (XRD) (using Cu Kα source, λ=1.541 Å). High-resolution transmission electron microscopy (HRTEM) was used for the characterization of microstructure, phase identification, and defect analysis. Rutherford backscattering ion channeling was used for determining the composition and crystal quality. Optical transmission measurements were applied for the optical-gap determinations.
5.3 Results and Discussion

Cubic ZnMgO thin films were realized on all the three types of substrates, sapphire (0001), MgO (001), and Si (001) with TiN buffer layer. Figure 5-3-1 shows XRD pattern of ZnMgO film on sapphire (0001) surface grown at the temperature of 750°C. This was done to demonstrate the formation of cubic phase of ZnMgO, whose lattice constant is close to MgO and TiN, but is quite different from that of sapphire. The (111) and (222) reflections of ZnMgO phase are clearly seen apart from the sapphire (0001) reflections. From the 2θ values of (111)-reflection, the lattice constant of ZnMgO was calculated to be 4.234 Å, which is very close to that of MgO (4.213 Å). Figure 5-3-2 shows the XRD pattern of ZnMgO/TiN/Si (001) heterostructure. On TiN/Si (100) surface, the XRD showed (200) reflection of TiN with (200) peak of ZnMgO superimposed on it. Whereas on MgO (100) substrates, closely spaced peaks corresponding to ZnMgO and MgO (200) were observed. According to the phase diagram, the lattice constant of MgO-ZnO alloy remains close to that of MgO and increases slightly with the fraction of ZnO in the lattice. This is in agreement with the present observations. All the compositions of ZnMgO synthesized herein gave similar XRD peaks as shown in Figures 5-3-1 and 5-3-2. The shift of peak position as a function of the composition of alloy was relatively small. The optimum growth temperature for ZnMgO was found to be 750°C at the oxygen partial pressure of 4X10⁻⁵ Torr on MgO and sapphire substrates.
Figure 5-3-1. X-ray diffraction pattern of cubic Zn$_x$Mg$_{1-x}$O (111)/$\alpha$-Al$_2$O$_3$ (0001) heterostructure. The observation of secondary peaks at the higher angles are the result of splitting due to Cu K$_{\alpha_1}$ and Cu K$_{\alpha_2}$ X-ray lines.

Figure 5-3-2. X-ray diffraction pattern of cubic Zn$_x$Mg$_{1-x}$O/TiN/Si(001) heterostructure. The (00l) reflections from TiN buffer and ZnMgO film superimposed each other.
Figure 5-3-3 shows RBS spectrum of ZnMgO film as seen in Figure 5-3-1. The RBS analyses were performed using a probe beam of 2.75 MeV He$^+$ ions and a standard, surface barrier detector positioned at 160°. Both random and aligned spectra were recorded to estimate the composition and the crystalline quality of the films. The atomic fraction of Zn in the alloy was calculated by simulating the random yield using a range of compositions to find the best fit to the acquired data. The Zn content in the films grown on MgO (100) substrates (shown in Figure 5-3-3) was estimated to be 13 at.%. The minimum channeling yield ($\chi_{\text{min}}$) from this sample is around 3%, which is close to the value for bulk single crystal. The low value of $\chi_{\text{min}}$ indicates that the defect content is as low as expected from single crystal material. The channeling yield does not increase appreciably near the interface in this
sample, which means a low defect density near the interface. This is consistent with cross-section TEM results. The Zn$_x$Mg$_{1-x}$O alloy films are good candidates to modify the surface of MgO and tailor its optical properties as a function of Zn-content. The maximum Zn content obtained in these films was estimated to be 18 at.% from the RBS data.

Figure 5-3-4. Cross-section TEM micrograph of ZnMgO epilayer deposited on TiN/Si (100) heterostructure. Contrast due to an interfacial layer as a result of reaction between ZnMgO and TiN is seen.

Figure 5-3-4 shows <100> cross-section TEM micrograph from the ZnMgO sample deposited on Si (100) substrate with TiN as a buffer layer. The ZnMgO films were deposited on TiN/Si heterostructure in this sample at 650°C. The deposition was performed first in background pressure for one minute, then performed at oxygen partial pressure of 4X10$^{-5}$
Torr. The <110> cross-section micrograph clearly shows four layers, ZnMgO/reacted layer/TiN/Si (substrate). From a fit to the RBS data of this sample, the composition of ZnMgO was determined to be Zn$_{0.18}$Mg$_{0.82}$O.

The <110> selected-area micro-diffraction patterns are given in Figure 5-3-5. The SAD patterns were taken from different layers. Figure 5-3-5 (a) shows the SAD pattern from the interface between ZnMgO film and the spinel layer. The SAD pattern from TiN buffer and Si substrate is given in Figure 5-3-5 (b). Figure 5-3-5 (c) shows the diffraction taken from all ZnMgO/spinel/TiN/Si (100) layers. In Figure 5-3-5 (a), the diffraction spots from ZnMgO were indexed as $b$ and that corresponding to spinel were indexed as $c$. Figure 5-3-5 (b) contained only the diffraction spots from TiN (denoted as $b$) and silicon (shown as $a$). Figure 5-3-5 (c) shows diffraction spots from all the layers, which are clearly aligned as expected from epitaxial growth. From these diffraction studies, it is clearly evident that we have synthesized epitaxial ZnMgO films possessing cubic symmetry with cube-on-cube alignment. The lattice constant of ZnMgO (4.23 Å) was found to be very close to that of TiN (4.24 Å), which is in agreement with the XRD results. The alignment of diffraction spots from TiN, spinel and ZnMgO phase also demonstrates the cube-on-cube epitaxial nature of the films on Si (100) substrates, where four lattice constants of TiN match with three of the substrate via domain epitaxy. From diffraction results, the lattice constant of spinel was estimated to be 8.44 Å corresponding to Mg$_{2-x}$Zn$_x$TiO$_4$ (a$_0$~8.44 Å).
Figure 5-3-5 The [011] zone axis selected area diffraction patterns from (a) cubic ZnMgO/spinel interface, b denotes ZnMgO diffraction spots, while c denotes spinel diffraction spots (b) TiN/Si interface, b corresponds to TiN spots and a denotes Si diffraction spots and (c) all the layers in this heterostructure. a, b, and c correspond to the same phases as assigned in upper two diffraction patterns.
Figure 5-3-6. High-resolution electron micrograph of (a) Si/TiN interface, (b) TiN/Spinel interface; (c) Spinel/ZnMgO interface.

Figure 5-3-6 shows the HR pictures of TiN/Spinel and Spinel/ZnMgO interfaces. The interface between TiN buffer and spinel phase is sharp on atomic scales. The same conclusion could be drawn from conventional cross-section image taken with lower magnification. However the interface between spinel phase and ZnMgO layer is rough enough on atomic scales. It indicates that the spinel phase was formed due to some diffusion process. As the consequence of this diffusion, the variation in the concentrations (content depletion) of some species should occur from the TiN/spinel interface to the spinel/ZnMgO interface. This is demonstrated by the Z-contrast STEM image shown in Figure 5-3-7. The
image indicates that some element with high-z diffuses into ZnMgO layer, which leads to this interfacial reaction. Titanium is the native candidate for this high-z element. On the other hand the origin of all these features becomes clear if we consider that extremely high concentration of Ti extent in TiN layer was generated during pulse layer deposition owing to decomposition of TiN. According to the phase diagram, MgO allows a maximum of 56 wt% ZnO (40 at%) at 1600°C and maintains NaCl structure with lattice constant increasing only slightly less than 1% with ZnO. We present results on synthesis of cubic ZnMgO phase with x varying up to a maximum 18 at%. With increasing Zn content inside this diapason no phase decomposition observed.

Figure 5-3-7. Z-contrast STEM image of ZnMgO/TiN/Si structure. The arrows indicate Ti-diffused regions.
Figure 5-3-8 shows the transmission spectrum of cubic Zn$_{0.18}$Mg$_{0.82}$O film on sapphire. A Cary 5E UV-VIS-NIR spectrophotometer was used to measure the optical transmission on these films. From these measurements, the band gap of cubic Zn$_{0.18}$Mg$_{0.82}$O was estimated to be close to 6.7 eV. This is higher than that obtained in previous measurements of wurtzite Mg$_{0.34}$Zn$_{0.64}$O films grown on sapphire where the band gap was determined to be 4.19 eV.$^{13,16}$ This is not surprising as the Mg content in these films is higher than that in wurtzite phase, and the advantage is the change of symmetry from hexagonal to cubic at high Mg contents.

Figure 5-3-8. Transmission spectrum of the ZnMgO film deposited on c-plane sapphire.
5.4 Conclusion

In conclusion, we have synthesized chemically stable cubic Zn$_x$Mg$_{1-x}$O films on MgO (100), c-plane sapphire and Si (100) substrates by pulsed laser deposition. TEM and XRD studies of these films revealed the cubic symmetry in this phase with $x$ varying between 0.0-0.18. The lattice constants of these films were close to that of MgO and identical to TiN. The TiN, therefore, is found to provide an excellent buffer layer for integrating these films with Si. The band gap of cubic Zn$_{0.18}$Mg$_{0.82}$O films was determined to be approximately 6.7 eV, which is higher than that obtained from the hexagonal Mg$_{0.34}$Zn$_{0.66}$O films. The design of electronic material such as cubic phase of ZnMgO provides another variable in this system namely Zn which could be varied to tailor the optical properties of the films in the UV range for integration with silicon microelectronic devices. In addition, ZnMgO thin films also have a great potential to be used as deep UV devices (such as deep UV photodetectors) due to the large, adjustable bandgap energies.
References


In this chapter we present the results of the investigation for phase separation in ZnO/MgZnO superlattice structures. We have synthesized Mg_xZn_{1-x}O alloy of wurtzite (x=0.0-0.34) and ZnO/MgZnO superlattice by using non-equilibrium pulsed laser deposition method on (0001) sapphire substrates. Using JEOL-2010 field-emission transmission electron microscope equipped with STEM and Gatan image filter, we can perform atomic structure, STEM-Z, electron energy loss spectroscopy and imaging simultaneously. Such studies on the ZnO/MgZnO superlattices provide first direct evidence of phase-separation. HRTEM results reveal the cubic-phase nanoinclusions and their epitaxial relationship with MgZnO hexagonal matrix. The Mg diffusion from the barrier layer to the well layer is considered as the origin of the phase separation. The diffusion process is also confirmed by PL and absorption measurements.

