ABSTRACT

WEI, WEI. Electrical and Optical Properties of Ga-Doped Mg$_{1-x}$Zn$_x$O System. (Under the direction of Prof. Jagdish Narayan).

The primary aim in this thesis is to investigate Ga-doped Mg$_{1-x}$Zn$_x$O, as well as undoped Mg$_{1-x}$Zn$_x$O for the application of transparent conducting oxide. For this thesis work, the films have been grown on sapphire using pulsed laser deposition technique. The films were grown under various deposition conditions in order to understand the effect of processing on the film properties. The grown films have been characterized using various techniques, including XRD, TEM, XPS, 4-probe resistivity measurements, Hall measurements and absorption/transmission spectroscopy.

Undoped Mg$_{1-x}$Zn$_x$O films have been grown at several temperatures between room temperature and 750 °C. Photoluminescence was correlated with Urbach energy values which were determined from absorption spectrum. The film grown at 350 °C exhibited lowest band-tail parameter values and highest photoluminescence values than the other films.

The optical and electrical properties of heavily Ga-doped Mg$_x$Zn$_{1-x}$O thin films were investigated. The film transparency is greater than 90% in the visible spectrum range. The absorption can be extended to lower wavelength range with higher magnesium concentration, which can improve the transparency in the ultraviolet wavelength range; however, conductivity is decreased. The optimum Ga concentration was found to be 0.5 at. %. At this Ga concentration, the film resistivity increased from 1.9×10$^{-3}$ to 3.62×10$^{-2}$ Ω.cm, as the magnesium concentration increased from 5 at. % to 15 at. %.

The optical and electrical properties of Ga-doped Mg$_x$Zn$_{1-x}$O thin films were investigated systematically. In these films, the Ga content was varied from 0.05 at.% to 7 at.% and the Mg
content was varied from 5 at.% to 15 at.%. X-ray diffraction showed that the solid solubility limit of Ga in Mg$_x$Zn$_{1-x}$O is less than 3 at.%. The absorption spectra were fitted to examine Ga doping effects on bandgap and band tail characteristics. Distinctive trends in fitted bandgap and band tail characteristics were determined in films with Ga content below 3 at.% and Ga content above 3 at.%. The effects of bandgap engineering on optical transparency were evaluated using transmission spectra. Carrier concentration and Hall mobility data were obtained as functions of Ga and Mg content. The electrical properties were significantly degraded when the Ga content exceeded 3 at.%. Correlations between conduction mechanisms and Ga doping of Mg$_x$Zn$_{1-x}$O thin films were described. In addition, the effect of bandgap engineering on the electrical properties of epitaxial single crystal Ga-doped Mg$_x$Zn$_{1-x}$O thin films was discussed.

Mott transition in Ga-doped Mg$_x$Zn$_{1-x}$O thin films was investigated. 0.1 at.%, 0.5 at.% and 1 at.% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O films were selected for resistivity measurements in the temperature range from 250 K to 40 mK. The 0.1 at.% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O thin film showed typical insulator-like behavior and the 1 at.% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O thin film showed typical metal-like behavior. The 0.5 at% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O film showed increasing resistivity with decreasing temperature; resistivity was saturated with a value of $1.15 \times 10^{-2}$ $\Omega \cdot$cm at 40 mK, which is characteristic of the metal-insulator transition region. Temperature dependent conductivity $\sigma(T)$ in the low temperature range revealed that the electron-electron scattering is the dominant dephasing mechanism.

Mg$_x$Zn$_{1-x}$O/TiN/Si(111) heterostructures were fabricated using pulsed laser deposition. X-ray diffraction and transmission electron microscopy studies showed that both TiN and Mg$_x$Zn$_{1-x}$O were grown epitaxially on Si(111). A thin spinel layer (~5 nm) was formed after
deposition at the Mg$_x$Zn$_{1-x}$O and TiN interface. Current-voltage measurements showed that the electrical contact between Mg$_x$Zn$_{1-x}$O and TiN is ohmic contact. These results suggest that the TiN provides a buffer layer to integrate Mg$_x$Zn$_{1-x}$O thin films with silicon substrate.
Electrical and Optical Properties of Ga-Doped Mg$_{1-x}$Zn$_x$O System

by
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DEDICATION

To my parents.
Wei Wei was born on Oct 28th, 1981 in Lujiang, a small town located in Anhui province, China. He completed his elementary school, middle school and high school in his hometown after twelve-year studies. At the year of 2000, he was admitted to the program of Special Class for Gifted Young in University of Science and Technology of China. His interest in sciences excited him to choose Physics as his major. He completed his Bachelor of Science degree in 2004. In the fall of 2004, he entered the Ph.D program in Physic Department at North Carolina State University and passed Ph.D qualifying exam in January 2005. He worked with Dr. David Aspnes in the summer of 2005. This experience led him to the research field of advanced electronic materials. In the fall of 2005, he joined the NSF Center for Advanced Materials and Smart Structures in Department of Materials Science and Engineering at NCSU. He has been working towards his Ph.D degree under the supervision of Prof. Jagdish Narayan.
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Chapter 1 Introduction

Transparent conducting oxides (TCOs) are a class of materials that are both electrically conductive and optically transparent. With these unusual properties, they are widely used for numerous applications, both high tech and low tech. These applications generally fall into two categories \[1\]. The first type of applications is known as transparent electronics, in which TCOs are used as optical and electrical coating materials. The most commercially important applications of TCOs include photovoltaic (PV) cells, flat panel displays (FPD), thin film transistors (TFT). Other than these important applications in modern electronic industry, TCOs are also used for many low tech applications, such as antistatic coatings, window defrosters and infra-red reflection coatings \[1\]. In this type of applications, TCOs are usually n-type materials. The second type of applications is termed as transparent oxide semiconductors (TOSs), which emerges after the discovery of CuAlO\(_2\), the first “real” p-type TCO, in 1997 \[2\]. This discovery leads to intensive researches on developing various p-type TCOs and electronic and opto-electronic devices such as light emitting diodes (LEDs) and photo-detectors \[3\].

Surprisingly, in comparison to the numerous applications, only a few TCO materials have ever been practically used. Historically, tin oxide doped with impurities such as fluorine and antimony were the first commercially developed TCOs. Currently, tin doped indium oxide, also known as indium tin oxide or ITO, is the most widely used material for TCO
applications. A detailed review of TCO can be found in Chapter 2.  

The diversity of applications leads to a complex issue of developing TCOs with balanced material and electro-optical properties for different applications. For a specific application, the most suitable TCO is the one that best meets particular criteria of properties such as optical, electrical, chemical and mechanical properties. The difference among these criteria has led to varied choices of TCOs for different applications. For example, in order to improve lighting efficiency of PV cell, the selection of TCO is determined by not only basic electrical and optical performance of the TCO material, but also other considerations, such as work function, band alignment, materials compatibility and material cost [4].

The issue of economy is always important in industrial products. Due to the growing market of electronic and opto-electronic applications mentioned above, the demand of ITO has been steadily increasing in recently years [5]. The market of FPDs is expected to grow to 150 billion US$ by 2012. Figure 1.1 shows the market forecast of LCD TV, which takes a significant share of the FPD market [6]. Similarly, the annual consumption of TCO coated windows, which is primarily used for infra-red reflection coating or known as low-emission coatings, is 100 million square meters in United States. It is predicted that the market of ITO-coated substrates should reach $ 8 billion by 2015 and the total market for TCOs used in displays, photovoltaics and lighting will reach $ 9.4 billion by 2015 [5].
On the other hand, indium supply is very limited to meet these commercial demands, which causes soaring of indium market price. There are several reasons for the failure to meet increasing demand of indium. The primary reason is that indium is a very rare chemical element \([7]\). The concentration of indium in earth’s crust is extremely low (0.1 ppb) and there is no direct mining of indium. It is usually produced as a by-product in the mining of other metals, such as zinc, tin and lead. In fact, improvement of indium mining itself is an intensive research topic \([8]\). The second reason is that roughly 30% of produced indium is consumed by other industrial applications. For example, indium based compound semiconductors like indium phosphor and indium antimony are widely explored for their applications as transistors and sensors. Indium is also a critical component in CIGS (CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\)) based
PV cell, which is one of the major commercial thin film PV cells in the solar industry. In addition to the economic issue connected with indium, there are other technological challenges that ITO has to overcome. For example, ITO has rather poor chemical stability in the hydrogen atmosphere, which limit its application in Si based PV solar cells since hydrogen passivation is a key processing step in the cell fabrication \cite{9}.

Therefore, development of new and cost-effective TCO materials to divergent applications requirement is an urgent need. This has driven researchers all over the world to explore alternative TCO materials. Table 1.1 summaries some of the most important TCO materials that have been investigated.

Table 1.1 Important TCO materials reported in the literature.

<table>
<thead>
<tr>
<th>n-type</th>
<th>p-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>CuAlO\textsubscript{2}</td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>CuGaO\textsubscript{2}</td>
</tr>
<tr>
<td>ZnO:Ga</td>
<td>ZnO:P</td>
</tr>
<tr>
<td>SnO\textsubscript{2}:F</td>
<td></td>
</tr>
<tr>
<td>In\textsubscript{2}O\textsubscript{3}:Sn</td>
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</table>

The main practical challenges in the development of TCOs lie in:

1. the search for a low resistivity while maintaining reasonable optical transparency
2. the extension of transparency window to a broader wavelength range \[^{10}\]

3. the development of high quality p-type TCO for p-n TCO junctions \[^{11}\].

These objectives require a better understanding of the correlation of material structure – process – physical properties, and the role of chemical bonding, chemical structure and thin film morphology in the charge transport \[^{12}\].

In this thesis, the focus is developing bandgap engineered gallium-doped magnesium zinc oxide thin films and evaluate the electrical and optical properties for their potential application as a transparent conducting oxide.

The following aspects are addresses in this work:

1. The process - properties - structure correlation to optimize the performance for TCO applications.

2. The effect of engineered bandgap on the electrical and optical properties.

3. The fundamental electrical transport properties.

The thesis is organized into 8 chapters. In chapter 2, recent progress on development of new TCOs is reviewed. In addition, the fundament properties of zinc oxide, magnesium oxide and magnesium zinc oxide are presented. Chapter 3 will describe the experimental techniques that were used to accomplish the goals set for the thesis. Chapter 4, 5, 6, 7 and 8 describe the experimental details and discusses the results. In chapter 9, the overall conclusions are summarized.
References

6 DisplaySearch, Quarterly Advanced Global TV Shipment and Forecast Report, 2009
7 http://en.wikipedia.org/wiki/Indium
Chapter 2 Literature review

2.1 Transparent conducting oxides

Transparent conducting oxides (TCOs) are one class of materials which uniquely possess combined physical properties of high conductivity and high transparency. According to Exarhos[^1], “The properties of TCO materials derive from the nature, number, and atomic arrangements of metal cations in crystalline or amorphous oxide structures, from the resident morphology, and from the presence of intrinsic or intentionally introduced defects”. The TCO materials have been widely used in a variety of applications, as has been mentioned in Chapter 1. The research of TCO materials have been a very active field since the first application of TCO as transparent de-icing heaters in aircraft windshields dating back to World War II[^2]. The research progresses of TCO materials have been repeatedly reviewed nearly every decade. Holland[^3] reviewed the early work of TCO films in 1958. Vossen[^4] and Haacke[^5] reported comprehensive reviews to the mid-1970s. Manifacier[^6], Jarzebski[^7], and Chopra et. al.[^8] covered the work in this area up to the early 1980s. Hartnagel et. al.[^9] presented a comprehensive review on the growth techniques, properties and applications of TCOs. Some critical issues related to new TCO materials, such as criteria for applications and theoretical models, were addressed in MRS Bulletin[^10] in 2000. More recently, Exharhos et. al.[^1] summarized up-to-date TCO research with an emphasis on the microscopic description of electronic conduction properties and guidelines for designing new
TCO materials. In this section, the research of TCO materials is briefly reviewed in the aim to provide a general background of this research field.

2.1.1 Materials

Cadmium oxide (CdO) was the first reported TCO material by Badeker in 1907.\[^{[11]}\] The CdO film was prepared by oxidation of thermally vaporized cadmium. The electrical conductivity of deposited CdO was due to the non-stoichiometry in the film. Later works on both thin films and bulk samples revealed that CdO is an n-type semiconductor in which interstitial cadmium donates free electrons. Due to the high toxicity of cadmium, CdO has not received much attention for practical applications.

Since then, various materials have been developed as TCOs. Among these investigated materials, three oxides have emerged as commercially important TCOs: indium oxide (In\(_2\)O\(_3\)), tin oxide (SnO\(_2\)), and zinc oxide (ZnO). These oxides are the highest-performance and best-understood materials in the TCO class. The basic electrical properties of the three oxides are summarized in Table 2.1.

Table 2.1 Electrical properties of In\(_2\)O\(_3\), SnO\(_2\) and ZnO.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Bandgap (eV)</th>
<th>Conductivity (S cm(^{-1}))</th>
<th>Electron concentration (cm(^{-3}))</th>
<th>Mobility (cm(^2) V(^{-1})s(^{-1}))</th>
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<tbody>
<tr>
<td>SnO(_2)</td>
<td>3.65</td>
<td>5,000</td>
<td>&gt;10(^{20})</td>
<td>15</td>
</tr>
<tr>
<td>In(_2)O(_3)</td>
<td>3.75</td>
<td>10,000</td>
<td>&gt;10(^{21})</td>
<td>35</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.35</td>
<td>8,000</td>
<td>&gt;10(^{21})</td>
<td>40</td>
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</tbody>
</table>
These materials have bandgap larger than 3 eV so that it is transparent in the full visible spectrum. The electron concentration and mobility are dependent on the preparation methods and process conditions. In general, the electron concentration is sufficiently high, usually in the order of $10^{20}$ cm$^{-3}$ or higher in order to gain higher conductivity. The mobility is in the order of 10 cm$^2$ V$^{-1}$s$^{-1}$, usually between 20 to 40 cm$^2$ V$^{-1}$s$^{-1}$. A low mobility at high carrier concentrations is, to a large extent, a consequence of intense ionized impurity scattering associated with high doping concentrations [9]. The theoretical absolute limit of mobility for a TCO has been estimated to be 90 cm$^2$ V$^{-1}$s$^{-1}$ and the limit of conductivity, taking into account the requirement of transparency, has been estimated to be 25,000 S cm$^{-1}$ [12]. Ellmer showed that in ZnO films deposited by various methods, the resistivity and mobility were nearly independent of the deposition method and limited to about $2 \times 10^{-4}$ Ωcm and 50 cm$^2$ V$^{-1}$s$^{-1}$, respectively [13]. Similarly, the conductivity and mobility limits are also held in ITO films [13]. Various dopants have been used in these three oxides to enhance the conductivity. These doping elements are listed in Table 2.2 [14].

### Table 2.2 List of investigated doping elements in SnO$_2$, In$_2$O$_3$ and ZnO.

<table>
<thead>
<tr>
<th>TCO material</th>
<th>Doping elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$</td>
<td>Sb, F, As, Nb, Ta</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>Sn, Mo, Ta, W, Zr, F, Ge, Nb, Hf, Mg</td>
</tr>
<tr>
<td>ZnO</td>
<td>Al, Ga, B, In, Y, Sc, F, V, Si, Ge, Ti, Zr, Hf, As, H</td>
</tr>
</tbody>
</table>
Multi-component oxides also have been reported as potential TCO materials. The development of multi-component oxides has largely driven by the possibilities of designing and discovering new TCO materials through combination as well as phase segregation of binary and ternary TCO materials. Minami et. al. have reported several TCO materials based on ZnO-SnO$_2$, ZnO-In$_2$O$_3$ and In$_2$O$_3$-SnO$_2$ systems [$^{15,16,17,18,19,20,21}$]. The combination of multi-oxides represents the opportunity to combine the advantages of individual oxide material. For example, ZnO-In$_2$O$_3$ based TCOs have the combined advantages of both ZnO and In$_2$O$_3$. Fig. 2.1 shows variation in the etching rate and bandgap with the compositional change of the ZnO-In$_2$O$_3$ films [$^{22}$]. It was also observed that other electrical properties, such as the carrier concentration and the resistivity could be changed systematically by altering the content of ZnO in the composite. Similarly, the compositional dependence of electrical, optical and chemical properties has been observed in ZnO-SnO$_2$ and In$_2$O$_3$-SnO$_2$ systems.
Various new ternary compounds have been found in these multi-component oxides systems, such as Zn$_2$In$_2$O$_5$, In$_4$Sn$_3$O$_{12}$, ZnSnO$_3$, Zn$_2$SnO$_4$, MgIn$_2$O$_4$, GaInO$_3$, (GaIn)$_2$O$_3$ [23]. It should be noted that these compounds, as well as composites, have been prepared by sputtering techniques. Table 2.3 lists the reported resistivities of these compounds [23].
<table>
<thead>
<tr>
<th>Materials</th>
<th>Resistivity (Ω·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$_2$SnO$_4$</td>
<td>1.7 x 10$^{-2}$</td>
</tr>
<tr>
<td>ZnSnO$_3$</td>
<td>4 x 10$^{-3}$</td>
</tr>
<tr>
<td>MgIn$_2$O$_4$</td>
<td>4.3 x 10$^{-3}$</td>
</tr>
<tr>
<td>GaInO$_3$</td>
<td>2.7 x 10$^{-3}$</td>
</tr>
<tr>
<td>(GaIn)$_2$O$_3$</td>
<td>5.8 x 10$^{-4}$</td>
</tr>
<tr>
<td>Zn$_2$In$_2$O$_5$</td>
<td>3.9 x 10$^{-4}$</td>
</tr>
<tr>
<td>In$_4$Sn$<em>3$O$</em>{12}$</td>
<td>2.0 x 10$^{-4}$</td>
</tr>
<tr>
<td>Zn$_2$In$_4$Sn$<em>3$O$</em>{14}$</td>
<td>4.0 x 10$^{-4}$</td>
</tr>
<tr>
<td>In$<em>3$Ga$</em>{1.5}$Sn$_{1.5}$O$_x$</td>
<td>3.0 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

The values of resistivity of ternary compound oxides, such as Zn$_2$In$_2$O$_5$ and In$_4$Sn$_3$O$_{12}$ are approximately 2~4 x 10$^{-4}$ Ω·cm, which is comparable to that of ITO.

Similarly, complex oxide composites, based on mixtures of binary – ternary compounds and ternary – ternary compounds are developed for TCOs. Table 2.4 lists the binary – ternary composites and ternary – ternary composites that have been investigated.
Table 2.4 The binary-ternary composites and ternary-ternary composites for TCO applications

<table>
<thead>
<tr>
<th>binary – ternary composite</th>
<th>ternary – ternary composites</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$O$_3$-MgIn$_2$O$_4$</td>
<td>Zn$_2$In$_2$O$_5$-MgIn$_2$O$_4$</td>
</tr>
<tr>
<td>In$_2$O$_3$-GaInO$_3$</td>
<td>Zn$_2$In$_2$O$_5$-In$_4$Sn$<em>3$O$</em>{12}$</td>
</tr>
<tr>
<td>Ga$_2$O$_3$-GaInO$_3$</td>
<td>GaInO$_3$-Zn$_2$In$_2$O$_5$</td>
</tr>
<tr>
<td>MgO-MgIn$_2$O$_4$</td>
<td>GaInO$_3$-In$_4$Sn$<em>3$O$</em>{12}$</td>
</tr>
<tr>
<td></td>
<td>ZnSnO$_3$-Zn$_2$In$_2$O$_5$</td>
</tr>
<tr>
<td></td>
<td>ZnSnO$_3$-In$_4$Sn$<em>3$O$</em>{12}$</td>
</tr>
</tbody>
</table>

Similar to these ternary compounds, it is found that TCO of complex oxides in the full compositional ranges can be obtained if the compounds involved are conducting. As a result, the physical properties and the chemical properties are monotonically changed with composition. Figure 2.2 shows the variation of carrier concentration, bandgap and work function in the Zn$_2$In$_2$O$_5$-In$_4$Sn$_3$O$_{12}$ system $^{22,23}$. If the TCO is composed of a conducting compound and an insulating ternary compound, the resistivity increases with increase in content of the insulating compound. Thus, the chemical, electrical, optical and physical properties in these multi-component oxides vary monotonically with composition of the different binary and/or ternary compounds.
Figure 2.2 The compositional dependence of bandgap, carrier concentration and work function in Zn$_2$In$_2$O$_5$-In$_4$Sn$_3$O$_{12}$ [22, 23].

Based on these results, the multi-component oxides show compositional dependences of resistivity and optical properties. The chemical properties of the multi-component oxides are primarily dependent on the type of the metal element present in the film. These observations provide guidelines for the design of a composition of TCO for a specific application. The results also indicate the wide variety of possibilities of developing new TCO systems through exploration of combination of multi-component oxides. These multi-component oxides are very interesting systems and show potential for commercial applications in the future.

Development of p-type TCO is an even greater challenge than the above mentioned n-type
TCOs. A number of materials have been investigated for p-type transparent electronics applications \(^{[24]}\). So far, the only commercially available p-type material is GaN:Mg\(^{[25]}\). Development of p-type TCO is motivated, to a large extent, by the CuAlO\(_2\) reported in 1997 by Kawazoe et. al. \(^{[26]}\). p-type TCO reported in recent years are listed in Table 2.5 \(^{[24]}\). A majority of p-type TCOs included are oxides, although several types of non-oxide based p-type materials are also listed.

Table 2.5 P-type TCOs in the literature \(^{[24]}\)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Conductivity (S cm(^{-1}))</th>
<th>Mobility (cm(^2) V(^{-1}) s(^{-1}))</th>
<th>Transparency</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO: Sb</td>
<td>5</td>
<td>20.0</td>
<td>fair</td>
</tr>
<tr>
<td>NiO</td>
<td>7</td>
<td>2</td>
<td>fair</td>
</tr>
<tr>
<td>CuAlO(_2)</td>
<td>1</td>
<td>10.4</td>
<td>excellent</td>
</tr>
<tr>
<td>SrCuO(_2):K</td>
<td>0.048</td>
<td>0.46</td>
<td>excellent</td>
</tr>
<tr>
<td>In(_2):O(_3)-Ag:O</td>
<td>100</td>
<td>17</td>
<td>Poor</td>
</tr>
<tr>
<td>LaCuOS:Sr</td>
<td>0.026</td>
<td>Excellent</td>
<td></td>
</tr>
<tr>
<td>CuInO(_2):Ca</td>
<td>0.0028</td>
<td>Excellent</td>
<td></td>
</tr>
<tr>
<td>CuScO(_2):O</td>
<td>30</td>
<td>&lt;0.5</td>
<td>Poor</td>
</tr>
<tr>
<td>CuScO(_2):Mg</td>
<td>0.01</td>
<td>Excellent</td>
<td></td>
</tr>
<tr>
<td>CuGaO(_2)</td>
<td>0.063</td>
<td>0.23</td>
<td>Excellent</td>
</tr>
<tr>
<td>CuYO(_2):Ca</td>
<td>0.3 (~1)</td>
<td>&lt;0.5</td>
<td>Fair</td>
</tr>
<tr>
<td>CuCrO(_2):Mg</td>
<td>220</td>
<td>&lt;0.5</td>
<td>Poor</td>
</tr>
<tr>
<td>AgMO(_2) (M =Sc, In, Cr, Ga)</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgCoO(_2)</td>
<td>0.2</td>
<td>Fair</td>
<td></td>
</tr>
<tr>
<td>CuGaO(_2):Fe</td>
<td>~1</td>
<td>Fair</td>
<td></td>
</tr>
<tr>
<td>BaCuS(_2)</td>
<td>17</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>CuNi(_0.6):Sb(_0.3):O(_2):Sn</td>
<td>0.05</td>
<td>Fair</td>
<td></td>
</tr>
<tr>
<td>LaCuOSe</td>
<td>24</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>LaCuOSe: Mg</td>
<td>140</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>ZnRh(_2)O(_4)</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Obtaining high conductivity and transparency from a p-type material is very challenging. To a large extent, the poor conductivity of p-type TCOs is due to the very low mobility of these materials, typically less than ~1 cm² V⁻¹ s⁻¹, which necessitates having a high hole concentration in order to obtain a high conductivity. However, there is often a trade-off between conductivity and transparency. For example, unintentionally doped CuScO₂ films are highly insulating and transparent, whereas oxygen intercalation greatly increases their conductivity and concomitantly degrades their transparency [27,28].

2.1.2 Fundamental electrical properties

The most fundamental properties of any TCOs are the electrical properties and optical properties. In this section, the fundamental electrical properties of TCOs are discussed. The optical properties will be discussed in next section.

The conductivity is one of the key issues in the studies of electrical properties of TCOs. The conductivity (σ) of a material is mainly determined by the carrier concentration (n) and mobility (μ). The formula of σ is defined as following:

\[ \sigma = n \cdot e \cdot \mu \]  

(2.1)

where e is the electron charge.

Since e is a constant, to achieve high conductivity of the films, the carrier concentration (n) and mobility (μ) should be simultaneously maximized. The conductivity (σ) is intrinsically limited for two reasons. First, n and μ cannot be independently increased for practical TCOs
with relatively high carrier concentrations. At high electron concentration, carrier transport is limited primarily by ionized impurity scattering, i.e., the Coulomb interaction between electron and the ionized dopant. Higher doping concentration reduces carrier mobility to a degree that the conductivity may start decreasing, and it decreases the optical transmission at the near-infrared edge. With increasing dopant concentration, the resistivity reaches a lower limit, and does not decrease beyond it, whereas the optical window becomes narrower. Bellingham et. al.\textsuperscript{12} were the first to propose that the mobility and conductivity of TCOs (ITO, SnO\textsubscript{2}, ZnO) are intrinsically limited by ionized impurity scattering for carrier concentration above 10\textsuperscript{20} cm\textsuperscript{-3}. Ellmer also showed that the conductivity and mobility of ZnO films were limited to about 2×10\textsuperscript{-4} cm\textsuperscript{-3} and 50 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}, regardless of deposition methods \textsuperscript{13}. In ITO films, the maximum carrier concentration was about 1.5×10\textsuperscript{21} cm\textsuperscript{-3}, and the same conductivity and mobility limits also held \textsuperscript{13}. In current discussion of electrical properties of TCO, the ITO is used as an example since ITO is well understood for its TCO application.

For indium oxide, as well as most other TCOs, the maximum carrier concentration can be achieved by intrinsic (oxygen vacancies) and extrinsic (impurity ions) doping. Moreover, the activation of the dopants and the carrier concentration are strongly dependent on the processing conditions, especially for intrinsic doping, like oxygen vacancies. If an oxygen vacancy is created in a perfect crystal, two electrons are created in the crystal and contribute to the electrical conduction as ionized donors. However, the creation of too many oxygen

\textsuperscript{12} Bellingham et al.

\textsuperscript{13} Ellmer
vacancies may degrade the electrical properties by several ways: the crystallinity of the films may be degraded which reduces the electron mobility; undesirable secondary phases may be formed which reduces both the electron concentration and mobility. To achieve controllable electrical properties, the relationship of processing - properties - structure in these films is required to be understood in depth. In terms of intrinsic doping, oxygen partial pressure and substrate temperature are the two most important process parameters [29,30]. Figure 2.3 shows the dependence of electron concentration on oxygen partial pressure.

Figure 2.3 The electron concentrations of ITO (black dot) and indium oxide (open circle) as a function of oxygen partial pressures [29].
As a result, the carrier concentration is varied as a function of oxygen stoichiometry of indium oxide films (In$_2$O$_x$), as is shown in Figure 2.4 $^{[29,30]}$.

![Figure 2.4 The dependence of carrier concentration on oxygen stoichiometry $^{[30]}$.](image)

Substrate deposition temperature is another important parameter to control the conductivity of films. The conductivity of the ITO films also increases as the substrate deposition temperature in the temperature range from room temperature to 300 °C $^{[31,32]}$. The increase in conductivity with an increase in the substrate deposition temperature can be explained by the increase of grain size with increasing growth temperature, which reduces the grain boundary scattering, and thus increasing the mobility. It should be noted that that the optical transmittance (T) in the visible range (400 - 700 nm) increases slightly with increasing the substrate temperature from room temperature to 300 °C. The magnitude of the change in electrical properties of ITO films with varying substrate deposition temperature may also depend on the other deposition conditions, such as target composition, plasma plume and
target-to-substrate distance.