6.1 Introduction

Recently, ZnO is attracting much attention since the material is considered as an alternative to GaN system for the applications in light-emitting devices operating in visible-ultraviolet regions. Corresponding to GaN/AlGaN heterostructure, ZnO/MgZnO superlattices play an important role for realizing the practical devices. Alloying ZnO films with MgO may
potentially permit the band gap to be controlled from 3.4 to 4 eV or even higher since up to
34 at.% Mg could be incorporated into hexagonal MgZnO thin films (see Chapter 4). This
means that MgZnO can be considered as an appropriate ternary alloy system that can
construct efficient ZnO-based heterojunctions with adjustable barrier height. However, since
the thermodynamic solubility limit of MgO in ZnO is less than 4 at.%,\(^3\) Mg\(_x\)Zn\(_{1-x}\)O solution
with 0.04<x< 0.34 should be considered as a metastable phase. It is the nonequilibrium
processes in PLD method that lead to the much higher Mg content in the solid solution while
maintaining the hexagonal structure with a lattice constant close to that of ZnO.

MgO has a rock salt (NaCl) structure with coordination number of six, whereas the structure
of ternary MgZnO alloy is hexagonal wurtzite. The wurtzite structure compound contains
1.5 times less atomic bonds as compared to the rock salt one. Since the formation enthalpy is
characterized by the total energy of all bonds, we could expect that the enthalpy would be
increased for rocksalt structure. The limit of metastability of the supersaturated solid alloy is
classified by spinodal decomposition.\(^4\)

Ohtomo et al\(^1\) shows that single-phase Mg\(_x\)Zn\(_{1-x}\)O thin films with wurtzite structure could be
prepared with x up to 0.25, as verified by XRD analysis. Our previous results extend this
limit up to x=0.34 (Mg content) by varying the growth parameters (Chapter 4).\(^2\) There is no
doubt that the higher Mg content implies that the phase of the alloy is more unstable. The
idea of this work is to investigate ZnO (Hex)- MgZnO (Hex) superlattices with the highest
barrier as possible. Here, Mg\(_x\)Zn\(_{1-x}\)O, where x is close to the solubility limit (x=0.33 - 0.34)
is used as the barrier layer. Although XRD measurements had shown that MgO-like
phase separation was observed for \( x > 0.34 \), the electron microscopic investigation had not been done for this kind of initial stage nucleation. The characterization of these objects by HRTEM and EELS measurements is the first purpose of this work. It has been demonstrated that the formation of nanoinclusions originated from the thermodynamic equilibrium phase separation in III-V ternary compounds at growth temperature.\(^5\)\(^6\) For example, it is this kind of phase separation that leads to the formation of In-rich phase in the InGaN alloy layers.\(^5\)

As for II-VI system, there are only a few cases of phase separations, e.g. the phase separations have been observed in ZnSeS, ZnMgSeS and ZnSeTe alloys.\(^7\)\(^8\)

### 6.2 Experimental Details

The superlattice heterostructure was deposited using pulsed laser deposition (PLD) technique with ZnO and composite ZnO-MgO targets. Pulsed excimer (KrF) laser (\( \lambda = 248 \) nm, pulse width=25 ns, repetition rate=10 Hz) beam was focused on the composite targets to achieve a fluence of 2.5-3.5 J/cm\(^2\). The substrates were mounted on a heater plate parallel to the target with the distance between the two around 5 cm. The laser beam is incident on the target at an angle close to 45\(^\circ\). A high vacuum environment (~10\(^{-7}\) Torr) is routinely obtained in this PLD chamber. The depositions in this work were carried out in an oxygen partial pressure ~1-5X10\(^{-5}\) Torr while the substrates were maintained at the temperature of 650-750\(^\circ\)C. The films were deposited on \( \alpha \) Al\(_2\)O\(_3\) (0001) substrates. The ZnO–MgZnO superlattice structure were fabricated by first depositing ZnO buffer layer for 6 minutes and then depositing ten alternating layers of MgZnO (20 seconds) and ZnO (15 seconds).
Thin film characterizations were carried out using X-ray diffraction (XRD) (using Cu Kα source, λ=1.541 Å) and high-resolution transmission electron microscopy (HRTEM) for microstructure, phase identification, and defect analysis, and Rutherford Backscattering ion channeling for composition and crystal quality. Optical transmission and photoluminescence of the heterostructure were also measured.

6.3 Results and Discussion

MgZnO-ZnO/Sapphire heterostructure is very delicate growth system. Although good quality uniform MgZnO have been grown up to 34 at.% of Mg, the composition of the superlattice structure become unstable when concentration of Mg is higher. Figure 6-3-1 shows the XRD pattern of MgZnO-ZnO layered structure on sapphire (0001) substrates grown at temperature of 650 °C. This XRD pattern demonstrates the formation of hexagonal phase MgZnO with Mg concentration as high as 34 at. %. The lattice constants of Mg_{0.34}Zn_{0.66}O alloy were found to change by 1% (a increased by 1% and c decreased by 0.9%) with respect to that of the pure ZnO, corresponding to the values of a=3.28 Å, c=5.15 Å. The full-width-at-half-maximum (FWHMs) of ω-rocking curve of the (0002) reflections were typically 0.40°, which is an indication of a high crystalline quality of the alloy films.²

As Mg content increases, this system becomes very sensitive to the growth parameters such as temperature, laser energy and the fluctuation of stoichiometry in the superlattice ZnO-
MgZnO. In our case, the stoichiometric deviation of MgZnO solution from the optimum leads to the decomposition of this ternary compound. Because vapor pressure of ZnO and Zn is much larger than that of MgO and Mg at the substrate temperature, Zn-related species can easily desorbs from the growing surface. This effect results in the condensation of Mg-related species on the surface. Desorption of Zn species is also the origin of Zn deficit in ZnO layers grown by pulsed laser deposition. The observation of high concentration of stacking faults in pure ZnO on sapphire is the indicator of this phenomenon. Unlike ZnO, uniform MgZnO is more stable at the optimum stoichiometry. And again the indicator of this effect is the lack of stacking faults. At this case threading dislocations are the primary defects in MgZnO/sapphire system. So we can draw an important conclusion here, the growth of MgZnO with high concentration of Mg demands the control for perfect stoichiometric conditions.
Figure 6-3-1. XRD pattern of MgZnO-ZnO layer structure on sapphire (0001) substrate grown at temperature of 650 °C.

Figure 6-3-2. Dark-field transmission electron micrograph taken under 2-beam condition. Interface between ZnO and superlattice is clearly visible.

Figure 6-3-2 shows the low-magnification dark field picture of ZnO-MgZnO superlattice (SL) grown on sapphire with ZnO buffer layer taken under 2-beam condition. The interface between buffer and superlattice is clearly observed, but the contrast from SL hardly exists. Figure 6-3-3 is the high-resolution TEM micrograph. No SL-related contrast (estimated thickness of alternating layers should be 6 nm) is observed. Only high concentration of stacking faults is found in the HRTEM image. Note that the growth condition for this superlattice structure is the same as that for the uniform MgZnO/Sapphire and in the latter case no stacking fault was observed. This phenomenon seems to arise from the additional flux of metal vacancies from the growing pure ZnO layers, which leads to the mixing of Mg and the decomposition of the ternary compound. After this phase decomposition, the cubic-phase nanoinclusions with structure similar to that of MgO originate. Figure 6-3-4 (c) shows
the HRTEM picture of the proposed superlattice area. The inclusions that really exist on this picture are very hard to detect since the interplanar distances of the inclusions are very small and the contrast is weak. Fourier spectrum transformation (insert in Figure 6-3-5 a) clearly shows additional reflexes associated with the cubic-phase nanoparticles. After the subtraction of the MgZnO hexagonal phase fringes, we visualize this nanoparticle (Figure 6-3-5 a). All these cubic phase nanoparticles have the epitaxial relationship with the MgZnO hexagonal matrix (see the position of additional reflex on FFT diagram).

![HRTEM Picture of Proposed Superlattice Area](image)

Figure 6-3-3. Transmission electron micrograph taken in [1120] zone axis. C-planes of MgZnO and ZnO resolved here.

The cubic phase structure of these precipitates is confirmed further by the analysis of electron energy loss spectroscopy. Figure 6-3-5 (b) shows the near-edge fine structure (ELNES) of the K-edge of Mg. This spectrum shows the same shape as the cubic MgO. We believe that this is the sufficient evidence for the MgZnO cubic phase with low content of Zn. The Mg map also shows the accumulation of the element in tiny inclusions in the area of proposed
superlattice (Figure 6-3-4. (a) and (b)).

Figure 6-3-4. (a) Zn elemental map taken by EELS, (b) Mg elemental map (EELS), (c) high-resolution transmission electron micrograph taken in [1120] zone axis in SL area.
Figure 6-3-5. (a) Visualization of cubic-phase MgZnO nanoparticle after subtraction of reflections of hexagonal MgZnO (or ZnO). Insert represents the FFT spectrum of picture in Figure 4c; reflections associated with cubic-phase nanoparticle indicated by arrows; (b) ELNES of Mg-K shows the same shape as the cubic MgO.

Figure 6-3-6. Absorption spectra of MgZnO/ZnO SL structures with different well deposition time (10, 15, 18 seconds).

The absorption spectra of MgZnO/ZnO superlattice structures were measured by using Cary 5 UV-VIS-NIR spectrometer at room temperature. Figure 6-3-6 shows the absorption spectra of three ZnO/Mg$_{0.34}$Zn$_{0.66}$O superlattice structures with different deposition times of ZnO well layers. The absorption spectra of pure ZnO and Mg$_{0.34}$Zn$_{0.66}$O films were also plotted for the purpose of comparison. The relative absorbance is scaled such that the “A” exciton peak is the same for each sample. In case of Mg$_x$Zn$_{1-x}$O sample, the thickness of the sample was such that the absorption above bandgap was approximately the same as the other
samples. In pure ZnO sample, A and B exciton peaks are well distinguished. For the spectra of three superlattice samples, the exciton peak shifts to the higher energy side as the deposition time decreases. The blue shift of the exciton peak of the well layer is widely observed in the superlattice structure and is usually considered as the consequence of the quantum confinement effect. However in our case, it should be noticed that the exciton absorption peak of the barrier MgZnO layer has a red shift for each of the three samples. Combining the result of TEM investigation, we conclude that there is serious diffusion of Mg from the barrier to the ZnO well layer. The blue shift of the ZnO well is due to the band gap increase since the diffusion process leads to the formation of MgZnO in the well region. On the other hand, the quantum-confine effect for ZnO well should be quite small due to the large exciton binding energy and the small exciton Bohr radius.

Figure 6-3-7 shows the PL spectra of three superlattice structures with well deposition time of 7, 10 and 15 sec. The PL spectrum of pure ZnO thin film is also shown in the figure. These spectra were measured with 270 nm line of an Ar\(^+\) ion laser at room temperature. The sample with the shortest well deposition time (7 sec) shows the strongest relative PL of barrier layers. The lower-energy emission band of this sample seems mainly from the ZnO buffer layer. In the spectra of the 10-second sample, the emission form the well layer is strong and is shifted to the higher-energy side due to the bandgap change arising from the Mg diffusion. For the 15-second sample, the emission from ZnO well layer occurs with a shoulder of the buffer layer. After all the PL spectra of these superlattice sample also demonstrate the Mg diffusion from the barrier to the well layer. This is in agreement with the TEM and absorption measurements.
**6.4 Conclusion**

Epitaxial films of MgZnO wurtzite structure have been grown on (0001) sapphire substrates. With higher concentration of Mg (higher than 34wt%) the composition becomes unstable even at optimum stoichiometry. The deviation of stoichiometry in ZnO-MgZnO superlattice leads to the phase decomposition of the ternary compound. HRTEM reveals numerous cubic-phase nanoinclusions. All these cubic phase nanoparticles have the epitaxial relationship with MgZnO hexagonal matrix. The near-edge fine structure (ELNES) of K-
edge of Mg demonstrates the cubic nature of these inclusions. The Mg and Zn mapping confirms the TEM data. The Mg diffusion in the superlattice structures was also confirmed by the absorption and PL observations.

References

In this chapter we present our results of the growth and characterization of Zn_{1-x}Mn_xO thin films. These films were deposited on (0001) sapphire substrate by a pulsed laser deposition technique. The nonequilibrium nature of PLD process allowed us to incorporate higher Mn contents (x=0.36) than that allowed by thermal equilibrium limit (x≈0.13) into the MnZnO alloy films. The epitaxial nature and single-crystalline quality of the films are demonstrated by the XRD and TEM results. As the Mn concentration increases in the system, the c-axis lattice constant was found to increase linearly. Optical transmittance study showed an increase in the band-gap ($E_g$) with increase in Mn atomic fraction $x$ following $E_g=3.270+2.760x-4.988x^2$ eV. DC magnetization measurements showed the paramagnetic nature of the system.

7.1 Introduction

With the band gap of 3.40 eV, ZnO in II–VI semiconductor family\textsuperscript{1–2} compares very favorably with GaN of III–V systems\textsuperscript{3} with almost identical bandgap. To vary the bandgap, GaN can be alloyed with AlN (6.2 eV) to increase the bandgap or with InN (1.9 eV) to decrease it. Similarly ZnO can be alloyed with MgO (8.2 eV) to increase the bandgap (see
or with CdO (2.0 eV) to decrease it. Furthermore, ZnO could be alloyed with MgO both in hexagonal (wurtzite) as well as cubic structure. The cubic structure has been integrated with Si(001) substrate via domain epitaxy, where four lattice constants of ZnMgO match with three of the underlying silicon (see chapter 5). In addition, ZnO and its alloys have higher exciton binding energy (60 meV) compared to III-nitride counterparts (25 meV), which results in higher luminescent efficiencies. Another possible application of ZnO is in the field of spintronics. Spintronics (spin+electronics) is a fast emerging field in physics focused on spin-dependent phenomena, which can be applied to the modern electronics devices such as new generation of random storage device. Diluted magnetic semiconductors (DMS) are considered as ideal systems for spintronics. Recently Dietl et al. using the approximation of Zener's model of ferromagnetism, predicted that Mn doped ZnO may have room temperature ferromagnetism ($T_c>300$ K).

Stimulated by Dietl et al.’s prediction, Mn doping of ZnO thin films have been reported. The maximum Mn fraction in these $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films was found to be 35 at. %, far exceeding the equilibrium value of Mn of 13%. These films were deposited by non-equilibrium pulsed laser deposition where the average energy of laser-ablated species (100–1000 kT) is 2–3 orders of magnitude higher than the equilibrium value. One of the drawbacks of the previous work was that these films were not characterized in terms of detailed microstructure and epitaxial growth. It was not clear if Mn replaces Zn or forms Mn precipitates. The microstructural information for these films is still lack.

In this work, we have placed a strong emphasis on Rutherford backscattering/channeling
for Mn lattice location and detailed high-resolution transmission electron microscopy (HRTEM) to observe the fate of Mn, particularly whether it forms Mn precipitates in MnZnO thin films. The epitaxial nature of these films is revealed by the XRD and TEM observation. The focus of this work is on the preparation and detailed microstructural characterization, and optical and magnetic property measurements of epitaxial Zn$_{1-x}$Mn$_x$O films.

7.2 Experimental Details

Epitaxial Zn$_{1-x}$Mn$_x$O ($x=0.01–0.36$) films were grown on two-side polished sapphire (0001) substrates by pulsed laser deposition technique with a KrF excimer laser (wavelength of 248 nm, repetition of 10 Hz, and pulse duration of 25 ns). Targets were prepared by standard solid state method. Stoichiometric amount of ZnO and MnO powders were mixed together and calcined at 450 °C for 6 h. Resulting powder was pressed in the form of circular pallets. These pallets were sintered at 900 °C for 12 h in flowing oxygen. Pallets thus prepared were used for laser ablation targets. Depositions were carried out at 610 °C in an ambient oxygen pressure of $5 \times 10^{-5}$ Torr. The energy density and repetition rate of the laser beam were 2–3 J/cm$^2$ and 10 Hz, respectively. Crystal structure of these films was determined by X-ray diffraction using a Rigaku X-ray diffractometer with Cu K$\alpha$ radiation and Ni filter. Exact stoichiometry of these films was determined by Rutherford backscattering technique. Microstructural characterization of these films was performed by cross-sectional TEM using JEOL-2010F analytical electron microscope with point-to-point resolution of 0.18 nm. Optical transmittance spectra of these films were recorded at room temperature in the
energy range 1–4 eV. Magnetic properties of these films were studied using superconducting quantum interference device (SQUID) magnetometer.

7.3 Results and Discussion

![X-ray diffraction patterns of Zn$_{1-x}$Mn$_x$O (x=0.20 and 0.01) films.](image)

Figure 7-3-1. X-ray diffraction patterns of Zn$_{1-x}$Mn$_x$O (x=0.20 and 0.01) films.

X-ray diffraction patterns of the films showed them to be single phase and having wurtzite structure with c-axis of the film aligned with that of the substrate. Figure 7-3-1 shows the typical X-ray diffraction patterns of Zn$_{1-x}$Mn$_x$O with x=0.01 and 0.20. As is clear from the figure, there are no other orientations except (000l) reflections of ZnO and sapphire substrates. Till x=0.36, all the films were in single phase but for x>0.36 some signatures of phase separation were observed. In Figure 7-3-2 we have shown the variation in the c-
axis lattice constant \( c \) as a function of Mn content in the system. A systematic increase in \( c \) without any observed change in crystal symmetry indicates that Mn is occupying the Zn site in the crystal structure. It is interesting to note that in this work we have succeeded in doping Mn in ZnO much above the thermal equilibrium limit of \( x \approx 0.13 \). This became possible because of the nonequilibrium processing involved during the pulsed laser deposition, where the average energy of the laser-ablated species is 2–3 orders of magnitude higher than the equilibrium value.

![Graph showing variation in the c-axis lattice parameter of Zn\(_{1-x}\)Mn\(_x\)O thin films with x. Solid line represents a linear fit to data.](image)

**Figure 7-3-2.** Variation in the c-axis lattice parameter of Zn\(_{1-x}\)Mn\(_x\)O thin films with x. Solid line represents a linear fit to data.

In Figure 7-3-3, we have presented our results (yield vs. energy) of Rutherford backscattering and channeling experiment on one of the films. The figure shows the random and channeling
spectra from which the minimum channeling yield was calculated to be less than 3.0% near the surface. The low channeling yield indicates that Mn is located at the lattice site rather than the interstitial site. The minimum channeling yield is close to the value of bulk single crystal, indicating a high quality of the film. From a fit to the random backscattering profile, the actual concentration of Mn in these films was determined. Mn contents in the films and the targets were found to lie within ±5%.

Figure 7-3-3. Rutherford back scattering random (●) and channeling (+) data for Zn$_{1-x}$Mn$_x$O (x=0.25) film.

Figure 7-3-4 shows the selected area diffraction pattern on the Zn$_{1-x}$Mn$_x$O (x=0.85)/ sapphire interface area taken along [01 10] zone axis of ZnMnO thin film. The aligned patterns clearly show that the film was epitaxially grown on the substrate with following epitaxial relationship: Zn$_{1-x}$Mn$_x$O(0001)\(\parallel\) sapphire(0001), Zn$_{1-x}$Mn$_x$O (01 10)\(\parallel\) sapphire( 12 10),
and Zn_{1-x}Mn_xO (\(\bar{1}2\bar{1}0\)) \parallel \text{sapphire (01 \bar{1}0)}. As in the case of ZnO and MgZnO thin films, this corresponds to a 30° or 90° rotation of the film about the substrate in the basal plane.