In terms of extrinsic doping, the efficiency of doping is the most important issue. In the case of ITO, ideally Sn is substitutionally incorporated in In$_2$O$_3$ to create an extra electron in the lattice, so that effective substitutional doping can be achieved. However, it has also been reported that Sn is not an effective donor in the amorphous ITO films because of the dominant role of oxygen partial pressure [29]. Similar results were obtained by several other researchers, which suggest strong interaction between the Sn and oxygen related defects [33, 34]. The creation of excess oxygen vacancies in a SnO$_2$ film may form suboxide such as SnO.

In reality, with both intrinsic and extrinsic doping, the films with high conductivity are usually degenerate. Increase of the conductivity of the TCO by increasing free carrier concentration in the films through the use of dopants and oxygen vacancies is the major strategy in developing TCO materials. Figure 2.5 shows a plot of resistivity as a function of electron concentration for indium oxide and ITO films [29]. The experimental results are compared with the values calculated using Dingle and Moore models. The degeneracy in these films has been confirmed by the temperature independence of the carrier concentration at low temperatures (down to 4.2 K). The observation of degeneracy is one of the most important realities for TCO films with high carrier concentrations and is a critical factor when attempting to derive stable performance for most applications.
Figure 2.5 Resistivity as a function of electron concentration for In$_2$O$_3$ and ITO films [29].

However, increasing the carrier density via intrinsic and extrinsic doping is self-limiting. At very high carrier concentration, the conductivity tends to decrease due to a decrease in mobility. This is attributed to enhanced scattering of ionized impurities, which are intentionally doped to increase carrier concentration. Hence, there is a trade-off between the carrier density and the carrier mobility for achieving low resistivity. In general, for a completely degenerate material, the relationship between the carrier density and carrier mobility can be expressed by $\mu \propto n^{2/3}$ [35].

The conductivity and mobility in degenerate semiconductors have been modeled for the experimental results obtained in ITO [36,37,38,39]. For degenerate semiconductors, the resistivity (inverse of conductivity) can be written as:
\[
\rho = \frac{N_iZ^2e^2m^*}{24\pi^3(e_0\varepsilon_r)^2h^3n^2} f(k_F) \quad \text{.......................... (2.2)}
\]

where \(N_i\) is the number density of impurity centers with charge Ze, \(\varepsilon_r\) is the low-frequency relative permittivity and \(m^*\) is the conduction band effective mass.

The function \(f(k_F)\) is given by:

\[
f(k_F) = \ln(1 + \beta^2) - \frac{\beta^2}{1 + \beta^2} \quad \text{.......................... (2.3)}
\]

where \(\beta = 2k_F/K_T\) and \(K_T\) is the Thomas-Fermi screening wave vector.

The mobility is calculated using the equation:

\[
\mu_{\text{ionized}} = \frac{2^{7/2}(4\pi\varepsilon_0)^2(kT)^{3/2}}{\pi^{1/2}Z^2e^3N_i[\ln(1 + Y_{BH}^2) - \frac{Y_{BH}^2}{1 + Y_{BH}^2}]} \quad \text{........ (2.4)}
\]

where

\[
Y_{BH} = \frac{2m^*}{h} \left(\frac{2}{m^*}3k_BT\right)^{1/2}L_D \quad \text{................................. (2.5)}
\]

and \(L_D\) is the Debye length, \(L_D = \left[\frac{4\pi\varepsilon_0\varepsilon_kT}{e^2n}\right]^{1/2}\).

Figure 2.6 shows the dependence of mobility on carrier concentration due to the ionized impurity scattering. The mobility predicted by the theory, after the correction for the carrier concentration due to ionized impurity centers, shows a good agreement with the experimental data [36].
Figure 2.6 Comparison of the experimental results with calculated mobility values (upper limit). The theoretical mobility values are modified with the effective mass correction and the carrier concentration due to ionized impurity center correction \(^{36}\).

The theoretical mobility determined by Equation (2.2) considers only the electrons donated from the fully ionized \(\text{Sn}^{4+}\). Each \(\text{Sn}\) ion can donate only one electron. However, since oxygen vacancies contribute electrons and an oxygen vacancy can donate two electrons, Equation (2.2) should be corrected accordingly. To accommodate the effect of additional carrier sources, the relationship between the ionized impurity centers and the carrier concentration is given by:
\( N_i = x n \) ....................................... (2.6)

where \( f(n) \) is the carrier concentration ionized impurity center correction function.

The \( x \) value was found to be more than one, indicating that the number of ionized impurity centers is higher than the actual carrier concentration and the ionization efficiencies of these centers are less than 1.0. The electrically inactive dopants only act as scattering centers, which further decreases the mobility. Another important correction in the calculation of mobility is the change of effective mass with the electron concentration. In Figure 2.5, the best fit between the calculation and the experimental result is obtained for the plot corrected for both the effective mass and carrier scattering effects.

An empirical equation between the effective mass and the carrier concentration was proposed by Chen et. al.\(^{[36]}\):

\[
k = \frac{m^*}{m} = 0.3 + 0.06192 \times f^{2/5} \quad \text{..........................} \quad (2.7)
\]

where \( f = \frac{n}{10^{35}} \).

Figure 2.7 shows Equation 2.7 is in good agreement with the fitted effective mass. The increase in effective mass is attributed to the change in Fermi energy and in the shape of the conduction band as the impurity bands overlap \(^{[36]}\).
Figure 2.7 Comparison of effective mass $m^*$ calculated using equation 2.7 with the experimental results [36].

It should be noted that other scattering mechanisms may also play a role in the theoretical corrections of mobility. A theoretical plot of combined acoustical deformation scattering and the ionized impurity scattering mechanism is also shown in Figure 2.6 (dashed line). Although, the plot shows good agreement with the experimental results (solid line), it has been attributed to the carrier impurity correction. Moreover, the plot deviates at lower carrier concentration range (less than $1 \times 10^{20}$ cm$^3$), which indicates that the phonon scattering has
less effect on the carriers scattering in degenerate TCOs. In addition, the temperature dependent studies of the electrical properties of these ITO films did not show any notable temperature dependence in the range 100 – 500 °C, which also suggests that the phonon scattering is not a dominant scattering mechanism in degenerate TCO films, although it has been suggested that the scattering due to the phonon scattering can play a role in the mobility of TCOs \[^{40}\].

In the degenerate region mentioned above, the mobility is mainly limited by ionized impurity scattering, which leads to a decrease of mobility with increasing carrier concentration. On the other hand, in the region where the carrier concentration is lower compared with typical degenerate semiconductors, the mobility usually increases with increasing carrier concentration. In this case, the grain boundary scattering is the dominant scattering mechanism. Grain boundaries can introduce defects which trap electrons and lead to formation of a potential barrier \[^{41,42}\]. The grain boundary barrier height may be of the order of 0.1 eV for films with low carrier concentrations \[^{41}\]. Petritz has modeled the effect of grain boundaries on the transport characteristics in the polycrystalline films \[^{43}\]. According to this model, the change in mobility is given by the following equation:

\[
\mu_s = \mu_0 \exp\left(-\frac{\phi_b}{kT}\right) \quad \cdots \cdots \cdots \cdots \cdots (2.8)
\]

where

\[\mu_0 = \left(\frac{L^2 e^2}{2\pi m^* kT}\right)^{1/2}\]

and L is the grain size and \(\Phi_b\) is the grain boundary potential.
Plots of calculated mobility using different $\Phi_b$ and grain size are shown in Figure 2.8.

It can be seen that the mobility decreases with decrease in grain size and increase in the grain boundary potential [36]. The calculated value of mobility is greater than 200 cm$^2$ V$^{-1}$s$^{-1}$, given the grain boundary potential is $\sim 0.01$ eV and the average grain size is $\geq 100$ nm [23,36,44]. However, this value of mobility is significantly larger than the values practically observed in the ITO films. In the literature, most of the reproducible data shows that the mobility is less than 100 cm$^2$ V$^{-1}$s$^{-1}$. This large deviation observed in the calculated mobility and the experimental data suggests that grain boundary scattering may not be a dominant scattering mechanism for ITO. The effect of grain boundaries scattering on the carrier mobility may be more important in other materials which have a high grain boundary potential, for example, ZnO [13].

![Figure 2.8 Theoretical calculation of mobility at different (a) grain boundary potentials and (b) grain sizes [36]](image-url)
In ITO films, the effect of grain boundaries on the scattering of carriers can be further understood by considering the mean free path of electrons. The mean free path $l$ is defined as below:

$$l = \left(\frac{\hbar}{2e}\right)\left(\frac{3n}{\pi}\right)^{1/3} \mu$$  

The calculated $l$ is less than 15 nm when using the experimental result for ITO films, as is shown in Figure 2.9. This value is much smaller than the actual grain size observed in ITO films with high conductivity. However, it is noted that in recent years, TCO films have been grown at relatively low substrates temperature (< 200 °C) which yields fine grain size (5-20 nm) in the films. In this case, grain boundary scattering may be important to determine the electron mobility at relatively low carrier concentration region.

Figure 2.9 Variation of mean free path with carrier concentration for ITO films [36]
Based on the above discussion of various carriers scattering mechanism, it is found that the ionized impurity scattering is critical for degenerate semiconductors. It is an intrinsic limit for the maximum achievable value of mobility and conductivity of TCOs. At lower carrier concentration regions, other carriers scattering mechanisms play roles in determining the mobility. Therefore, the presence of grain boundaries and doping atoms can significantly alter the transport characteristics of the TCOs. In additional, it should be mentioned here that other scattering mechanisms such as defects (dislocation) scattering, electron – electron interaction, electron – neutral impurity scattering are also sometimes considered to analyze the observed electrical properties in TCO films.

2.1.3 Fundamental optical properties

As has been mentioned before, TCO thin films must have a very low absorption coefficient in the near UV-VIS-NIR region. A typical transmittance spectrum of a TCO film is shown in Figure 2.10, which exhibits three distinct regions of transmission [45]. The optically transparent region is limited by the absorption edge ($\lambda_{\text{gap}}$) and the plasma edge ($\lambda_{\text{pl}}$). The region is also known as transparent window. The absorption edge ($\lambda_{\text{gap}}$) is associated with fundamental bandgap absorption. The plasma edge ($\lambda_{\text{pl}}$) is determined by free electron plasma absorption.
Figure 2.10 Illustration of transmission spectrum of a typical TCO with $\lambda_{\text{gap}}$ and $\lambda_{\text{pl}}$ indicating the wavelength of bandgap absorption and free electron plasma absorption, respectively [45].

The optical properties of TCOs - transmission (T), reflection (R), and absorption (A) - are determined by its refraction index n, extinction coefficient k, band gap $E_g$, and geometry. Geometry includes film thickness, thickness uniformity, and film surface roughness. T, R and A are intrinsic, depending on the chemical composition and solid structure of the material, whereas the geometry is extrinsic.

The transmittance and the absorption can be explained by considering the energy band diagram of the TCOs. Fan et. al. proposed the first energy band model to explain the observed optical spectra in ITO [46]. Since then there have been considerable investigation on the band structures of various TCOs with the aim to explain the experimental measured optical properties [47]. Inspite of its schematic nature, the band energy model proposed by Fan et. al. is widely recognized as the basis to explain the observed high transmittance across
the visible region in the TCOs. In this model, the conduction band consists mainly of \( s \) electrons from the cations and the valence band is formed by O2p electrons. The two bands are separated by a large bandgap (\( E_g > 3.2 \text{ eV} \)), which leads to the transparency of TCOs in the visible spectrum region. Upon radiation with energy higher than the bandgap, electrons can absorb photons to be excited from the valence band to conduction band. The intrinsic semiconductor has a Fermi energy (\( E_f \)) lying in the midgap (\( E_g/2 \)). As the electron concentration increases, \( E_f \) is shifted towards the conduction band. With high concentration of electrons generated from the shallow donors (impurities and vacancies), the \( E_f \) can move above the conduction band. At sufficiently high electron concentration, the measured optical bandgap can increase with increasing carrier concentration, leading to a shift of the absorption edge towards shorter wavelength region. The bandgap widening phenomenon is known as the Moss-Burstein effect, which is due to occupation of the lowest states by electrons in the conduction band. Figure 2.11 shows schematically the proposed band structure of a TCO and the Moss-Burstein effect [{48}].

Assuming the conduction band (CB) and valence band (VB) are parabolic, the dispersions of the CB and VB in the doped material are given by:

\[
E_c^0(k) = \frac{\hbar^2 k_c^2}{2m_c} \quad \text{.................................. (2.10)}
\]

\[
E_v^0(k) = E_g - \frac{\hbar^2 k_v^2}{2m_v} \quad \text{.................................. (2.11)}
\]
The measured bandgap is given by:

\[ E_g^0(k) = E_g + \Delta E_{g}^{BM} \]  
\[ \text{(2.12)} \]

where

\[ \Delta E_{g}^{BM} = \frac{\hbar^2 k_F^2}{2} \left( \frac{1}{m_v} - \frac{1}{m_c} \right) \]  
\[ \text{(2.13)} \]

\[ \text{Figure 2.11 The schematic of the proposed band structure of a TCO and the Burstein-Moss effect [48].} \]

Assuming that the Fermi surface is spherical, the Fermi wave vector is given as:

\[ k_F = (3\pi^2 n)^{1/3} \]  
\[ \text{(2.14)} \]

Adding Equation 2.14 into Equation 2.13, \( \Delta E_{g}^{BM} \) is given as:

\[ \Delta E_{g}^{BM} = (3\pi^2 n)^{2/3} \cdot \frac{\hbar^2}{2} \left( \frac{1}{m_v} - \frac{1}{m_c} \right) \]  
\[ \text{(2.15)} \]

Equation 2.15 shows that the measured optical bandgap is proportional to \( n^{2/3} \). As is shown in
Figure 2.12, the measured $E_g$ does show correlation with electron density $n^{2/3}$ [49]. However, this theory does not take into account additional effects related to the electron-electron interactions and impurity scattering. It is believed that scattering effects also contribute to the observed change in the bandgap in the doped materials.

Figure 2.12 The correlation of $E_g$ with electron density $n^{2/3}$. The solid curve is calculated using the B-M theory [49].

The effect of the scattering events can be accommodated by adding a correction term to the dispersion of energy bands. As a result, the actual change in the bandgap is given by:

$$E_g = \Delta E_g^{BM} + W \quad \text{………………. (2.16)}$$

where $W$ represents a decrease of bandgap due to scattering terms. [49,50]
The degenerate nature of the degenerate TCOs not only affects the transmittance and absorption but also the reflectivity. The effect is most predominant in the near-IR region, where the plasma edge ($\lambda_{pl}$) tends to shift as a function of electron density. The calculation of the optical properties of TCOs in the near-IR region is based on Maxwell’s equations and the Drude theory of free electrons. The Drude theory used to describe the degenerate semiconductors can correlate the electrical parameters $n_e$ and $\mu$ with the optical constants $n$ and $k$, which will be shown at the end of this section. Maxwell’s equations enable us to define a complex permittivity, which is a function of frequency and conductivity. Using the Lorentz oscillator model for entire collection of free electron gas, $^[51]$, a complex conductivity is obtained, which is a function of carrier concentration, relaxation time, effective mass of free carriers, and frequency of the applied electric field. From the complex permittivity and conductivity, the real and imaginary parts of the permittivity are derived as functions of material parameters. The real and imaginary parts of the refractive index can then be calculated. These enable us to obtain the reflectance, as well as absorptance and transmittance of a film–substrate combination as functions of wavelength and film thickness.

The real and imaginary parts of permittivity are expressed as below,

$$\varepsilon_1 = \varepsilon_{\infty} (1 - \frac{\omega_p^2}{\omega^2}) \quad \text{.......................... (2.17)}$$

$$\varepsilon_2 = \frac{\varepsilon_{\infty} \omega_p^2}{\omega^2 \tau^2} \quad \text{.......................... (2.18)}$$
where $\tau$ is the relaxation time and $\omega$ is the frequency of applied electric field.

The $\omega_p$ is known as the plasma frequency, at which the free electron gas resonates with the applied electric field and is given by:

$$
\omega_p = \left( \frac{ne^2}{\varepsilon_0 \varepsilon_{\infty} m^*_c} \right)^{1/2}
$$

(2.19)

where $\varepsilon_0$ is the permittivity of free space, $\varepsilon_{\infty}$ is the high-frequency permittivity, and $m^*_c$ is the conductivity effective mass.

At the plasma frequency, $\varepsilon_1 = 0$, which leads the dramatic change of material’s optical properties. As is shown in Figure 2.13 [52], the reflectance can be very different at different carrier concentrations.

![Figure 2.13](image)

Figure 2.13 Calculated reflectance from 0.4 to 2.4 µm at different carrier concentrations. The mobility is 100 cm$^2$V$^{-1}$s$^{-1}$. The $\varepsilon_{\infty}$ is taken as 4 and the $m^*_c$ is assumed to be 0.3 $m_e$. The film thickness is 0.5 µm [52].
The real (n) and imaginary (k) parts of the refractive index can also be derived from Equations 2.17 and 2.18 [53]:

\[
n = \sqrt{\frac{1}{2} \left( \varepsilon_1^2 + \varepsilon_2^2 \right)^{1/2} + \frac{\varepsilon_1}{2}} \hspace{1cm} \text{……………………… (2.20)}
\]

\[
k = \sqrt{\frac{1}{2} \left( \varepsilon_1^2 + \varepsilon_2^2 \right)^{1/2} - \frac{\varepsilon_1}{2}} \hspace{1cm} \text{……………………… (2.21)}
\]

It should be noted that the absorptance and transmittance are also affected. The calculated absorptance at different carrier concentrations is shown in Figure 2.14. The material parameters are same as the one used in Figure 2.13.

![Figure 2.14 Calculated absorptance in the wavelength from 0.4 to 2.4 µm at different carrier concentrations [52].](image-url)

Figure 2.14 Calculated absorptance in the wavelength from 0.4 to 2.4 µm at different carrier concentrations [52].
The absorption coefficient ($\alpha$) can also be obtained from extinction coefficient ($k$), which is given as:

$$\alpha = \frac{4\pi k}{\lambda} \quad \text{................................... (2.22)}$$

### 2.1.4 Other critical issues

In addition to the fundamental electrical and optical properties discussed in the two sections above, several other important technical factors need to be considered when developing new TCO material. In this section, the most frequently discussed issues in the literature are briefly reviewed here.

**1) Thermal stability**

Long term stability of properties of the TCOs is critical for the life span of devices. Depending on the applications of devices, the TCO may be exposed to various extreme environments. For example, PV cells are usually under long time and repeated solar irradiations. Therefore, the thermal stability of developed TCOs is essential to their applications.

The thermal stability temperature is a threshold temperature, above which appreciable changes can be observed in the properties of TCO films. The change in film properties can be either an isolated or combined effect of the chemistry, structure, chemical reaction and/or formation of new phases. The reported thermal stability temperatures for ZnO, SnO$_2$ and Cd$_2$SnO$_4$ are 250, 500 and 700 °C, respectively [54]. Above these temperatures, chemical
decompositions of the films occur, which degrade the quality of the films.

In many practical cases, processing temperatures are restrained by substrates such as substrate softening and interfacial reactions. Many commercial substrates are temperature sensitive (glass < 500 °C, polymer < 200 °C). Observations of chemical reaction of the TCO films with the substrate and the subsequent layers have been reported in the literature [55]

(2) Chemical stability and etchability

Chemical stability of a TCO is determined by its ability to resist corrosive environment. The etchability of a material is inversely related to the chemical stability. The chemical stability and/or etchability are dependent on various factors, such as chemical composition of thin films, chemical atmosphere, microstructures and deposition conditions.

The stability and/or etchability are mainly determined by metal elements presented in the TCO films. Among ZnO, ITO and SnO₂, ZnO exhibits poor chemical stability while having high etching rates; SnO₂ is one of the most resistive TCOs to chemical etching. ITO exhibits intermediate stability and/or etchability [54]. The presence of foreign chemical species is also known to affect chemical stability etchability of films. In the case of ZnO, the chemical stability was reported to be improved significantly with addition of dopants (Al, Ga, F, Co). The most stable films were co-doped with (F,Ga):ZnO and (Al,Co):ZnO [56].

The sensitivity of TCO films exposed to either reducing atmospheres or hydrogen plasmas is another important concern. SnO₂ can be readily reduced in the hydrogen plasma, which
causes undesirable absorption of radiation \(^{[56]}\). Similarly, ITO also undergoes heavy reduction when exposed to hydrogen environments \(^{[54,56]}\). In comparison to \(\text{SnO}_2\) and ITO, doped ZnO are much more stable in reducing atmospheres and hydrogen plasmas \(^{[54,56]}\). Therefore, ZnO based TCOs may be preferred for the applications involving hydrogen plasma processing. In contrast, ITO shows better stability compared to other TCOs in oxidizing atmosphere, especially at high temperatures \(^{[56]}\).

Microstructure is also known to play a role in the stability and/or etchability. It has been observed that amorphous ITO exhibits higher etch rate than single crystal or polycrystalline ITO films \(^{[57,58]}\). This effect may be related to the increased defect content and number of chemically activated sites in the amorphous ITO. Van den Meerakker et. al.\(^{[59]}\) has proposed that the lack of well-defined structures facilitates the bond-breaking. Kithara et. al. \(^{[60]}\) has conjectured that the existence of residual \(\text{H}_2\text{O}\) and \(\text{H}\) related species may control the etch rate in the films.

Films with high etchability are desirable for the etching process, which is employed to pattern the TCO films. Wet etching, also known as chemical etching is currently being used to etch TCO films. Table 2.6 lists the chemicals that are used for wet etching of TCOs \(^{[54]}\).
Table 2.6 Various etchants for different TCOs [54].

<table>
<thead>
<tr>
<th>TCO</th>
<th>Etchant</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>Dilute acids and alkalis (HCL, KOH)</td>
</tr>
<tr>
<td>ZnO</td>
<td>Ammonium chloride</td>
</tr>
<tr>
<td>TiN</td>
<td>H$_2$O$_2$ + NH$_3$</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>HCl + HNO$_3$ or FeCl$_3$</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>Zn+HCl</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>CrCl$_2$</td>
</tr>
</tbody>
</table>

(3) Mechanical hardness

Mechanical hardness is another important factor that contributes to the stability of TCOs and devices. TCO films with high hardness can provide good mechanical durability and endurance, which can stabilize the devices performance and life span. The hardness of the three common TCOs increases in the following order: Ag < ZnO < In$_2$O$_3$ < SnO$_2$ < TiN. The Ag and TiN are two widely used metal coatings.

The mechanical hardness also shows slight dependence on the deposition parameters, mainly oxygen pressure and the nature of the substrates. Wu et. al. systematically studied the effect of the oxygen pressure of sputtering on the microhardness of ITO films and found that the hardness increased with increasing oxygen pressure [61]. They also observed that the increase
in oxygen pressure improved the adhesion and the scratch resistance of the ITO films. However, on alternative substrates such as polymer and glass, the evaluation of mechanical properties is limited by the early failure of the substrate rather than the films.

(4) Surface morphology

Surface roughness of TCOs can affect both their optical and electrical properties, which can drastically alter device performances. For most of opto-electronic devices (e.g. organic LEDs, solar cells) smooth surface with RMS less than 5nm is required. Due to the small dimension of devices (~100 nm or less), surface asperities with the dimensions comparable to the devices can hamper the device performance \([62]\). Furthermore, smooth surfaces usually yield low specific contact resistance by reducing surface scattering and minimizing localized field effects \([57,63]\).

However, a textured surface may be preferred in certain cases, for example, amorphous Si:H and/or nanocrystalline (nc) Si:H solar cells \([64]\). The textured surface can trap the incident light through enhanced light scattering within the absorption layer in the solar cell. Fig. 2.15 illustrates schematically the trapping of the incident light by corrugated surface of the TCO layers \([64]\). The increasing optical path length of the incident light can significantly increase the absorption in the absorption layer, which can improve the efficiency of these solar cells.
Post-deposition treatments such as plasma processing and etching have been used to modify the TCO surface properties, such as the work function and chemical activity [63]. It has been found that oxygen plasma treatment combined with acid etching gives the best effect on the properties of the TCO film and the device performance. However, it should be noted here that the post-deposition treatment may lead to some undesirable effects. For example, the adsorption of extraneous species such as H, Ar, and O on the film surface can significantly alter the electrical resistivity of the films.
(5) Work function

Work function ($\varphi$) is defined as the energy difference between the Fermi level and the ionization potential. In semiconductors, since the Fermi level usually lies in the bandgap, the work function is given as:

$$\varphi = \chi + (E_f - E_c) \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdOTS
Table 2.7 Work function values of some common TCOs [54].

<table>
<thead>
<tr>
<th>TCO</th>
<th>Work Function (eV)</th>
<th>Carrier concentration (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:F</td>
<td>4.2</td>
<td>2×10$^{20}$</td>
</tr>
<tr>
<td>ZnO</td>
<td>4.5</td>
<td>7×10$^{19}$</td>
</tr>
<tr>
<td>In$_2$O$_3$:Sn</td>
<td>4.8</td>
<td>&gt; 10$^{20}$</td>
</tr>
<tr>
<td>SnO$_2$:F</td>
<td>4.9</td>
<td>4×10$^{20}$</td>
</tr>
<tr>
<td>ZnSnO$_3$</td>
<td>5.3</td>
<td>6×10$^{19}$</td>
</tr>
</tbody>
</table>

Work function is an important factor in the PV solar cells. Matching the work function between the transparent electrode and the active layers can maximize the device efficiency.

(6) Toxicity

A growing concern over the long term impact of TCO materials on the environment has risen in recent years. For the elements commonly studied for TCO applications, the toxicity levels are as follows: Zn < Sn < In < Cd [54].

The use of toxic material in large scale manufacturing facility requires strict regulations and safe operation procedures. Once properly and securely handled, toxic materials used in manufacturing processes may be rendered harmless. Recycling of these toxic materials after usage is required. All this increases the costs of the finished product and should be taken into account for development of new TCOs.
2.2 Zinc oxide

ZnO has attracted a lot of research interests due to its properties. The wurtzite ZnO is a direct band semiconductor with a wide bandgap of 3.3 eV, which gives great prospects in opto-electronic devices. The advantage it has over GaN, another wide band gap semiconductor widely used in production of LEDs and laser diodes, is its large exciton binding energy (~60 meV) which is more than twice that of GaN. The large exciton energy leads to a strong near-band-edge excitonic emission even at room temperature since its value is more than twice of room temperature thermal energy (k_B T= 25 meV for room temperature) [65,66].

ZnO is intrinsically n-type. This n-type conductivity has been attributed to the presence of intrinsic defects like oxygen vacancies and zinc interstitials. By doping with group III elements, the carrier concentration can be as high as ~ 10^{21} cm^{-3}, which makes ZnO show metallic conductivity. The wide bandgap of ZnO makes it transparent in the visible range. As a result, ZnO is a promising material for the applications of transparent conducting oxide [67].

2.2.1 Crystal structure

The crystal structure of ZnO appears in three different phases: a) wurtzite (hexagonal) structure, b) Zinc blende and c) rock salt (NaCl). Wurtzite is the most thermodynamically stable phase under ambient conditions, although the other two structures also exist under specific conditions. The zinc-blende state is stable only when grown on cubic substrates and
the rock salt structure can be obtained only at very high pressures. The wurtzite structure has a hexagonal close packed (hcp) bravais lattice and belongs to the P63mc space group \(^{68}\). The ZnO structure consists of two interpenetrating hcp sub-lattices of cation (Zn) and anion (O) which are displaced along the c-axis by the Zn-O bond length. Figure 2.17 shows a schematic of the wurtzite structure and the HCP Bravais lattice \(^{69}\). 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 slightly smaller than the ideal value of 1.633 for 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.