![Selected area diffraction pattern (SAD) from 10 \(\mu\text{m}\) area for Zn_{1-x}Mn_xO (x=0.15) thin films on sapphire (0001) substrate. The white numbers correspond to ZnMnO and the black numbers in white blocks correspond to sapphire.](image)

In Figure 7-3-5 (a), we present the HRTEM image carried out on the Zn_{1-x}Mn_xO/sapphire interface. The interface between the film and the sapphire is atomically sharp and free from any other phase. There are no precipitates of MnO or otherwise, which is consistent with RBS/channeling results in that Mn is incorporated into the Zn sites substitutionally. Due to the large in-plane mismatch (~18%) between the film and the substrate, the epitaxial growth of the film occurs via domain epitaxy.\(^{10-11}\) Figure 7-3-5 (b) is the inverse FFT picture of the image shown in Figure 7-3-5 (a). This is done by masking two reflexes (\(\bar{1}2\bar{1}0\)) and (01 \bar{1}0) in the corresponding FFT picture. The misfit dislocations were observed at the interface in the IFFT image. The dislocation occurs at every 6-th (\(\bar{2}\ 2 \bar{1}0\)) plane of
sapphire (average). The unit cell of ZnMnO film rotates by 30° about the c-axis with respect to the sapphire unit cell as reported in pure ZnO on sapphire substrate.\textsuperscript{10-11}

Figure 7-3-6 shows the optical absorbance spectra of Zn\(_{1-x}\)Mn\(_x\)O films. It can be seen from this figure that as the Mn content increases, the absorption edge moves towards the higher energy side. This indicates the increase in the band-gap (\(E_g\)) of the system. Significant amount of midgap absorption is also observed in these samples. This phenomenon had been reported in earlier studies\textsuperscript{8} and was attributed to the charge-transfer transition between donor and acceptor ionization levels of Mn ions and the band continuum. In Figure 7-3-7, we have plotted the band-gap of these films as a function of Mn content. A systematic increase in the value of \(E_g\) with Mn concentration can clearly be envisaged. More than 12% increase in the band-gap is caused by 25% doping of Mn in ZnO.

Figure 7-3-5 (a) High-resolution picture of single crystal Zn\(_{1-x}\)Mn\(_x\)O (x=15) film grown on sapphire (0001) substrate.
Figure 7-3-5 (b) IFFT picture from Fig.7-3-5 (a). Two reflexes ( 12 10) and (01 10) have been masked in corresponding FFT picture, so only (01 10) planes of ZnMnO and ( 12 10) planes of sapphire are observed. The places corresponding to the misfit dislocations are indicated here.

DC magnetization data from SQUID measurements showed the paramagnetic behavior for all the samples. No signature of ferromagnetic ordering could be detected in any of these films down to 10 K. This is in contradiction with the theoretical predictions of Dietl et al.\textsuperscript{7} A typical magnetization vs. temperature variation for \( x=0.05 \) film is shown in Figure 7-3-8. Magnetic susceptibility (\( \chi=M/H \)) data fits well in an expression of the kind \( \chi=x_0+C/T \). By using the value of the parameter \( C \) in the expression \( C=N_p^2\mu_B^2/3k_B \) for Curie paramagnetism,\textsuperscript{12} we derived a value of effective Bohr magnetron number \( p \) for Mn to be 5.9, which gives a value of \( J\approx5/2 \). This is consistent with the doubly ionized ionic state of Mn, substituting Zn sites in the Zn\textsubscript{1-x}Mn\textsubscript{x}O lattice.
Figure 7-3-6. Optical absorbance spectra of Zn$_{1-x}$Mn$_x$O films. Symbols a, b, c, d and e correspond to $x=0.01$, 0.05, 0.12, 0.18 and 0.25 respectively. Absorbance is related to the percentage transmittance (T) by the relation absorbance=$-\log(\%T/100)$.

Figure 7-3-7. Variation in the band-gap of Zn$_{1-x}$Mn$_x$O films with $x$. Data fits well in a second order polynomial equation $E_g=3.270+2.762x-4.988x^2$ eV (see solid line).
7.4 Conclusion

In conclusion, we have prepared high quality epitaxial Zn$_{1-x}$Mn$_x$O (x=0.05) films on sapphire (0001) substrates using a pulsed laser deposition technique. A systematic study of the structural properties of these high quality epitaxial films showed a 30° rotation of the film with respect to the substrate, similar to III-nitride growth on the sapphire substrate. Both the $c$-axis lattice parameter as well as the band-gap $E_g$ is found to be sensitive functions of Mn content. Bandgap was found to follow the relationship $E_g=3.270+2.760x-4.988x^2$ eV. SQUID measurements showed paramagnetic behavior. No ferromagnetic ordering could be detected in any of these films down to 10 K. However, here we find it appropriate to mention that
though the system does not exhibit any long range ferromagnetic ordering but still the possibility of local ferromagnetic ordering cannot be overruled at this point. Recently it has been shown\textsuperscript{13} that paramagnetism may emerge from clusters that are locally ordered ferromagnetically, magnetic moments of these clusters point randomly and cancel each other resulting in the overall paramagnetic behavior of the system.

References


Chapter 8 INTEGRATION OF ZnO THIN FILMS WITH SILLICON SUBSTRATE

The research work in this chapter is focused to exploit the way to integrate epitaxial ZnO thin films onto silicon substrate. Epitaxial ZnO thin films were grown on Si (111) substrates by using AlN buffer layer and MgO/TiN buffer layers. The resultant films are evaluated by transmission electron microscopy, x-ray diffraction, electrical measurements, and PL measurement. The epitaxial relationship of ZnO thin film in ZnO/AlN/Si(111) heterostructure was found to be ZnO[0001] || AlN[0001] || Si[111] along the growth direction and ZnO[2 \bar{1} \bar{1} 0] || AlN[2 \bar{1} \bar{1} 0] || Si[0 \bar{1} \bar{1}] along the in-plane direction. For ZnO/MgO/TiN/Si(111) heterostructure, domain-matching epitaxial growth of TiN on Si(111) substrate provides a template for the epitaxial growth of the MgO and ZnO layers. Epitaxial relationships in this heterostructure system are ZnO(2\bar{1}10) || MgO/TiN/Si(011) and ZnO(111) || MgO/TiN/Si(111).

8.1 Introduction

ZnO has a hexagonal wurtzite structure with lattice constant of a=3.2498Å and c=5.2066Å. ZnO thin films have been grown by using several different techniques including pulsed laser deposition (PLD),\textsuperscript{1-2} rf-magnetron sputtering,\textsuperscript{3} spray pyrolysis\textsuperscript{4} etc. (see also chapter 2). The
c-axis oriented sapphire ($\alpha$-Al$_2$O$_3$) substrates are widely used for developing epitaxial ZnO thin films. The mechanism for this epitaxial growth is characterized by domain-matching epitaxy, in which the in-plane epitaxial orientation relationship between the film and the substrate corresponds to $30^\circ$ or $90^\circ$ rotation of the film with respect to the substrate in the basal plane. However, for the practical applications, the integration of ZnO thin film with Si substrate is more desirable. In this work, we report the epitaxial growth of ZnO thin films on Si(111) substrates. Two kinds of buffer layers were used to achieve the epitaxial growth, AlN and MgO/TiN. AlN has hexagonal wurtzite structure with lattice constants of $a=3.112$ Å and $c=4.982$ Å. The epitaxial growth of AlN thin film on Si(111) substrate occurs by the domain matching epitaxy, where integral multiples of major lattice planes of the film and the substrate match across the interface. Epitaxial ZnO thin film can be grown on AlN layer via lattice-matching epitaxy since the lattice misfit between the lattice constants of the two materials is only 4%. TiN has a cubic sodium chloride structure with lattice constant of 4.24 Å. The epitaxial mechanism of TiN thin films on Si (001) substrate was found to be cube-on-cube domain-matching epitaxy of less than 4% misfits with 4-TiN unit cells matching 3-Si unit cells. There is a good epitaxial compatibility between TiN and MgO, since both the epitaxial growths of TiN thin films on MgO substrates and MgO thin films on TiN substrates had been realized. MgO has a sodium chloride (NaCl) structure with the lattice constant of 4.216 Å. Small lattice misfit between TiN and MgO allows the epitaxial growth of MgO thin film on TiN layer with lattice-matching epitaxy.
8.2 Experimental Details

ZnO/AlN/Si(111) and ZnO/MgO/TiN/Si(111) heterostructures were grown by pulsed-laser deposition using a KrF excimer laser (λ=248 nm, t=25 ns) in a high vacuum chamber. Before deposition, the silicon (111) substrate was cleaned to remove the surface oxide layer using 5% HF solution. The stoichiometric hot pressed AlN, TiN and MgO targets obtained commercially were used to grow the buffer layers. ZnO target was synthesized by using standard calcine-sintering method in our lab (see chapter 4 for details). During the AlN buffer deposition, the Si (111) substrate was maintained at 750 °C, and the background pressure rose to 1×10⁻⁶ Torr. The AlN buffer layer was deposited at a laser energy density of 5J/cm² and pulse repetition rate of 10 Hz. ZnO thin films were deposited directly on the AlN buffer layer at 630 °C. The laser energy density and repetition rate were 2 J/cm² and 10 Hz, respectively. ZnO film was deposited first in vacuum (1×10⁻⁶ Torr) for 1 minute and then deposited at the oxygen partial pressure of 5×10⁻⁵ Torr. The total deposition times for AlN and ZnO thin films were 15 minutes each.

For ZnO/MgO/TiN/Si(111) heterostructures, TiN layer was deposited at background pressure of about 1×10⁻⁶ Torr at 650 °C. The laser energy density is 2.3 J/cm². After 15 minutes growth of TiN layer, MgO was grown at the same temperature with laser energy density of 4J/cm². The deposition of MgO layer was first performed at the background pressure for 1 minute, then performed at oxygen pressure of 5×10⁻⁵ Torr. The deposition time for MgO layer is also 15 minutes. ZnO thin film was deposited at the same temperature and oxygen
partial pressure. The laser energy density for ZnO thin film is 2.5 J/cm². The deposition time of ZnO thin film was 20 minutes.

X-ray diffraction and transmission electron microscope (TEM) were used to characterize the crystalline structure and the microstructure. PL spectra of the films were measured at room temperature. The conductivity of the films was also measured.

8.3 Results and Discussion for ZnO/AlN/Si(111) Heterostructure

The x-ray diffraction pattern of the resultant ZnO/AlN/Si(111) heterostructure is given in Figure 8-3-1. The diffraction pattern shows the expected reflections from Si(111) planes together with AlN (002), AlN (004), ZnO (002), and ZnO(004) reflections. The XRD result shows that the ZnO and AlN films were crystalline with epitaxial characterizations on Si(111) substrate. The c-axis lattice parameter of ZnO calculated from XRD data is found to be 5.199Å.