Figure 2.17 schematic of wurtzite structure and HCP lattice of ZnO.

ZnO is an-isotropic crystal with the point group symmetry of C6v (or 6mm). Group C6v 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.

2.2.2 Band structure

In a single atom, the electrons form discrete atomic orbitals at different energy levels. When several atoms are close enough to allow the interactions between electrons, the atomic orbitals split. When a large number of atoms are brought together to form a solid, the number of orbitals are so that the levels can be considered to form continuous bands of orbitals rather than the discrete energy levels. In certain energy region without any bands, the bandgaps are formed.

The band structure of a solid is determined by the crystal structure and the chemical bindings in the solid. Many theoretical methods such as first principle calculation, Local density approximation (LDA) and density functional theory (DFT) [70,71] and experimental techniques, such as X-ray or UV reflection/absorption or emission techniques, photoelectron spectroscopy (PES), angle-resolved photoelectron spectroscopy (ARPES) [1] have been used to investigate the band structure.

Density of states (DOS) calculation based on first principle method has been used to calculate the electronic band structure of ZnO. The valence bands extend down to about 10eV below the Fermi level. The deepest valence band is mainly the O3s orbital and the
upper valence band is composed of Zn3d, Zn4s, Zn4p and O2p orbitals. The conduction band consists of Zn4s, Zn4p and O2p orbitals. Figure 2.18 shows calculated density of states and the band structure of ZnO. Close to the Fermi level, the uppermost valence band was mainly composed of O2p. Compared to this the lowermost conduction band is predominantly Zn4s and 4p with contributions from the O2p and 3s states being negligible. The O2p orbital in ZnO is rather sharp without much overlap with other orbitals. This implies that the O2p is tightly bound to the oxygen atoms, which inhibits much contribution of electron states to the conduction band. The electronic band structure of ZnO (wurtzite) matches well with the experimental data. But the calculated direct band gap of ZnO is 1 eV which is much smaller than the measured value of 3.4 eV. A self-interaction correction (SIC) is incorporated in these calculations to correct the bandgap to the experimental values [72]. The influence of Zn 3d states on the s and p derived valence states can be accounted for the band structure when using a SIC-psuedo potential, which is in good agreement with the experimental values.
2.2.3 Excitons

In the effective mass model, excitons are formed by the Coulomb interaction between an electron and a hole. Assuming parabolic bands of a direct semiconductor, the relative motion of electron and hole can be separated from the motion of the center of mass. Then the calculation of exciton energy is simplified to calculate the hydrogen-like electron-hole pair in the media of the semiconductor. The energy dispersion relation of excitons with wave vector can be written as \[^{73}\]:

Figure 2.18 The density of states and band structure of wurtzite ZnO \[^{72}\].
\[ E_{ex}(n_B K) = E_g - R_y^* \frac{1}{n_B^2} + \frac{\hbar^2 K^2}{2M} \]  
\[ \ldots \ldots \ldots (2.23) \]

where \( E_g \) is the band gap and \( n_B = 1, 2, 3 \ldots \) is the principle quantum number adn \( M = m_e + m_h \). \( K = k_e + k_h \) are the translational mass and wave vector of the exciton.

\( R_y^* \) is the exciton binding energy, given as:

\[ R_y^* = 13.6 \cdot \frac{\mu}{m_0} \frac{1}{\varepsilon^2} \]  
\[ \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2.24) \]

where \( \mu \) is the reduced mass of the electron and hole and \( \varepsilon \) is the dielectric constant.

The second term is the Coulomb interaction energy of the electron and hole pair. The third term represents the kinetic energy of the exciton. Exciton states are a series of separated energy levels below the conduction band bottom, as is illustrated in Figure 2.19.

![Figure 2.19 Schematic of exitons in direct band semiconductors.](image-url)
Excitons can be classified into two types. The free excitons can move in the semiconductor without any trap or bound. Excitons can also be associated with other particles and point defects to form ion-like or molecule-like complex. In this case, they are called bound excitons \(^{[74,75]}\).

### 2.2.4 Native defects

The effect of native defects on the electrical properties of ZnO can be well understood by analysis of the electronic band structure. As-deposited ZnO is intrinsically n-type due to its oxygen deficiency under normal growth conditions. The main reason for the n-type conductivity has been proposed to be a native defect, either O vacancies or Zn interstitials, acting as a shallow donor, although the role played by either of these two defects in the origin on n-type conductivity in pure ZnO is still controversial. Usually these point defects appear in crystals as Schottky (pair of anion and cation vacancy) or Frenkel (vacancy-interstitial pair of the same ion). But the type of defects that will be present in ZnO crystal and their effect on the band structure is very complex and far from complete understood \(^{[76]}\).

Theoretical calculations have showed that mid-gap states are formed by the introduction of defects such as \(V_O\), \(V_{Zn}\), \(O_i\) and \(Zn_i\) \(^{[77]}\). But still the energy levels of these defects in the mid-gap are debated. By performing numerous studies on optical and electrical properties of ZnO and on the diffusion process, Krueger \(^{[78]}\) estimated the energy levels of these native defects in ZnO, which is shown schematically in Figure 2.20. He assigned \(V_O\) and \(V_{Zn}\) as the
dominant donor and acceptor, respectively. In oxygen rich conditions Zn vacancies ($V_{\text{Zn}}$) will dominate while under Zn rich or oxygen deficient conditions O vacancies ($V_{\text{O}}$) will dominate. Theoretical calculations which predict lower energy of formation energy for $V_{\text{O}}$ as compared to $\text{Zn}_i$ also suggest that films when grown under high vacuum would have oxygen vacancies which could be responsible for the n-type conductivity. In the Figure 2.20 Zn vacancies are represented as $V_{\text{Zn}}'$ and $V_{\text{Zn}}''$ with effective charges of -q and -2q respectively. $\text{Zn}_i^x$ and $\text{Zn}_i^*$ represent Zn interstitials with effective charges of zero and +q, respectively, and oxygen vacancies are denoted by $V_{\text{O}}^x$ and $V_{\text{O}}^*$ with effective charges of zero and +q, respectively. It was proposed that both $V_{\text{O}}$ and $\text{Zn}_i$ can act as shallow donors but there is a great debate about which one is the dominant donor defect responsible for n-type conductivity [79].

Figure 2.20 Electronic energy levels of native defects in ZnO [79].
2.3 Magnesium oxide

MgO has a sodium chloride (NaCl) structure with the lattice constant of 4.216 Å as shown in Figure 2.21. Each Mg (or O) atom forms bonds with six surrounding O (or Mg) atoms. Due to the ionic nature of Mg-O bond, MgO is a insulator with a bandgap of 7.8 eV and it is transparent in a wide wavelength range from 0.3µm to 6 µm. The physical and chemical properties of MgO are summarized in Table 2.3.

![Crystal structure of MgO.](image)

Figure 2.21 Crystal structure of MgO.

Table 2.8 The basic physical and chemical properties of MgO [80]

<table>
<thead>
<tr>
<th>Structural properties</th>
<th>Structure</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant</td>
<td></td>
<td>4.216 Å</td>
</tr>
<tr>
<td>Space group</td>
<td></td>
<td>O₅h</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td>3.576 g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td></td>
<td>3073 K</td>
</tr>
<tr>
<td>Dielectric constants</td>
<td>ε(0)=9.83, ε(∞)=2.94</td>
<td></td>
</tr>
<tr>
<td>Bandgap</td>
<td></td>
<td>7.833 eV (85 K)</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td></td>
<td>161 meV</td>
</tr>
</tbody>
</table>

53
MgO has also been demonstrated as substrate and buffer material for heteroepitaxial growth of thin films. The thin films that have been grown epitaxially on MgO includes metal \(^{[81]}\), metal-nanoparticles composite \(^{[82]}\), phosphors \(^{[83]}\), ferromagnetic materials \(^{[84,85]}\), ferroelectric materials \(^{[86,87]}\), semiconductor oxides \(^{[74,75]}\), superconductor \(^{[88]}\). MgO can be grown epitaxially with TiN \(^{[89]}\) which makes MgO a useful buffer layer for heteroepitaxy. TiN is well known as a metal used in the Si-based electronic devices as a diffusion and wet etching barrier layer \(^{[90]}\). Since TiN thin films can be epitaxially grown on Si substrates \(^{[91]}\), the heteroepitaxial MgO/TiN provides a route to integrate oxides with Si substrate. One of the most successful examples is PZT/YBCO/STO/MgO/TiN/Si(100) heterostructures, in which all the five layers have been grown epitaxially on Si (001) \(^{[92]}\).

### 2.4 Magnesium zinc oxide

ZnO can form Mg\(_x\)Zn\(_{1-x}\)O alloy with MgO \(^{[93]}\). The Mg\(_x\)Zn\(_{1-x}\)O alloy is considered to be one of the promising candidates for opto-electronic devices, such as UV LED \(^{[94]}\), laser diode \(^{[95]}\), and deep UV photodetector \(^{[96]}\). Another interesting application of Mg\(_x\)Zn\(_{1-x}\)O is Mg\(_x\)Zn\(_{1-x}\)O based heterostructures. Quantum wells and superlattices can be fabricated with ZnO/Mg\(_x\)Zn\(_{1-x}\)O or Mg\(_x\)Zn\(_{1-x}\)O/MgO heterostructures. A ZnO/Mg\(_{0.2}\)Zn\(_{0.8}\)O superlattice with a band offset of 0.5 eV has been reported \(^{[97]}\).

Figure 2.22 shows the phase diagram of MgO-ZnO system \(^{[98]}\). The solubility of MgO in wurtzite ZnO is less than 4%, although the solid solution limit of ZnO in periclase MgO was
extended to approximately 56 wt. % of ZnO (40 at.%) at 1600 °C.

Figure 2.22 Phase diagram of ZnO and MgO [98].

The thermal stability of the supersaturated Mg$_x$Zn$_{1-x}$O thin films had been investigated by Ohtomo et. al.[99]. The Mg$_x$Zn$_{1-x}$O thin films were deposited using laser molecular-beam epitaxy (LMBE) on sapphire at 550 °C. The as-deposited films were annealed from 700 °C to 1000 °C. The segregation of MgO occurred at 850 °C in the film with Mg content above 15 at. %. As the annealing temperature exceeds 1000 °C, the film with Mg content of 15 at. % or lower showed no segregation of MgO. However, the nonequilibrium nature of PLD
enables the growth of Mg$_x$Zn$_{1-x}$O with Mg content higher than the thermodynamic solubility limit. The growth of Mg$_x$Zn$_{1-x}$O thin films with the Mg content up to 34 at.% has been achieved on sapphire (0001) substrate [100]. With Mg content of 34%, the bandgap of the Mg$_x$Zn$_{1-x}$O thin films is found to be 4.15 eV.

Mg$_x$Zn$_{1-x}$O alloy has two phases: wurtzite (hexagonal, a = 3.24 Å and b = 5.20 Å) and NaCl-type (cubic, a = 4.24 Å) [101]. At low MgO content, the alloy is wurtzite. With high content of MgO, the structure is changed from hexagonal to cubic. A cubic Mg$_{0.82}$Zn$_{0.18}$O thin film with a bandgap of 6.7 eV has been reported [102]. In general, the bandgap of Mg$_x$Zn$_{1-x}$O alloy can be adjustable from 3.3 to 7.8 eV by controlling the MgO content. Figure 2.23 shows the wurtzite and cubic Mg$_x$Zn$_{1-x}$O alloy and corresponding bandgap values as a function of MgO composition [103].
Figure 2.23 MgO compositional dependence of phases and bandgap values of Mg$_x$Zn$_{1-x}$O [103].
References


61 W.F. Wu and B.S. Chiou, Thin Solid Films, 293, 244 (1997).


Chapter 3 Experimental techniques

3.1 Pulsed laser deposition

3.1.1 Overview

Pulsed laser deposition (PLD) is a versatile thin film growth technique based on physical vapor deposition. Basically it involves the vaporization process of target materials and the deposition process of the vaporized species on the substrates. The idea of vaporization of materials using a high power laser was proposed in 1960s \(^1\), after the invention of high power ruby laser. The prototype PLD was first demonstrated by Smith et. al. in 1965 \(^2\). PLD was developed as a predominant thin film deposition technique in 1980s, after a series of successful demonstrations of developing novel thin films and heterostructures using PLD technique. Cheung et. al. \(^3\) reported the first successfully synthesis of epitaxial Hg\(_x\)Cd\(_{1-x}\)Te/CdTe and CdTe/GaAs heterosturctures in 1983. Dijkkamp et. al. \(^4\) demonstrated the growth of YBa\(_2\)Cu\(_3\)O\(_7\) superconducting thin films on sapphire in 1987. Since then PLD has been widely used to grow a variety of metals, oxides and nitrides thin films as well as nanocomposites.

In general, the PLD system is favorable for academic studies due to the simplicity of the experimental set-up, easy operation and low maintenance costs. The PLD system consists of three main components: 1) the high power laser, 2) the vacuum system including vacuum chamber and pumps, 3) the optics system that manipulate the laser beam by using a set of
optical elements such as lenses, beam splitter, apertures, mirrors. Figure 3.1 shows the schematic of a typical PLD system.

![Schematic diagram of a PLD system](image)

Figure 3.1 Schematic diagram of a PLD system.

Most high power lasers can generally be used in a PLD system. Lasers that have been used in PLD technique include ruby laser [5], CO₂ laser [6], Nd-YAG laser [7,8], Nd-glass laser [8] and excimer lasers [6,8,9]. Since most materials of interest exhibit strong absorption in the range 200 – 400 nm, the wavelength of desired lasers must match this working wavelength.
The most widely used lasers in PLD system are the Nd:YAG and the excimer laser. The Nd:YAG laser is a solid state neodymium doped yttrium aluminum garnet laser, with a fundamental wavelength of 1064 nm. The high-intensity pulses may be efficiently frequency doubled, tripled or quadrupled to 532 nm, 355 nm and 262 nm by nonlinear high order harmonic generation process. However, the use of these crystals causes energy loses and reduced system efficiency, which make Nd:YAG laser less desirable for PLD. The excimer lasers have several advantages compared with Nd:YAG laser. Excimer lasers can emit radiation directly in the UV range with a repetition rate up to several hundred hertz and the energies up to 1 J/pulse. The excimer laser is a chemical laser which uses a mixture with precise rations of an inert gas and a reactive gas. The term excimer is a short form of excited dimer. The typical inert gases used are Argon, Krypton and Xenon. The reactive gases typically used are highly toxic fluorine and chlorine. 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 lists most commercial excimer laser systems along with their wavelengths and energies. Among these excimer lasers, the KrF laser (wavelength 248 nm, photon energy 5eV) is the highest gain system for electrically discharged pumped excimer lasers and can deliver pulses with much higher energy than other excimer lasers [10]. This makes the KrF laser the most popular laser source in PLD growth technique. In the present work, KrF excimer laser was used as the source.
Table 3.1 Operating wavelengths of excimer lasers when using different gases.

<table>
<thead>
<tr>
<th>Excimer gas</th>
<th>Wavelength (nm)</th>
<th>Laser energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>157</td>
<td>7.9</td>
</tr>
<tr>
<td>ArF</td>
<td>193</td>
<td>6.4</td>
</tr>
<tr>
<td>KrCl</td>
<td>222</td>
<td>5.6</td>
</tr>
<tr>
<td>KrF</td>
<td>248</td>
<td>5.0</td>
</tr>
<tr>
<td>XeCl</td>
<td>308</td>
<td>4.0</td>
</tr>
<tr>
<td>XeF</td>
<td>351</td>
<td>3.5</td>
</tr>
</tbody>
</table>

In the PLD systems, thin films are grown in a high vacuum chamber in order to generate high quality plasma plumes. Depending on the vacuum system used, the vacuum may vary from $10^{-6}$ Torr to $10^{-11}$ Torr (also known as ultra high vacuum). The basic elements inside the vacuum chamber include substrate holder, targets holder, vacuum gauges, etc. The multiple-target mounting carousel is usually applied in the PLD system for growth of multilayer heterostructures. In the chamber used for this thesis work, the target mounting assembly has six targets holds which allows six targets to be loaded at the same time.

In the PLD systems, the optical elements are used to guide the laser beam onto the target and achieve the optimized energy density of the focused beam. 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.

The quality of grown films can be controlled by varying different growth parameters, such as substrate temperature, ambient gas, laser fluence, substrate to target distance and pulse...
repetition rate. For the growth of thin films, the chamber was evacuated to a vacuum in the order of $10^{-6}$ torr. The substrate is placed parallel to the target at a distance of 4.5 cm. The substrate temperature can be varied from room temperature up to 650 °C. By using a gas flow meter, a specific ambient gas (usually oxygen) partial pressure can be maintained during deposition.

3.1.2 Physics of laser-material interaction

During deposition, the target material interacts with the focused laser beam to form a plasma plume. The plasma plume subsequently reaches and sticks to the substrate to form a thin film. In contrast to the simplicity of PLD system itself and the operation to grow films, the real laser-solid interaction involves very complicated physics.

The laser-solid interaction was analyzed and modeled by Singh et. al. [6,11]. It should be noted that the model is only valid in the regime that the energy densities of laser beam is above the threshold of vaporization of materials. Depending upon the interaction of the laser with the target material, Singh et. al. [6,11] divided the interaction into three stages. These three stages are schematically shown in Figure 3.2.

Stage 1. Evaporation of the target surface layer due to the interaction of laser beam and the target material. This regime is termed as the evaporation regime. It starts with the laser pulse and continues through the duration of the laser pulse.

Stage 2. Formation of a high-temperature, isothermally expanding plasma plume due to the
interaction of the laser beam with the evaporated material. This regime prevails when the target starts to evaporate and continues until the end of the laser pulse.

Stage 3. Anisotropic three-dimensional adiabatic expansion of plasma plume. The elliptical shape of expanding plasma plume is characteristic of forward directed nature of PLD. This regime starts after the termination of the laser pulse.

Figure 3.2. Schematic diagram showing the different stages during laser irradiation of a target: (A) uneffected target, (B) evaporated target material, (C) dense plasma absorbing laser radiation [6].
The underlying physics of each of the three stages are briefly discussed as follow:

Stage 1

When a laser pulse reaches the target surface, the electromagnetic energy is absorbed to excite free electrons in the target material. The excited electrons interact with phonons to conversion the electromagnetic energy to thermal energy. This conversion results in rapid localized heating, melting and evaporation of the surface layer. It should be noted that the interaction time for this process is on the order of picoseconds \([6, 11]\). The thickness of evaporated layer on the target is given by:

\[
\Delta x_i = \frac{(1 - R)(E - E_{th})}{\Delta H + C_v \Delta T} \tag{3.1}
\]

where, \(\Delta x_i\), \(R\), \(\Delta H\), \(C_v\), and \(\Delta T\) are the evaporated thickness, surface reflectivity, latent heat, volume heat capacity, and the maximum temperature rise, respectively. Here \(E_{th}\) is the threshold energy beyond which the evaporation process takes place. Equation 3.1 is valid for materials where the thermal diffusion distance \(\sqrt{2D\tau}\) is larger than the penetration depth, \((1/\alpha_t)\), of the laser beam on the target. In the case of metals and small band-gap semiconductors, this condition is satisfied. But for \(1/\alpha_t > 2D\tau\) the thermal diffusivity no longer plays a role in the evaporation of the material, and the evaporated depth depends on the penetration depth, \((1/\alpha_t)\), of the laser beam on the target. This will happen for materials with small thermal diffusivities and absorption coefficients such as polymers and insulators. The \(\Delta x_i\) is dependent both on the laser parameter (energy density) and material properties.
(surface reflectivity, latent heat, volume heat capacity). $E_{th}$ only depends on material properties, which may vary during deposition since the ablation may change the properties of target surface layer. Depending on the laser wavelength and the porosity and surface roughness of the target, typical values of threshold energy vary from 0.11 to 0.40 J/cm$^2$ $^6$. A target with high surface roughness, low reflectivity and high absorption coefficient ($\alpha_t$) allows for efficient laser-solid interaction and thus provides a low threshold energy.

Stage 2

The evaporated material induces emission of particles, such as positive ions and electrons, from the target surface due to the high surface temperature. The laser-material interaction can yield a surface temperature in the range of 2000-3200 K. The ions and electrons form in the vacuum a plasma plume (also known as plasma) which extends normally to the target surface. The plasma plume may also contain charged and neutral particles of molecules atoms. The plasma plume can absorb the incoming laser beam, which can generate a higher plasma plume temperature compared with the vaporization temperature. The absorption of laser energy into the plasma plume occurs by an inverse Bremsstrahlung process that involves the absorption of a photon by a free electron $^12$. The absorption coefficient of the plasma plume is given by $^6$:

$$\alpha_p = 3.69 \times 10^8 \left( \frac{Z^2 n_i^2}{T^{0.5} \nu^2} \right) \left( 1 - e^{-\frac{hv}{k_B T}} \right)$$

where $Z$, $n_i$ and $T$ are the average charge, ion density, and temperature of the plasma plume,
respectively. The \( h \), \( K_B \) and \( \nu \) are the Plank constant, Boltzman constant, and the frequency of the laser beam respectively. The term \( 1 - e^{-\frac{hv}{K_BT}} \) corresponds to the losses due to stimulated emission. Since the absorption of the plasma is proportional to \( n_i^2 \), the largest fraction of the laser beam will be absorbed in the region close to the target surface since the particle density in the plasma plume is highest there.

The particle density decreases rapidly as the plasma plume move away from the target surface with a very high expansion velocities \( (10^5 - 10^6 \text{ cm/sec}) \). A dynamic self-regulating equilibrium mechanism between the plasma plume absorption coefficient and the rapid transfer of the thermal energy into kinetic energy establishes the isothermal temperature near the target surface. These complex processes result in a plasma plume particle density that can be approximated by a Gaussian profile that decreases away from the surface of the target.

The interaction between the laser beam and the evaporated material resulted in highly energetic species having energies in the range \( 10 - 100 \text{ eV} \) and temperatures of the order of \( 2 \times 10^4 \text{K} \) \(^6,13\).

The variation of density, pressure and expansion velocity (along the direction perpendicular to the target surface) has been modeled by Singh et. al. \(^6,11\). Figure 3.3 shows the profile of variation of density, pressure and expansion velocity. The direction perpendicular to the target surface is defined as the x direction. It is clear from the figure that the density of particles is a maximum in the near surface regions, while the velocity is the minimum. The
particle density in the plasma plume follows a Gaussian distribution approximately.

Figure 3.3: Distribution of density (n), pressure (p) and expansion velocity (v) of the plasma plume as a function of distance in the perpendicular direction from the target surface [6].

Stage 3

After termination of the laser pulse, an adiabatic expansion of the plasma plume occurs. This process can be described by using fundamental gas equation for adiabatic expansion:

$$T[X(t) Y(t) Z(t)] \gamma - 1 = \text{const} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3.3)$$

Here $\gamma$ is the ratio of specific heats at constant pressure to that at constant temperature. In the adiabatic expansion regime, the plasma plume temperature drops continuously as the
expanding plasma plume attains very high expansion velocities (10 times higher than the velocity of sound). The increase in velocity takes place by conversion of the thermal energy into kinetic energy. Once the thermal energy is converted into kinetic energy, there is not enough energy left to sustain the plasma plume and the plasma plume elongates in the shorter dimensions and retains this profile during the deposition process. In Figure 3.4 it is shown that initially the plasma plume is larger in the Y direction than in the Z direction, thus the plasma plume would accelerate more along the Z direction. As the plasma plume expands adiabatically, the resulting shape of the plasma plume is as shown in Figure 3.4 with Z-axis as the major axis. Since the plasma plume dimension is the smallest along the perpendicular direction, the acceleration is maximal along this dimension giving rise to a characteristic forward directed shape to the plasma plume.
3.1.3 Advantages and disadvantages of PLD

PLD technique has several advantages compared with other thin film deposition techniques, such as sputtering, molecule beam epitaxy and chemical vapor deposition. Most advantages arise due to the highly energetic plasma plume of the ablated species [6]. The plasma plume
energy can be as high as 10 to 100 eV (i.e. about 100-1000 kT). In comparison, the average kinetic energies of the impinging atoms in MBE are just of the order of a few hundreds meV [6] and that of the species in sputtering are a few eV. The advantages of the PLD technique are summarized as below:

1. The non-equilibrium nature of the PLD growth process permits the growth of novel materials with metastable phases and introducing dopant concentrations in excess of the thermodynamic limits. In the case of magnesium zinc oxide, single crystal, hexagonal magnesium zinc oxide with magnesium content up to 36 at.% can be grown by PLD [14].

2. A variety of materials, including metals, ceramics and polymers can be deposited by using PLD technique. Since nearly all materials absorb laser energy via either linear or non-linear processes, the laser ablation of materials, which generates the plasma plume for PLD, can be achieved as long as a laser with an appropriate wavelength is used.

3. Stoichiometric multi-component material systems, such as YBCO can be grown by PLD. The forward directed, highly energetic of the plasma plume helps to maintain the stoichiometry in the grown films [6,15].

4. Multi-layered heterostructured thin films can easily be synthesized using PLD. The target carousel can be suitably manipulated to hold multiple targets (4 to 6 targets). This means multi-layered films can be deposited without breaking the vacuum. For example, using PLD epitaxial growth of PZT/YBCO/STO/MgO/TiN/Si(100) was demonstrated by
Sharma et. al [16].

On the other hand, there are some disadvantages of the PLD technique. The major drawback is the non-uniform distribution and/or spatial thickness variation, which significantly prevent PLD technique from immediate industrial application. The variation of thickness is due to the forward-directed nature of the plasma plume. The spatial variation of film thickness is given by a factor of \( \cos^p \theta \), where \( \theta \) is the angle between the radial vector and the surface normal to the plane of the target and \( p \) is the exponential factor varying between 8-12 depending on laser fluence, irradiated spot-size, etc. On contrast, the thickness variation in case of thermal processes is only \( \cos \theta \), leading to much more uniform films. For a substrate with relatively small sizes, for example, 1 cm × 1cm or less, fairly uniform growth can be achieved by controlling the deposition. Deposition on larger substrates and uniformity of film thickness can be achieved to some extent by rastering the laser beam over a large target and/or rotation and translation of the substrate [17]. The other important drawback of PLD is the formation of particulates (also known as chunks) due to improper ablation of target materials. The particulates have been proved to be detrimental to the quality of the film [18]. Generation of particulates involve various mechanisms such as subsurface boiling, expulsion of the liquid layer by shock wave recoil and exfoliation [6,11,18]. Generation of particulates can be minimized by various ways, including adjusting the laser parameters, increasing the absorption coefficient and making a compact targets for ablation.
3.1.4 Epitaxial growth of thin films by PLD

Thin film growth mainly involves two critical steps: nucleation and growth. On arrival at the substrate, the incident atoms can have a series of different processes including re-evaporation, surface diffusion, incorporation to existing nucleus, and nucleation. Figure 3.5 schematically shows the various processes during the early stages of thin growth [19]. These competing processes affect the nucleation and growth of the films.

![Schematic diagram of various processes on the substrate at the initial stage of film growth](image)

Figure 3.5: Schematic diagram of various processes on the substrate at the initial stage of film growth with (a) deposition, (b) surface diffusion, (c) nucleation, (d) addition to existing clusters, (e) dissociation of clusters, and (f) evaporation.

Depending on the interaction between the substrate and adatoms, three different nucleation modes can be observed in the thin film growth processes: (1) Volmer-Weber growth mode (three dimensional island growth); (2) Frank van Merwe growth mode (two dimensional full-mono-layer growth); (3) Stranski-Krastanov growth mode (two dimensional...
full-mono-layer growth followed by island growth mode). The three growth modes are illustrated in Figure 3.6.

Figure 3.6. Schematic diagram of three basic growth modes. (a) three dimensional island growth; (b) two dimensional full-mono-layer growth; (3) two dimensional full-mono-layer growth followed by island growth mode.