The choice of AlN as a buffer layer was motivated by the earlier work of Narayan et al⁶ in which they developed a method to grow single crystal AlN films on Si(111) by domain matching epitaxy. Here it is to be noted that there is a large difference between the lattice parameters of AlN and Si. The lattice misfit, \( f \) [defined as \( f = 2(b-a)/(a+b) \), where \( a \) and \( b \) are the lattice parameters of the substrate and the AlN film, respectively] is 22.3%. This is a quite large value for lattice matching epitaxial growth. The epitaxial relationship between
AlN film and Si(111) substrate was formed by the so-called domain-matching epitaxy mechanism (DEM). In each domain, ‘m’ lattice parameters (or interplanar distances) in the substrate match with ‘n’ in the epilayer, where, m and n are simple integers. The residual domain mismatch is given by $f_d = \frac{2(nb-ma)}{(nb+ma)}$. In the case of AlN epitaxy on Si(111), 4 interplanar distances of Si(110) closely match with the 5 interplanar distances of AlN for AlN[2 1 10]∥Si[0 1 1] epitaxial growth. This yields a domain misfit ($f_d$) of 1.2%, which is much smaller than the lattice misfit of 22.3%.

![X-ray diffraction pattern of ZnO film on AlN/Si(111).](image)

Figure 8-3-1. X-ray diffraction pattern of ZnO film on AlN/Si(111).

Transmission electron diffraction studies confirmed the single crystalline epitaxial nature of ZnO film. In Figure 8-3-2 (a), we have shown the selected area diffraction pattern from the ZnO film, well aligned spots clearly establishes the high quality of the film. Figure 8-3-2(b)
shows the selected area diffraction pattern taken from the ZnO/AlN interface. The orientational relationship between ZnO and AlN was ZnO[0001]||AlN[0001] along the growth direction and ZnO[2 \bar{1} \bar{1} 0]||AlN[2 \bar{1} \bar{1} 0] along the in-plane direction. The lattice misfit between ZnO and AlN is –4.3% by choosing AlN as substrate. This value is within the feasible range for lattice-matching epitaxial growth. The negative sign means that ZnO is under compress stress corresponding to the tensile stress on the AlN buffer layer. Figure 8-3-3 shows the cross sectional image along direction <01 \bar{1}0> containing ZnO, AlN and silicon substrate. The micrograph clearly shows that the ZnO/AlN interface is clean and sharp. The film has a high concentration of stacking faults and dislocations, but still has very high crystalline quality.

![Figure 8-3-2](image)

Figure 8-3-2. (a) Selected area diffraction pattern from ZnO film; (b) selected area diffraction pattern from ZnO/AlN interface.
Current versus voltage characteristics of ZnO films are shown in Figure 8-3-4. A linear relationship can clearly be seen. It again confirms the excellent quality of film and much less number of dislocations and stacking faults compared to films grown on sapphire. As mentioned earlier, the epitaxial feature for ZnO thin films on sapphire (0001) substrates occurs by the domain-matching epitaxy mechanism. There are edge dislocations on the boundaries of the domains. At least, one dislocation exists in each domain. As a result, there is a large density of dislocations on the ZnO/α-Al2O3 interface, which gives nonlinearity in the I-V characteristics. Since the growth of ZnO films on AlN occurs by lattice-matching epitaxy, the density of dislocations is expected to be reduced significantly on the interface.
Figure 8-3-4. Current versus voltage (I-V) characteristics of ZnO film at 12K and 300K
8.4 Results and Discussion for ZnO/MgO/TiN/Si(111) Heterostructure

Figure 8-4-1 shows the XRD pattern for the ZnO/MgO/TiN/Si(111) heterostructure. The reflections from Si (111) planes and ZnO (000l) planes are clearly seen in the figure. The reflections from TiN and MgO (111) planes are not distinguished due to the small lattice constant difference between the two lattices. XRD results clearly demonstrate that the three thin-film layers are aligned along [111] direction with the Si (111) substrates. The figure also shows a very clean base line and all the layers are single phase.

![XRD θ-2θ scan of ZnO/MgO/TiN/Si(111) heterostructure. The reflections from TiN and MgO (111) plane are not distinguished due to the small lattice constant difference.](image)

Figure 8-4-1. XRD θ-2θ scan of ZnO/MgO/TiN/Si(111) heterostructure. The reflections from TiN and MgO (111) plane are not distinguished due to the small lattice constant difference.
Figure 8-4-2 is the low magnification TEM image of the heterostructure. As seen from the figure, thin-film layers are clearly distinguished and the interfaces between the layers are clean and sharp. Figure 8-4-3 shows the selected area diffraction pattern taken from the structure. Figure 8-4-3 (a) is the SAD pattern taken from all the three thin-film layers and the Si (111) substrate. The zone axis of the substrate SAD pattern is [011]. The SAD patterns from TiN and MgO layers are not distinguished due to the small lattice constant difference. Again, the zone axis for the two cubic structured films is [011]. The SAD pattern of ZnO layer is from the $[2\bar{1}10]$ zone diffraction. From the SAD pattern and XRD result, we can conclude that the three thin film layers have been grown epitaxially on the Si substrate.
Figure 8-4-3 (b) is the SAD pattern taken from the Si/TiN interface, which further confirms the epitaxial relationship between this buffer layer and the substrate. The SAD pattern in Figure 8-4-3 (c) is taken from the ZnO thin film layer alone. The diffraction of this pattern arises from the contributions of the [2110] zone planes of ZnO film. The clear, sharp SAD pattern shows that the film has a single crystalline quality. Based on the XRD results and the TEM SAD patterns, we can figure out the epitaxial relationship for this heterostructure. As expected, TiN layer is epitaxially grown on Si(111) via domain-matching epitaxy with cube-on-cube relationship. MgO is grown on the TiN buffer with lattice-matching epitaxial mechanism. The ZnO thin film layer is grown with domain-matching epitaxy. The epitaxial relationship between the ZnO thin film and the underlying buffer + substrate layers are as follows: ZnO(2110) \parallel MgO/TiN/Si(011) and ZnO(111) \parallel MgO/TiN/Si(111).

Figure 8-4-3 (a). TEM SAD patterns of ZnO/MgO/TiN/Si(111) heterostructure from all the layers.
Figure 8-4-3 (b). TEM SAD patterns of ZnO/MgO/TiN/Si(111) heterostructure taken from TiN/Si interface.

Figure 8-4-3 (c). TEM SAD patterns of ZnO/MgO/TiN/Si(111) heterostructure taken from ZnO film only.
Compared to the other ZnO heterostructure on Si substrate such as ZnO/GaN/Si(111) and ZnO/AlN/Si(111), the ZnO/MgO/TiN/Si(111) heterostructure has its unique advantage. The main purpose for using buffer layer is to prevent the oxidization of the silicon surface, which will significantly lower the thin film quality. However it is still a challenge to grow high quality III-nitride on silicon substrate, which makes the growth of ZnO/III-nitride/Si heterostructure even more difficult. On the other hand, the potential oxidization of the nitride surface has to be overcome when the ZnO thin film is deposited. The high quality TiN thin film on silicon substrate is relatively easier to achieve. One of a striking feature of TiN is that MgO can be grown epitaxially on it even there is oxidization occurred on the interface. No doubt, there is no oxidization need to be considered when ZnO is growing on MgO layer. It should be also noticed that, MgZnO layer has the same wurtzite structure with ZnO and very small lattice difference. The bandgap of MgZnO alloys is higher than that of ZnO, which makes the MgZnO layer always be the barrier layer if the two materials are contacted together. So ZnO can be grown on the MgO buffer without concerning the Mg diffusion or reaction.

Figure 8-4-4 shows the PL spectrum measured with Hitachi F2500 fluorescence spectrophotometer. The spectrum was measured with 300 nm line from Xe lamp source at room temperature. As seen from the spectrum, the excitonic emission band peaked at 380 nm is quite strong compared to the green band emission. The emission from this ZnO heterostructure is extremely bright. Figure 8-4-5 shows the PL spectrum for green band emission. The green band emission composed of two bands around 495 nm and 570 nm. As discussed in chapter 2, the mechanism for green band emission is not clear yet. The origins
of these two emission bands can not be identified at this point, but we believe that the native defects in ZnO are responsible. Figure 8-4-6 shows the excitation spectrum for the green band emission, which is measured by monitoring the green band emission at 500 nm. From the spectrum, we can see that both the band-band transitions and excitonic transitions contribute to the emission. This indicates that the excitation of the green band emission is mainly from the charge transformation processes.

![Figure 8-4-4. PL spectrum of ZnO/MgO/TiN/Si(111) heterostructure.](image)
Figure 8-4-5. Green band emission of ZnO/MgO/TiN/Si(111) heterostructure.

Figure 8-4-6. Excitation spectrum of ZnO/MgO/TiN/Si(111) heterostructure measured by monitoring the green band emission at 500 nm.
8.5 Conclusion

In conclusion, we have grown the single-crystalline ZnO films on ZnO/AlN/Si(111) and ZnO/MgO/TiN/Si(111) heterostructures. For ZnO/AlN/Si(111) system, XRD and TEM results demonstrate that AlN layer was grown epitaxially on Si (111) substrate by means of domain-matched epitaxy. The epitaxial ZnO thin film was grown on the AlN buffer layer with lattice-matching epitaxy. For ZnO/MgO/TiN/Si(111) heterostructure, the epitaxial mechanism of TiN buffer on Si (111) is domain-matching epitaxy with cube-on-cube alignment. MgO layer was grown epitaxially on the TiN buffer with lattice-matching epitaxy. The epitaxial mechanism of ZnO film on MgO buffer is again domain-matching epitaxy.

A linear relationship of current versus voltage characteristics was observed for the ZnO film on AlN/Si (111). This is believed to be the consequence of much less number of dislocations and stacking faults since ZnO was grown on AlN buffer via lattice matched epitaxy. ZnO films grown on MgO/TiN/Si(111) shows a very bright luminescence at room temperature. The PL spectrum for the sample is featured with a strong excitonic emission and a relatively weak green band emission.