The three growth modes can be understand by considering the thermodynamic equilibrium of a nucleus with thermodynamic parameters, such as the surface energy of the substrate (Γ_{vs}),
the surface energy of the film (Γ_{nv}) and the interfacial energy (Γ_{ns}). At the thermodynamic equilibrium at the interfacial between thin film and substrate, the surface energies satisfy the following equation:

$$\Gamma_{vs} = \Gamma_{ns} + \Gamma_{nv} \cos \theta$$  

(3.4)

Figure 3.7. Schematic diagram of a nucleation with thermodynamic equilibrium on a substrate surface.

1. Volmer-Weber growth mode

In this growth mode, since θ value satisfies the condition that $\theta > 0$, $\Gamma_{vs} < \Gamma_{ns} + \Gamma_{nv}$. As a result, small cluster-like islands are nucleated directly on the substrate and then form large 3-dimensional islands on the substrate. The islands can coalesce together and form a single continuous film. This type of growth can be widely observed in metals thin film grown on
oxide substrates.

2. Frank – van der Merwe growth mode

In this growth mode, the film “wets” the substrate leading to $\theta = 0$. In this case, nuclei tend to grow in 2 dimensional. The first atoms to arrive on the substrate will form a continuous monolayer film on which second layer of atoms will be grown. This mode can be commonly found in homoepitaxially grown films.

3. Stranski-Krastanov growth mode

In this mode, the surface and interfacial energies satisfy $\Gamma_{vs} < \Gamma_{ns} + \Gamma_{nv}$. The 3-dimensional islands tend to grow on underlying wetting layer, rather than directly on the substrate. It should be noted that the islands grown in this mode are coherently strained and dislocation free. The accumulated strain switches the growth mode from 2D to 3D is relieved by forming coherently strained islands instead of generating dislocations \([20,21]\). This mode has been observed in many heteroepitaxial semiconductor systems.

Thin film growth processes in PLD can be characterized by the properties of the laser-induced plasma plume. The plasma plume flux has characteristics of high density, high ionization degree (up to 70%), and high particle energy (from several eV to 2000 eV) \([22]\).

The dominant thermodynamic parameters determining the thin film growth are the substrate temperature $T$, plasma plume energy and supersaturation $\Delta m$. The $\Delta m$ is defined as \([23]\):

$$\Delta m = kT \ln\left(\frac{R}{R_e}\right)$$  \hspace{1cm} (3.5)
where $k$ is the Boltzmann constant, $R$ is the actual deposition rate, and $R_e$ is the equilibrium deposition rate at the temperature $T$. The supersaturation $\Delta m$ in PLD can be as high as $10^5$ J/mol.

The effect of plasma plume energy on thin film growth can be discussed as follows [22]:

1. The thermal energy of the evaporated particles.

When the thermal energy of evaporated particles is less than the dissociation energy of atomic bond of the target material, the grown thin films can keep the same stoichiometry as the target material. However, in the case of multi-component target, the stoichiometry may not be maintained in the grown films. If the thermal energy of evaporated particles is of the order of the dissociation energy, the target material may be partially or completely dissociated. As a result, stoichiometric films with high crystallinity and smooth surface can be obtained.

2. The kinetic energy of the evaporated particles.

When the kinetic energy of the particles is comparable to the defect formation energy of substrate material, radiative defects (vacancies) can be induced in the substrate. These defects may be used as additional nucleation sites. As a result, epitaxial growth can be realized at relatively low substrate temperature. At high laser beam intensity ($10^8$-$10^9$ W/cm$^2$), high density of energetic particles in the plasma plume can generate a thin layer ($\sim 30$ Å) of individual vacancies on top of the substrate. These vacancies diffuse into the substrate and
recombine in a time $\sim 10^{-8}$ s, which can increase the diffusion coefficient of grown films. This radiation stimulated diffusion process provides excellent adhesion of grown films on the substrate. This radiation-stimulated diffusion process may also be used to create abrupt doping profiles in semiconductors materials.

3.1.5 Principles of domain matching epitaxy

The term epitaxy is referred to the formation of extended single-crystalline thin films on single-crystalline substrates [24,25]. Epitaxy can be classified into two categories. If the grown film and substrate are same material, it is called homoepitaxy. Otherwise, it is termed as heteroepitaxy. The heteroepitaxy plays a critical role in modern electronic industrials. A variety of opto-electronic, optical and magnetic devices have been successfully developed [25].

Conventionally, the heteroepitaxy is restricted to small lattice misfit systems. Namely, the films can be grown epitaxially when lattice misfit between the film and the substrate is less than 7-8%. At higher misfits the films can be grown only textured or polycrystalline. This experimental observation leads to development of conventional lattice matching epitaxy (LME). In this theory, films will grow pseudomorphically up to a “critical thickness” where it then becomes energetically favorable for nucleation of dislocations [26]. The dislocations are created at the film surface and glide down to the interface of film and substrate. As a result, the burgers vector and planes of the dislocations are determined by the slip systems of
the thin films. In the case of 3-dimensional island growth, the dislocations are generated at
the edge of the islands during island coalescence. The schematic of LME is illustrated in
Figure 3.8.

![Schematic of LME](image)

**Figure 3.8.** Schematic illustration of thin films growth in the LME theory.

The advantages of PLD technique have lead to successful development of various
heteroepitaxial structure systems with large misfits (higher than 7 - 8\%) [27]. Narayan et. al.[28] has proposed the paradigm of domain matching epitaxy (DME) to describe the
heteroepitaxial growth of large lattice misfit systems. In this film growth paradigm, epitaxial
film growth occurs by matching of domains of lattice planes across the interface, where the
size of the domain is an integral multiple of planar spacings. For the film and substrate
having similar crystal structure, the matching of lattice planes reduces to matching of lattice
constants. The matching planes across the interface need not necessarily require the same
crystalline structure for the film and the substrate. Figure 3.9 illustrates the thin film growth paradigm of DME.

![Diagram showing domain-matching epitaxy growth](image)

Figure 3.9 Schematic illustration of domain-matching epitaxy growth. Five lattice planes of film match six lattice planes of substrate in the figure.

The misfit between the film and the substrate is accommodated by matching of integral multiple of planes, with one extra half plane (dislocation) existing in each domain. The accommodated lattice misfit can range from very small to very large values (1-50%). The matching of integral multiples of planes results in a residual misfit $\varepsilon_r$ which is defined by:

$$\varepsilon_r = \frac{md_f - nd_s}{nd_s} \quad \text{.................................................} \quad (3.6)$$

where $m$ planes of film with planar spacing match with $n$ planes of substrate with planar
spacing \(d_s\). It should be noted that Equation 3.6 will yield the definition of misfit \(\varepsilon_r\) in the LME if \(m\) and \(n\) are equal to one.

In the case of a perfect matching, \(\varepsilon_r\) is zero. If the misfit cannot be accommodated by a perfect integral matching of lattice planes, then two domains of different size can vary alternately with a frequency factor \(\alpha\).

\[
(m + \alpha) \cdot d_f = (n + \alpha) \cdot d_s \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3.7)
\]

Figure 3.10 shows a unified plot of strain vs film-substrate planar spacing ratio. The LME region was found to be above 12/13 ratio or below about 7.7% strain. Here \(n - m = 1\) for \(\varepsilon = 0 \sim 50\%\) and \(n - m = f(m)\) for \(\varepsilon = 50 \sim 100\%\). The basic assumption underlying the DME model is that complete relaxation strain takes place within the first couple mono layers without any dislocation barrier. Table 3.2 summarizes DME of various heteroepitaxial systems.

Figure 3.10 Unified plot of strain versus film-substrate planar spacing ratio [28].
Table 3.2 List of various heteroepitaxial systems based on DME \cite{28}.

<table>
<thead>
<tr>
<th>( m/n )</th>
<th>Planar spacing ratio</th>
<th>Experimental examples</th>
<th>Strain ( \varepsilon ) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/10</td>
<td>0.1</td>
<td>Mo, Nb, Ta, W/Si, NiAl/Si(100)</td>
<td>90.0%</td>
</tr>
<tr>
<td>1/9</td>
<td>0.11</td>
<td>Fe/Si, Cr/Si, NiAl/Si(100)</td>
<td>88.8%</td>
</tr>
<tr>
<td>1/8</td>
<td>0.125</td>
<td>Cu/Si(100)</td>
<td>87.5%</td>
</tr>
<tr>
<td>1/7</td>
<td>0.143</td>
<td>TiN/Si(100)</td>
<td>85.7%</td>
</tr>
<tr>
<td>1/6</td>
<td>0.166</td>
<td>AlN/Si(111)</td>
<td>83.3%</td>
</tr>
<tr>
<td>1/5</td>
<td>0.20</td>
<td>ZnO(0001)</td>
<td>80.0%</td>
</tr>
<tr>
<td>1/4</td>
<td>0.25</td>
<td>α-AlO(_3)/GaN(0001)</td>
<td>75.0%</td>
</tr>
<tr>
<td>1/3</td>
<td>0.33</td>
<td>Fe/Si(100)</td>
<td>66.7%</td>
</tr>
<tr>
<td>1/2 and 1/3</td>
<td>0.33–0.50</td>
<td>Mo, Nb, Ta, W/Si, NiAl/Si(100)</td>
<td>50.0%</td>
</tr>
</tbody>
</table>

3.2 Thin film characterization

The thin films grown by PLD in this study were characterized for the following properties:

1) X-ray diffraction (XRD) for structural characterization.

2) Transmission electron microscopy (TEM) for micro structural characterization.

3) Hall measurements and temperature dependent resistivity measurements for electrical
characterization.

4) Absorption/transmission spectroscopy for optical properties.

In the following sections the characterization techniques are discussed.

3.2.1 X-ray diffraction

XRD is a fundamental and characterization technique which is widely used for structure-related properties, such as lattice constant, identification of structure of unknown solids, orientation of single crystals, texture of thin films, phase compositions and defects, stress and strain \(^{[29]}\).

The basic principle of XRD is the constructive diffractions of X-ray beams by crystalline planes in the materials. In the case of solid materials, a parallel and monochromatic X-ray beam with a wavelength \(\lambda\) and incidence angle \(\theta\) is diffracted by a set of specific planes with certain orientation. Sharp diffraction peaks corresponding to certain set of planes can be detected when the conditions of the Bragg’s law are satisfied:

\[
2d \sin \theta = n \lambda \quad \cdots \quad (3.9)
\]

where \(n\) is an integer that indicates the order of the reflection, \(\theta\) is the Bragg angle, \(\lambda\) is the wavelength of incident x-ray beam and \(d\) is the planar spacing. The Bragg diffraction is illustrated in Figure 3.11
The relative intensity of the diffracted beam can be written as [30]:

\[
I = |F_{hkl}|^2 \frac{p}{\sin^2 \theta} \left(1 - \cos^2 2\theta \right)
\] ................................. (3.10)

\( P \) is the multiplicity factor representing the relative proportion of the planes contributing to the same reflection. The term in the bracket is known as Lorentz polarization factor. \( F_{hkl} \) is the structure factor which is the resultant complex wave scattered by all the atoms of the unit cell, given by:

\[
F_{hkl} = \sum_{n=1}^{N} f_n \exp\left\{2\pi i \cdot (h \cdot x_n + k \cdot y_n + l \cdot z_n)\right\}
\] ........................ (3.11)

where \( f_n \) is the atomic scattering factor and \((hkl)\) are the plane indices.

Various experimental methods can be used in the XRD technique, including X-ray
diffractometer, Laue method, rotating crystal method. For this study we used a Rigaku DMax A Powder diffractometer with Cu Kα radiation (λ = 1.54 Å). The Cu Kα beam is generated by a X-ray tube containing a tungsten filament (cathode) and a Cu target (anode). A high voltage (25 KV) induces the emission of electrons from the filament. The electrons are accelerated to bombard Cu target in order to produce X-ray beams. In this thesis work, 2θ scan is commonly used method. The diffractometer configuration of 2θ scan is shown in Figure 3.12.

![Figure 3.12 Schematic diagram of 2θ scan using X-ray diffractometer.](image)

3.2.2 Transmission electron microscopy

TEM is a very effective and direct technique for detailed microstructural characterization [31]. The high resolution (about a few Å) of TEM enables the atomic scale characterization of a
material. In this dissertation TEM analysis was done using a JEOL-2010F field-emission transmission electron microscope configured with GIF (Gatan Image Filter) for high resolution TEM.

The spatial resolution of a TEM is directly proportional to the wavelength of the probing electron beam. The wavelength of an electron beam accelerated with a voltage $V$ is given by:

$$\lambda = \frac{h}{\sqrt{2m_e eV}} \hspace{1cm} \text{(3.11)}$$

where $m_e$ is the rest mass of electron, $e$ is the electron charge and $h$ is Planck constant.

For a 200 KeV electron beam, the wavelength is $0.02507 \text{ Å}$.

According to the Raleigh criterion (shown below) resolution is directly proportional to wavelength $^{[31]}$.

$$\delta = 0.61 \frac{\lambda}{\beta} \hspace{1cm} \text{(3.12)}$$

However, the actual resolution of a TEM is limited by spherical aberrations and stigmatism. The actual resolution of JEOL 2010F TEM is about $0.12 \text{ nm}$ in high resolution Z-contrast mode and $0.18 \text{ nm}$ in high resolution TEM mode.

In general, a TEM consists of two major parts: the illumination system and the imaging system. The illumination system consists of the electron beam source and a series of electromagnetic lenses. $^{[31]}$. The electrons generated by an electron source are accelerated by a high voltage (200 KeV) and focused onto the sample using multiple electromagnetic lenses.
The electron beam interacts with the TEM sample. The scattered electron beam is captured by imaging system and recorded using a CCD camera or on a film. The important imaging techniques in this study were; diffraction/image, bright field and dark field and high resolution TEM.

1. Diffraction/image

The TEM generally operates in two modes: the diffraction mode and the image mode. The two modes can be switched by removal of SAD apertures and adjustment of focal length of intermediate lens. The two operational modes are illustrated in Figure 3.13.