Finally, the successful growth of high quality ZnO films with silicon opens the opportunity for the integration of ZnO based optical and lasing devices with the next generation microelectronic devices.
References

Chapter 9  THE GROWTH AND CHARACTERIZATION OF ZINC OXIDE THIN FILMS ON AMORPHOUS SUBSTRATES

In this work, ZnO thin films were grown on amorphous fused silica and pre-oxidized silicon substrates by using pulsed laser deposition technique. X-ray diffraction patterns showed that the films were highly crystalline and c-axis oriented. The surface morphologies of the films were observed by using scanning electron microscope and optical microscope. Free exciton absorption was observed at room temperature for the film grown on fused silica substrate. The strong near-UV luminescence peaked at 380 nm were observed for all the films and was attributed to the phonon-related exciton emission. The effect of oxygen partial pressure on the luminescence intensity is also investigated.

9.1 Introduction

Encouraged by the potential applications, the growth and characterization of ZnO thin films have become a very active research field in the past years. As a II-VI semiconductor, ZnO has a wide direct bandgap of 3.39 eV at room temperature and a larger exciton binding energy up to 60 meV. These characteristics make the material an ideal candidate for light emitting diode (LED)\(^1\) and UV-blue semiconductor laser.\(^2\) ZnO has also the potentials for many other applications such as flat panel displays,\(^3\) solar cell,\(^4\) gas sensor,\(^5\) and surface acoustic wave devices.\(^6\) Many different techniques were used to develop ZnO thin films, for examples, chemical vapor deposition\(^7\), pulsed laser deposition,\(^8\) rf magnetron sputtering\(^9\), and spray pyrolysis.\(^10\)
Most ZnO thin films were grown on $\alpha$-Al$_2$O$_3$ substrates on which ZnO films can be grown epitaxially by domain-matched epitaxial mechanism. Single crystalline ZnO thin films grown on a lattice-matched substrate was also reported. Another substrate that was frequently used is fused silica (glass). This is an amorphous substrate and is more practical for the future applications of planar displaying. The deposition of ZnO thin films on amorphous substrates is also strongly encouraged by the recent developments in the researches of random lasers. Lasing effects in polycrystalline ZnO thin films have been reported.

In this chapter, we report the growth and characterization of ZnO thin films on amorphous substrates. All films were deposited by using pulsed laser deposition technique. The resultant thin films were characterized by using x-ray diffraction, scanning electron microscope (SEM), absorption, emission and excitation spectra. The effects of oxygen partial pressure on the optical properties of the films were also investigated.

9.2 Experimental Details

An excimer KrF laser operated at 248 nm with the pulse width of 25 ns was used to ablate a sintered ZnO target made in our laboratory. Commercial fused silica slides (Alfa Aesar) and pre-oxidized silicon (100) wafers were used as substrates. The films were grown at the optimized temperature of 630 °C at different oxygen partial pressures from $2 \times 10^{-5}$ to $4 \times 10^{-1}$ Torr. The structure of the films was characterized by using x-ray diffraction technique.
with Cu Kα line. Surface morphology was observed by using scanning electron microscope (SEM) and optical microscope. Absorption spectra were recorded at room temperature with a Hitachi U-3010 spectrophotometer. Photoluminescence and excitation spectra were measured at room temperature using Hitachi F-2500 Fluorescence spectrometer.

9.3 Results and Discussion

Figure 9-3-1. X-ray diffraction patterns for the ZnO thin films grown on fused silica and SiO₂/Si(100) substrates.

Figure 9-3-1 (a) and (b) show the XRD patterns of ZnO films grown on fused silica and pre-oxidized silicon substrates at oxygen partial pressures of 2×10⁻⁵ Torr. Only ZnO (000l) reflections were observed in the XRD patterns for both films. This indicates that ZnO thin films were textured with c-axis orientation on the amorphous SiO₂ surfaces. The SEM image
for the film grown on fused silica substrate is given in Figure 9-3-2 (a). It can be seen that
the film consists of nano-size microcrystals with about 200 nm grain sizes. Figure 9-3-2 (b)
and (c) show the optical microscope image for ZnO thin films on fused silica and SiO$_2$/Si
substrates. From the images, we can see that ZnO film grown on fused silica cracked due to
the large difference of thermal expansion coefficients between the silica substrate and the
ZnO thin film. Opened circuits were confirmed for the cracked films from the electrical
measurements. It is impossible to use such open-circuit films for any electrical applications,
but it may not be a serious problem for cathode-luminescence applications. In fact, such
cracks were observed for all the films deposited on fused silica substrates at different oxygen
partial pressures. However, no cracks were found for the films grown on SiO$_2$/Si substrates,
which means the stresses between the ZnO thin films and the amorphous SiO$_2$ layers were
released by the underlying silicon body. Electrical measurements gave a sheet resistance
about $5 \times 10^4 \Omega$ for ZnO thin film deposited on SiO$_2$/Si substrate.

Figure 9-3-2. Surface morphologies of the ZnO thin films. (a) SEM image of ZnO thin
film grown on fused silica. (b) Image of optical microscope for ZnO thin film grown on
fused silica. (c) Image of optical microscope for ZnO thin film grown on SiO$_2$/Si(100)
substrate.
Figure 9-3-3. Absorption, excitation, and photoluminescence spectra of ZnO thin film grown on fused silica substrate. The excitation spectrum was recorded by monitoring 510 nm emission. (a) Absorption spectrum (solid line) and excitation spectrum (dash line). (b) Photoluminescence spectra with 300 nm excitation. The green-band emission was enlarged 3.5 times.

Figure 9-3-3 shows the absorption, emission (photoluminescence), and excitation spectra measured at room temperature for the films deposited on fused silica substrate at oxygen partial pressure of $2.1 \times 10^{-3}$ Torr. The absorption spectrum is featured with two distinguished exciton peaks just below the bandgap as seen in Figure 9-3-3 (a). The two peaks at 372 nm (3.33 eV) and at 364 nm (3.40 eV) are attributed to the free exciton absorption (A and B excitons). The bandgap is deduced to be about 3.39 eV by considering the exciton
binding energy of 0.06 eV. Figure 9-3-3 (b) shows the photoluminescence spectrum that was measured with 300 nm excitation. PL spectrum consists of two emission bands. One is centered at 380 nm (3.26 eV) with a HFWM of 0.14 eV. The peak position of this band is 0.07 eV (close to the LO phonon energy of 0.071 eV\textsuperscript{16}) below the free exciton absorption peak and is attributed the phonon-related excitonic emission. The other emission band (around 500 nm (2.48 eV)) is quite wide, and is structured with steps. This band is usually called the green-emission band. The energy separations among the steps are 0.13 eV and 0.12 eV, respectively. These two values are close to the 0.142 eV of 2LO-phonon energy. This indicates that some phonon-assisted processes also occurred in the defect-related emission transitions. The excitation spectrum was measured by monitoring the green-band emission at 510 nm (2.43 eV) and is given in Figure 9-3-3 (a). The excitation spectrum is quite similar to the absorption spectrum for the region below 370 nm. The excitations due to exciton absorption were also observed. Two separated excitonic features are clearly shown in the spectrum. Except the excitations due to charge-transformation, the direct excitation was also observed for the wavelength larger than 420 nm.

Figure 9-3-4 shows the integrated intensity (area) for the two emission bands as a function of oxygen partial pressures. As seen in Figure 9-3-4 (a), the integrated intensity of 380 nm emission band increase monotonically except for the sample deposited at oxygen partial pressure of 2×10\textsuperscript{-5} Torr. Oxygen vacancies are the dominant point defects in ZnO due to the oxygen deficiency. It is easy to understand that the intensity of 380 emission increases since the number of defect states decreases as a result of increasing oxygen partial pressure. The exception for the film deposited at oxygen partial pressure of 2×10\textsuperscript{-5} Torr may be due to
less number of structure defects, such as dislocations, and stacking faults. However, this monotonic increase was not followed for the green-emission band. The mechanism for the green-emission band is not clearly understood yet. Several different models were proposed in the literatures. Certainly, the models agreed with the corresponding observations for the different reports. The question is that we may not have the same defect type in the different films. In fact, we found that the green-emission bands were different for our five samples deposited at different oxygen partial pressures. These differences can be distinguished with the spectrum profiles, peak positions, etc. We also found that these differences occurred even for the films deposited at the same deposition parameters (substrate temperature, oxygen partial pressure, laser intensity, substrate, etc.). This means that the green-emission band is very sensitive to the growth conditions and that some unintended effects may play an important role. These may help us to understand the behavior of green-emission band under different oxygen partial pressures.

9.4 Conclusion

High quality, c-axis-oriented ZnO thin films had been grown on amorphous substrates by using pulsed laser deposition technique. Surface morphology was observed with SEM and optical microscope. The films are of high optical quality. Excitonic absorption was observed at room temperature with clearly distinguished A and B exciton peaks. The strong near-UV luminescence peaked at 380 nm were observed for all the films and was attributed to the phonon-related exciton emission. The effect of oxygen partial pressure on the luminescence
intensity was also investigated. The overall optical quality of ZnO thin films on amorphous substrates is comparable with that deposited on sapphire substrate.

Figure 9-3-4. The integrated-intensities of 380 nm emission band (a) and 500 nm emission band (b) as a function of oxygen partial pressures for the ZnO thin films grown on fused silica substrates.
References


In this chapter, we report the effect of the ultraviolet radiation on the photoluminescence characteristics of thin ZnO films. It has been observed that when ZnO films are continuously exposed to ultraviolet light, the intensity of excitonic peak as well as the green band, increasing with exposure time until they achieve a maximum value. We have proposed a phenomenological model to explain this behavior.

10.1 Introduction

ZnO is an II-VI semiconductor with a wide bandgap of 3.39 eV at room temperature. In recent years, the research interest for ZnO has been increasing due to its potential applications in UV-laser and planar displaying. One of the most attractive characteristics of ZnO is its large exciton binding energy of 60 meV, compared to 25 meV of GaN, which makes this material an ideal candidate for blue-UV semiconductor laser and light emitting diode (LED) even at room temperature. In addition, ZnO is also a low-voltage phosphor with high efficiency. This leads to a promising potential for the material to be used in vacuum fluorescent displays (VFDs) and field emission displays (FEDs). All these applications strongly depend on the luminescent properties and numerous efforts have been
made to understand the mechanism behind the photoemission process and to improve the light-emitting efficiency.

Although ZnO has been an attractive topic for more than 50 years, there are still some questions unanswered. First, for the future applications p-type ZnO with high conductivity is required for constructing p-n junction, but it is still a highly challenged topic. Second, the mechanism of green-band emission in the material is not clear yet. Luminescence spectra of ZnO material in all forms (bulk single crystal, powder and thin films) usually exhibit two bands at room temperature. One of them occurs at around 380 nm in the near UV-range and is attributed to the free-exciton emission. The other one occurs at around 510 nm, which is usually called the green-band emission. The mechanism of the green-band emission is still unclear although a large number of reports can be easily found in the literature. In the earlier reports, this green-band emission was associated to the copper impurities. However in the later studies, more researchers had attributed it to the intrinsic defects such as interstitial zinc or oxygen vacancies. Donor-acceptor pair (DAP) was also associated to this green-band emission. Although the researches have already lasted about half century, it seems that there is still a long way ahead to understand the mechanism behind this green-band emission. Third, slow excitation processes have already been reported in the photoconductivity measurements in ZnO, in which the dark conductivity increased after the sample was exposed for a long time. However this process is rarely related to the PL process even though there may be the same physical process behind.
In this work, we investigated the effect of UV-irradiation on photoluminescence (PL) intensities for both exciton and green-band emissions in ZnO thin films. We found that PL intensities increase as a function of the UV-exposure time. The clear understanding of this effect may help to obtain ZnO material with high luminescence efficiency that is highly desired for the applications mentioned above. The clear understanding of the effect may also give the clue for the mechanisms behind the photoemission processes.

10.2 Experimental Details

The ZnO thin film samples used in this work were grown on fused silica substrates (amorphous) by using pulsed laser deposition technique. Thin films were grown at O₂ partial pressure of 5×10⁻⁵ Torr at 630 °C for 12 minutes. Background pressure was 5×10⁻⁷ Torr. A KrF excimer laser operated at 248 nm with 10 Hz repetition rate was used to ablate a high purity ZnO target. Crystal structure of the film was determined by using x-ray diffraction technique. The absorption spectra of the films were recorded at room temperature with a Hitachi U-3010/UV/VIS spectrometer. The photoluminescence spectra (PL) were measured at room temperature with a Hitachi F-2500 Fluorescence spectrophotometer by using a 150 W Xenon lamp as the light source.
10.3 Results and Discussion

Figure 10-3-1 shows the X-ray diffraction pattern of a typical ZnO thin film grown by our method. This indicates that the thin films are highly crystalline with a wurtzite hexagonal structure. From the figure we can see that only the reflections from the $(000l)$ planes exist in the XRD pattern, which implies that the films are highly aligned (textured) with c-axis perpendicular to the substrate surface.

![X-ray diffraction pattern of ZnO film grown on silica substrate.](image)

Figure 10-3-1. X-ray diffraction pattern of ZnO film grown on silica substrate.

The room temperature absorption spectrum is shown in Figure 10-3-2. This spectrum is
similar to that measured for the epitaxial single-crystalline ZnO thin films grown on sapphire (0001) substrate.\textsuperscript{12} Two distinguished peaks can clearly be observed in this spectrum, one occurs at 372 nm (3.33 eV) and another occurs at 365 nm (3.40 eV). These two absorption peaks have been attributed to the free exciton absorption. Considering the exciton binding energy of 60 meV, the bandgap of our ZnO thin film is estimated to be 3.39 eV, which is close to the value in the other report.

![Absorption Spectrum](image)

**Figure 10-3-2.** Room temperature absorption spectrum of ZnO film.

The PL spectrum of the sample is shown in Figure 10-3-3. This spectrum consists of two emission bands, centered at 380 nm (3.26 eV) and 536 nm (2.31 eV), respectively. The emission peak of the higher energy band is 0.07 eV below the free exciton absorption peak.
This energy difference is quite close to the phonon energy, so we attribute this band to the exciton-related transitions although sometimes it has been called the near band-edge emission in the literature.\textsuperscript{11} The wide emission band at 536 nm is the so-called green-band emission. The origin for this emission band has not been clarified yet (see also chapter 2).\textsuperscript{2} Different models have been proposed and it seems that none of these models can account for all the characteristics\textsuperscript{3-10}. Even though the determination of the real mechanism responsible for green band emission is beyond the scope of this work, we find that most of the previous reports have attributed this emission band to the point defects present inside the body of the material.

![Figure 10-3-3. Room temperature photoluminescence spectrum of ZnO film.](image)

Figure 10-3-3. Room temperature photoluminescence spectrum of ZnO film.
In Figure 10-3-4, we show the excitation spectrum of our ZnO film, which was recorded by monitoring the green-band emission at 530 nm. This excitation spectrum shows a similar behavior that occurs in the absorption spectrum (Figure 10-3-2). The excitation peaks of 365 nm (3.40 eV) and 372 nm (3.33 eV) from the exciton-related transitions were also observed, indicating that the energy transformation from the excitons to the defect states exists in the sample. Band to band transitions provided another sources of the excitation as shown in the spectrum in the energy range higher than the band gap. Excitation from the direct transitions of the point defects also exists as shown in the spectrum in energy range below 2.88 eV (430 nm).

Figure 10-3-4. Excitation spectrum of ZnO film, recorded by monitoring the green band emission at 530 nm.
The most important observation of this study is the ultraviolet-radiation-enhanced photoluminescence in ZnO films. We find that when ZnO films are continuously exposed to ultraviolet radiation, the intensity of the excitonic emission peak as well as that of green-band emission increases with the illumination time. We call this effect UV-illumination-enhanced photoluminescence effect. To observe this effect, the ZnO films were continuously exposed to 300 nm ultraviolet radiation and the photoluminescence spectra were recorded at different times. In Figure 10-3-5 we have shown the photoluminescence spectra as a function of time. As seen in the figure, the intensity of both the excitonic emission band and green-band emission increases with the illumination time. In the inset of Figure 10-3-5, we have shown the plots of the integrated intensity vs. illumination time. The integration ranges are 350 to 420 nm for the exciton-related emission band and 420 to 750 nm for the green-band emission, respectively. It can be seen that the intensities of the two emission bands vary in a similar fashion as a function of illumination time.

In following, we discuss the physical processes that may be responsible for this behavior and would present a phenomenological model to explain this phenomenon.

No significant change was observed in the absorption spectrum before and after the sample was exposed to the uv-light beam. This indicates that the uv-enhanced effect is not from the increment of electron-hole generation rate. Therefore the increase in PL intensity implies that more electron-hole pairs recombine through the radiative recombination than that through the nonradiative recombination. The factors that can be taken into account may
include: (i) the transition probability for radiative or nonradiative recombination is changed, (ii) number of nonradiative centers is decreased or number of electron-hole pairs that recombine nonradiatively is decreased, (iii) number of photoluminescence centers that involved in the emission processes is increased. Transition probability is determined by the intrinsic nature of the material and hence is unlikely to be changed by the UV-radiation. So the second and third factors look more likely to be the cause of the phenomenon of UV-illumination-enhanced photoluminescence.

![Photoluminescence spectra as a function of exposure time. Insets show the plots of the integrated intensity vs. illumination time.](image)

Figure 10-3-5. Photoluminescence spectra as a function of exposure time. Insets show the plots of the integrated intensity vs. illumination time.

Photoinduced change of electronic properties of ZnO had been reported as early as nineteen fifties in the photoconductivity measurements. The development of research for this topic
gives rise to the idea that oxygen desorption on the surface is responsible for the observed slow increase of conductivity. Oxygen adsorption induces negative surface charges. The surface charges lead to a depletion region beneath the surface. The low density of electrons in the depletion region results in a low conductivity. It is widely accepted that photo-generated hole can be attracted to the negative O$^-$ ion or other traps on the surface.$^1$ These results in substable complex or desorption of oxygen. As a result, the negative surface charges are reduced, leading to a decreased depletion region. It is quite straightforward that same oxygen desorption may exist in our sample. We tentatively attribute the origin of the uv-enhanced PL effect to the desorption of oxygen.

The detailed model is discussed as follows:

As mentioned above, the increase in PL may come from the reduced number of electron and hole pairs that recombine through the nonradiative channels. Three types of nonradiative recombination are usually considered in semiconductor, Auger recombination, phonon emission, and surface recombination. The first two processes are related to the intrinsic features of the material and are difficult to be changed by the uv-irradiation. So we tend to believe that changes of emission processes associated to the surface sates are responsible to the uv-enhanced PL effect. The effect may occur by decreasing the number of nonradiative recombination centers near the surface or by decreasing the number of electron-hole pairs that can be captured by the surface centers. Depending on the rest time in each band, electrons inside the depletion region will be swept into the material but holes will move to
the surface. The holes then will be attracted on the surface traps, which are most likely the negative oxygen ions adsorbed on the surface. Some of the electrons can reach the surface either by tunneling or by diffusion. The trapping process of holes will decrease the depletion width dynamically. This will increase the possibilities for electrons moving to the surface. As long as both electrons and holes are near the surface they combine nonradiatively through the surface states. The trapping process of holes on the surface has to compete with other recombination processes. These processes may occur in a very short time since the lifetime for the free exciton emission is in the order of several hundreds of picosecond. The number of holes trapped in the surface states is proportional to the number of the surface traps and the depletion width. The more negative surface charges, the more holes will be attracted on the surface, so that more electron-hole pairs will recombine radiationlessly. The holes attracted on the negative O⁻ ions on the surface will lead to desorption of oxygen in a slow process also. The direct result of photo-desorption of oxygen is the decrease of depletion width and the decrease of oxygen traps so that the number of electron-hole pairs recombine nonradiatively through the surface states is decreased. It is very clear that both the free exciton and green emission can be increased by the decrease of the nonradiative recombination of electron and hole pairs. The above discussion can be considered as one of the mechanisms for uv-enhanced PL effect.

Another possible way for increasing in PL intensity due to the slow photo-desorption of oxygen may be considered as following:
First, since the electrons and holes move to opposite direction under the electrical filed inside the depletion region, the possibility that free electron and hole form the bound state (an exciton) is decreased. So the number of electron-hole pairs that recombine through free-exciton transition inside the depletion region is lower than that outside the depletion region. As a result, more free-exciton emission can be expected if the depletion width is decreased. Second, according to results reported by K. Vanheusden et al.\textsuperscript{13}, the band bending in the depletion region would lead to a redistribution of defect states that are responsible for the green-band emissions. For example, in the depletion region $V_o^-$ ions will be ionized to $V_o^{2-}$ ions so that the number of electron and hole pairs recombine through the green-band centers is decreased. Although the mechanism for green-band emission is not clear yet, less green-band emission can be always expected as long as the recombination depends on defect states that can be reduced by the band bending.

Figure 10-3-6 shows the PL spectra measured with different excitation wavelengths. It can be seen that the spectral profiles were changed and the PL intensities were decreased for both green-band emission and free exciton emission as the wavelength of excitation light is decreased. According to the report given by Muth et al.\textsuperscript{12}, ZnO have a relative large absorption coefficient of ~ 200000 cm\textsuperscript{-1} at 370 nm (3.35 eV), which leads to a small penetrating depth of about 50 nm. This means that the effective excitation region in the PL measurement is very small, which results in a very sensitive change of PL spectra if the excitation wavelength is decreased (penetrating depth is decreased too). The results shown in Figure 10-3-6 support the idea that the depletion region width has the strong influence on the
PL intensity since the depletion region could be comparable to the small penetration depth. Another evidence that indicates the surface depletion region may effect the PL spectrum of ZnO sample is given in Figure 10-3-7. Figure 10-3-7 (a) shows the PL spectra measured from the front side (film side) and the backside (substrate side) of ZnO film. We found that the PL intensity measured from the substrate side is about ten times the value of that measured from the film side. The spectrum profiles are also quite different as seen from the normalized plots shown in Figure 10-3-7 (b). These results indicate that the surface depletion region has a strong effect on PL intensity of ZnO sample.

![Figure 10-3-6](image)

Figure 10-3-6. PL spectra of ZnO film measured with different excitation wavelengths at room temperature.
Figure 10-3-7. (a) PL spectra of ZnO film measured from film and substrate sides, respectively. (b) Normalized plots of the spectra in (a).
Based on these discussions, we propose that the uv-enhanced PL effect comes from two possible effects due to the slow photo-desorption of oxygen: (1) the reduced number of electron-hole pairs through the surface states, and (2) the increased number of electron-hole pairs through the free exciton and green-band emissions.

The time evolution of the PL intensity can be easily deduced from the simple rate equations. Consider a simple exponential decay process for the photo-desorption of oxygen, we can write the density of oxygen ions on the surface as

\[ n_{ox} = N_s \exp\left(-\frac{T}{\tau}\right) \]

where \( T \) is the exposure time, \( N_s \) is a constant, and

\[ \frac{1}{\tau} = \frac{A_p I}{1} \]

with \( A_p \) being the cross section for photodesorption and \( I \) being the UV-irradiation intensity.

Figure 10-3-8 shows the schematic diagram for the possible transition processes. Let \( N, N_{GB}, N_{gb}, N_{NR}, \) and \( N_{nr} \) represent the number density of total electron-hole pairs, green-band centers, occupied green-band centers, nonradiative surface centers, and the occupied nonradiative surface centers, respectively. Then the rate of change of total number density of electron-hole (e-h) pairs can be written as:

\[ \frac{dN}{dt} = G_{net} - \gamma_{ex}N - \gamma_{gb}N_{GB}N_{gb} - \gamma_{nr}N_{NR}N_{nr} \]

The first terms, \( G_{net} \) on the right side of the equation represents the net excitation rate of the e-h pairs, which can be considered as the summation of photo-generation rate and
recombination rate for all the transition processes other than the free exciton, green band and the surface centers. The second, third, and forth terms represent the transformation rate of e-h pairs to excitons, green-band centers, and nonradiative centers, respectively. In the equation, \( \gamma \)'s are the corresponding constants for each process.

![Diagram of electron and hole recombination channels](image)

Figure 10-3-8. Schematic illustration of the possible channels for the recombination of photo-induced electron-hole pairs.

As discussed above, the rate that holes are captured by the surface traps is proportional to the depletion width and, in turn, is proportional to the density of surface oxygen ions, so we have \( \gamma_{nr} = \sigma n_{os} \) (where \( \sigma \) is a constant). On the other hand, the second mechanism for the uv-effect should be included in the rate equation too. For the sake of simplification, we assume that the area outside the depletion region dominates the free-exciton and green-band emissions.
So a weight factor can be added to eq. (3) by considering that both the emission processes are proportional to \((l_{\text{pen}} - l_{\text{dep}})\) with different constant factors. Here \(l_{\text{pen}}\) and \(l_{\text{dep}}\) are penetration depth and depletion width, respectively. Now we can rewrite eq. (3) as

\[
\frac{dN}{dt} = G_{\text{net}} - \alpha(l_{\text{pen}} - l_{\text{dep}})\gamma_{\text{ex}} N - \beta(l_{\text{pen}} - l_{\text{dep}})\gamma_{\text{gb}} N(G_{\text{GB}} - N_{\text{gb}}) - \gamma_{\text{nr}} N(N_{\text{NR}} - N_{\text{nr}})
\]  

(4)

where \(\alpha\) and \(\beta\) are constant factors for the two emission processes, respectively. The depletion width can be written as 

\[l_{\text{dep}} = \frac{n_{\text{os}}}{N_{\text{d}}}\]

and \(N_{\text{d}}\) is the donor density. We also have the following individual rate equations for excitons, green-band centers and nonradiative centers,

\[
\frac{dN_{\text{ex}}}{dt} = \gamma_{\text{ex}} N - \frac{N_{\text{ex}}}{T_{\text{ex}}}, \tag{5}
\]

\[
\frac{dN_{\text{gb}}}{dt} = \gamma_{\text{gb}} (N_{\text{GB}} - N_{\text{gb}}) - \frac{N_{\text{gb}}}{T_{\text{gb}}}, \tag{6}
\]

\[
\frac{dN_{\text{nr}}}{dt} = \gamma_{\text{nr}} (N_{\text{NR}} - N_{\text{nr}}) - \frac{N_{\text{nr}}}{T_{\text{nr}}}, \tag{7}
\]

where \(T_{\text{ex}}, T_{\text{gb}},\) and \(T_{\text{nr}}\) are the net spontaneous transition times for excitonic, green-band and nonradiative processes, respectively. Eq. (4) can be rewritten as

\[
\frac{dN}{dt} = G_{\text{net}} - \alpha(l_{\text{pen}} - n_{\text{os}}/N_{\text{d}})\gamma_{\text{ex}} N - \beta(l_{\text{pen}} - n_{\text{os}}/N_{\text{d}})\gamma_{\text{gb}} N(G_{\text{GB}} - N_{\text{gb}}) - \sigma n_{\text{os}} N(N_{\text{NR}} - N_{\text{nr}}) \tag{4a}
\]

Under the steady-state condition, we have \(dN/dt = dN_{\text{ex}}/dt = dN_{\text{gb}}/dt = dN_{\text{nr}}/dt = 0\). Further, considering only the condition of weak excitation, so that \(N_{\text{GB}} \gg N_{\text{gb}}\) and \(N_{\text{NR}} \gg N_{\text{nr}}\), we can get the expression for the density of electron-hole pairs as a function of exposure time \(T\) as
\[ N = \frac{G_{\text{net}}}{I_{\text{pen}}(a\alpha_{\text{ex}} + b\gamma_{\text{ex}}N_{\text{GB}}) + (a\sigma_dN_{NR} - \alpha_{\text{ex}} + b\gamma_{\text{GB}}N_{\text{GB}})\frac{N_{\text{s}}}{N_{\text{d}}} \exp(-T/\tau)} = \frac{A}{1 + B \exp(-T/\tau)} \]  \hspace{1cm} (8)

where

\[ A = \frac{G_{\text{net}}}{I_{\text{pen}}(a\alpha_{\text{ex}} + b\gamma_{\text{ex}}N_{\text{GB}})}, \]  \hspace{1cm} (9)

\[ B = \frac{(a\sigma_dN_{NR} - \alpha_{\text{ex}} + b\gamma_{\text{GB}}N_{\text{GB}})\frac{N_{\text{s}}}{N_{\text{d}}}}{I_{\text{pen}}(a\alpha_{\text{ex}} + b\gamma_{\text{ex}}N_{\text{GB}})}. \]  \hspace{1cm} (10)

Now the changes of luminescence intensity as illumination time \( T \) are straight,

\[ I_{\text{ex}} = \frac{N}{T_{\text{ex}}} = \gamma_{\text{ex}}N = \frac{\gamma_{\text{ex}}A}{1 + B \exp(-T/\tau)}, \]  \hspace{1cm} (11)

and

\[ I_{\text{gb}} = \frac{N}{T_{\text{gb}}} = \gamma_{\text{GB}}N_{\text{GB}} = \frac{\gamma_{\text{GB}}N_{\text{GB}}A}{1 + B \exp(-T/\tau)}. \]  \hspace{1cm} (12)

Equations (11) and (12) were used to fit the experimental data shown in Figure 7. Since the time-evolution functions for the two emissions differ only on the constants, we used the same parameters \( B \) and \( \tau \) for the exciton emission and the green-band emission during the simulation process. The results of the simulation are shown in Figure 10-3-9 with solid lines. The excellent fitting results confirm our explanation about the mechanisms of UV-illumination-enhanced photoluminescence effect.
Figure 10-3-9. (a) Experimental data of PL intensity of excitonic emission as a function of illumination time and least square fitting to Eq. (11); (b) Experimental data of PL intensity of green-band emission as a function of illumination time and least square fitting to Eq. (12).
10.4 Conclusion

We have observed an ultraviolet radiation enhanced photoluminescence effect in ZnO films. The effect was attributed to the photoinduced desorption of surface oxygen. The oxygen desorption will reduce the surface depletion depth since it will reduce the surface negative charges. This is supported by results of the PL measurements with changing the excitation wavelength and by the PL measurements taken from the different side of the film sample. The time-dependent PL intensity change with the exposure time was deduced based on the discussion of rate equations for the C-V band transitions. The resultant equations give the good fitting for the experimental data for both the exciton and green-band emissions. It should be pointed out that the discussion and the model are only phenomenological. For a complete understanding of the effect, more research efforts are required.

References