![Figure 3.13 Illustration of two basic operational modes of TEM](image)

Figure 3.13 Illustration of two basic operational modes of TEM \[\text{[31]}\].
Diffraction patterns can be formed on the screen by placing the back focal plane on the objective plane of the intermediate and projector lens. The electrons elastically diffracted from the sample represent the reciprocal lattice of the material. Since the Ewald sphere will have a large radius, the low order diffraction spots are almost in a flat plane and can be projected on the screen \(^{[31]}\). Single crystal samples scatter the electron coherently and thus produce a spot diffraction pattern. The central spot is the transmitted beam of electrons and other spots are the diffracted electrons. Polycrystalline samples produce concentric ring patterns. Sample with nano-sized grains produce discontinuous arcs. The diffraction pattern of an amorphous sample will show a broad diffused ring.

2. Bright field and dark field image

In the diffraction mode, the diffraction pattern is formed on the back focal plane. The objective aperture is inserted into this plane so that only the beam from a selected diffraction spot can pass. If the central spot is selected in the aperture, the corresponding image in the image mode is bright field image. If any of other diffraction spots is selected, the corresponding image is a dark field image. The bright field and dark field imaging give opposite contrast. In a bright field image the vacuum is bright and in a dark field image, the film is bright. The best contrast is obtained in a two beam condition \(^{[31]}\). To get two-beam condition, the sample is titled such that only one strong diffracted beam is left. This is done usually using in the kikuchi pattern by tilting the sample so that the “deficient” line of one of
the pairs of the kikuchi lines is brought to the center.

3. High resolution TEM

HRTEM is an imaging technique where an atomic resolution image is formed due to the phase contrast which is caused by the difference of phases of scattered electron beams. It is very important to reach the Scherzer defocus condition to obtain the best resolution. The “Scherzer defocus” is an underfocus value, which minimize the objective astigmatism to obtain atomic scale HRTEM image.

3.2.3. Electrical characterization

The resistivity $\rho$ is an important parameter for electronic materials as well as for electronic devices. It is defined as follow:

$$\rho = \frac{1}{\sigma} = \frac{1}{q(nu_n + pu_p)} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \l
is elimination of parasitic voltage drops. Figure 3.14 illustrates the two-point and four-point probe measurement setup. In the two-point probe measurement, the total measured resistance \( R_T \) is given by:

\[
R_T = 2R_W + 2R_C + R_{DUT} \quad \text{(3.11)}
\]

where \( R_W \) is the wire or probe resistance, \( R_C \) is the contact resistance, and \( R_{DUT} \) is the resistance of the device under test. The \( R_{DUT} \) can only be determined if \( R_W \) and \( R_C \) are negligible compared with \( R_{DUT} \). However, in the case of four-point probe technique, the voltage is measured by two additional probes. Although the voltage path still contains \( R_W \) and \( R_C \), the current flowing through the voltage path is very low due to the high input impedance of the voltmeter (\( 10^{12} \) ohms or even higher). Hence, the voltage drops across \( R_W \) and \( R_C \) are always negligibly small and the measured voltage is essentially the voltage drop across the DUT.

![Diagram](image)

Figure 3.14 Arrangements of two-point and four-point probe measurement schemes [32].
Although the four probes can be arranged in a random manner, the dominant probe configuration is collinear, i.e., arranged in-line with equal probe spacing.

The voltage \( V \) is related to the current density \( J \) and the resistivity \( \rho \) through the relationship:

\[
\frac{dV}{dr} = -\frac{I\rho}{2\pi r^2} \quad \text{........................................... (3.12)}
\]

For a sample with semi-infinite geometry, the voltage at a particular point can be obtained by integrating over the entire sample:

\[
\int_{r}^{\infty} dV = -\int_{r}^{\infty} \frac{I\rho}{2\pi r^2} \cdot dr \quad \text{........................................... (3.13)}
\]

This integration yields the expression of voltage at this point:

\[
V = \frac{I\rho}{2\pi r} \quad \text{........................................... (3.14)}
\]

In the collinear configuration, the voltage at probe 2 and probe 3 can be written as:

\[
V_2 = \frac{I\rho}{2\pi s_1} - \frac{I\rho}{2\pi(s_2 + s_3)} \quad \text{........................................... (3.15)}
\]

\[
V_3 = \frac{I\rho}{2\pi(s_2 + s_3)} - \frac{I\rho}{2\pi s_3} \quad \text{........................................... (3.16)}
\]

where \( s_1, s_2 \) and \( s_3 \) are the distances between probes 1, 2, 3, 4, respectively.

Since \( s = s_1 = s_2 = s_3 \), the measured voltage between probe 2 and 3, the voltage measuring probes, can be reduced as:

\[
V = 2\pi s I\rho \quad \text{........................................... (3.17)}
\]
The equation 3.17 can be re-written as:

\[ \rho = 2\pi \frac{V}{I} \]  \hspace{1cm} (3.18)

In reality, the measured sample is not semi-infinite in extent in either the lateral or the vertical dimension and Equation 3.18 must be corrected for finite geometries. A thickness correction factor should be applied to Equation 3.18:

\[ F = \frac{t}{s} \cdot \frac{1}{2 \ln \left( \frac{\sinh(t/s)}{\sinh(t/2s)} \right)} \]  \hspace{1cm} (3.19)

where \( t \) is the sample thickness.

In the case of thin films, Equation 3.18 is reduced to:

\[ F = \frac{t}{s} \cdot \frac{1}{2 \ln 2} \]  \hspace{1cm} (3.20)

Combined with Equation 3.18, this resistivity of thin films can be expressed as:

\[ \rho = \frac{\pi}{\ln 2} \cdot t \cdot \frac{V}{I} \]  \hspace{1cm} (3.21)

Thin films are also characterized by their sheet resistance \( R_{sh} \) in units of ohms per square:

\[ R_{sh} = \frac{\rho}{t} = \frac{\pi}{\ln 2} \cdot \frac{V}{I} \]  \hspace{1cm} (3.22)

In this dissertation all resistivity measurements were performed using the four-point probe technique.

The Hall effect measurement is another widely applied technique in the materials
characterization, especially semiconductor materials, because it gives the resistivity, the carrier density and the mobility. The basic physical principle underlying the Hall effect is that the Lorentz force applied on the charge carriers in the presence of a magnetic field and internal electric field:

\[ F = q(E + v \times B) \]  

where B is magnetic field, E is internal electric field and v is the velocity of moving charge.

When an electron moves along a direction perpendicular to an applied magnetic field, it experiences a force acting normal to both the motion of the electron and the magnetic field and moves in response to this force. The Hall effect in the Hall bar configuration is illustrated in Figure 3.15. Electrons subject to the Lorentz force initially drift away from the current line toward the negative y-axis, resulting in an accumulation of surface charge on one side of the sample. This results in the voltage drop, known as Hall voltage (VH) across the two sides of the sample:

\[ V_H = \frac{I B}{e n d} \]  

where, I, e, n and d are the current, electron charge, electron density and thickness of the material, respectively.

Therefore the carrier density can be determined:

\[ n = \frac{I B}{e V_H d} \]
The mobility of the carriers can be determined once we know the carrier density and the resistance by using the following relation:

\[ \mu = \frac{1}{enR} \]  

(3.26)

Figure 3.15 Illustration of Hall effect in the bridge-type Hall bar configuration. The material is n-type and the majority carriers are electrons \(^{[33]}\).

The van der Pauw configuration is widely used in the semiconductor industry due to its convenience \(^{[34]}\). Instead of doing Hall measurement in relatively complicated Hall bar geometry, the Hall measurement can be carried out simply by making four point contacts on a flat sample with arbitrary shape. The van der Pauw configuration is extremely preferable
for the thin films, in which the Hall bar configuration can not be fabricated easily. The resistivity, carrier density, and mobility can be determined without knowing the current pattern in the sample. Van der Pauw has shown, based on conformal mapping theory, that the van der Pauw configuration is equivalent to the Hall bar configuration if the following conditions are met: the contacts are at the circumference of the sample and are sufficiently small, the sample is uniformly thick, and does not contain isolated holes.

In van der Pauw configuration, the resistivity can be expressed as:

$$\rho = \frac{\pi}{\ln 2} \cdot I \cdot \frac{V_{12,34} + V_{23,41}}{2} \cdot F \quad \text{........................................... (3.27)}$$

In Equation 3.26, $R_{12,34} = V_{34}/I$. The current I enters the sample through contact 1 and leaves through contact 2 and $V_{34} = V_3 - V_4$ is the voltage between contacts 3 and 4. $R_{23,41}$ is
similarly defined. F is defined as:

\[
\frac{R_r - 1}{R_r + 1} = \frac{F}{\ln 2} \cdot \arccosh \left( \frac{\exp(\ln 2 / F)}{2} \right) \quad \text{.......................... (3.28)}
\]

where \( R_r = R_{12,34}/R_{23,41} \).

The F value reduces to one if the sample is symmetric (circle and square).

The van der Pauw Hall mobility is determined by measuring the resistance \( R_{24,13} \) with and without a magnetic field. The definition of \( R_{24,13} \) is similar to \( R_{12,34} \) above. The Hall mobility is then given by

\[
\mu_H = \frac{\Delta R_{24,13}}{B \rho} \quad \text{.......................... (3.29)}
\]

where \( \Delta R_{24,13} \) is change of \( R_{24,13} \) due to applied magnetic field.

Practically, there are several issues need to be considered when carrying out Hall measurement, including ohmic contact quality and contact resistance, sample uniformity and thickness, photoconductive and photovoltaic effects.

3.2.4. Optical characterization

A variety of experimental techniques are used to characterize the optical properties of solid materials, including absorption/transmission spectroscopy, photoluminescence, and Raman spectroscopy. For semiconductor thin films, the absorption/transmission spectroscopy is the most fundamental technique to determine the material properties such as the absorption coefficient, transmission, bandgap, as well as thin film thickness.
In general, when a light beam travels through a medium, absorption, transmission and reflection can occur, as is shown in Figure 3.17. The absorbed, transmitted and reflected lights satisfy Equation 3.30:

\[ \%A + \%T + \%R = 1 \]  \hspace{1cm} (3.30)

The absorption coefficient \( \alpha \) is defined by the following differential equation:

\[
\frac{dI(\lambda)}{dx} = -\alpha(\lambda) \cdot I(\lambda) \hspace{1cm} \text{ (3.31)}
\]

where \( I(\lambda) \) is the intensity of light and \( x \) is the distance that the light propagates. This equation yields another equation, known as Beer-Lambert law:

\[
I(\lambda) = I_0(\lambda) \cdot e^{-\alpha(\lambda) \cdot x} \hspace{1cm} \text{ (3.32)}
\]

The absorption coefficient \( \alpha \) can be calculated as following:

\[
\alpha(\lambda) = -\frac{1}{d} \ln \left( \frac{I(\lambda)}{I_0} \right) \hspace{1cm} \text{ (3.33)}
\]

This equation is convenient to determine the absorption coefficient with a given thickness.

Figure 3.17 Illustration of absorption, transmission and reflection when a light travels through a medium.
An absorption spectrometer (or transmission spectrometer) is generally composed of one or two monochromators, light sources, and a photomultiplier. Figure 3.18 illustrates the absorption/transmission spectrometer used in this thesis work.

Figure 3.18 Schematic layout of Hitachi U-3010 UV-Visible spectrometer.
The spectrometer is equipped with a W lamp as a light source in the visible range (from 1000 nm to 320 nm) and a deuterium lamp for the ultraviolet range (from 320 nm to 200 nm). The incident light is first split into a monochromatic beam by a pre-monochromator. The monochromatic beam is then split into two beams for the dual-beam measurement configuration. One of the beams transmits through the sample and the other one transmits through the reference. The transmitted beams are then passed through the main monochromator and their intensities are measured by a photomultiplier. Given the thickness of measured film, the absorption coefficient can be determined from logoritm of the ratio of $I(\lambda)/I_0$. 
References


33 http://www.nist.gov/eeel/semiconductor/hall.cfm

Chapter 4 Growth of Mg$_x$Zn$_{1-x}$O thin films

4.1 Abstract

Pulsed laser deposition was used to deposit magnesium zinc oxide films on amorphous fused silica substrates at several temperatures between room temperature and 750 °C. The optical properties of the films were investigated by absorption and photoluminescence spectra. Photoluminescence spectra were measured for the films deposited at 250 °C, 350 °C, 450 °C and 650 °C, and photoluminescence behavior was correlated with Urbach energy values. The film grown at 350 °C exhibited lower band-tail parameter values and higher photoluminescence values than the other films. These results suggest that Mg$_{0.15}$Zn$_{0.85}$O thin films grown using pulsed laser deposition have numerous potential applications, including use in ultraviolet-blue laser diodes, flat panel displays, and medical devices.
4.2 Introduction

Zinc oxide (ZnO) is a wide bandgap semiconductor. It has a direct bandgap of 3.4 eV and larger excitonic binding energy of about 60 meV, which makes it very promising material for use in a variety of optoelectronic applications, such as blue-ultraviolet (UV) light emitting diodes, lasers diodes and ultraviolet detector. One interesting feature of zinc oxide is that it can be alloyed with magnesium oxide in order to form Mg$_x$Zn$_{1-x}$O semiconductor alloys [1,3]. The alloys have tunable bandgap in the UV wavelength range, which raises the possibility of bandgap engineered heterostructure for optoelectronic applications in the UV range. For example, McClintock et al. have recently developed Mg$_x$Zn$_{1-x}$O alloy quantum wells for use in light emitting diodes [4].

Mg$_x$Zn$_{1-x}$O thin films have been deposited by various deposition techniques, such as molecular beam epitaxy (MBE), metalorganic vapor-phase epitaxy (MOVPE), magnetron sputtering, sol-gel and pulsed laser deposition. The atomic radii of zinc and magnesium have similar values (~1.36 Å). As a result, zinc can be substituted for magnesium in the cubic magnesium oxide structure, and magnesium can be substituted for zinc in the hexagonal wurzite zinc oxide structure. The equilibrium solid solubility of magnesium in hexagonal zinc oxide is limited to a maximum of 4% [2]. However, this value can be exceeded in magnesium zinc oxide alloys that are prepared using non-equilibrium processes.

In our earlier work, we used high-power pulsed laser deposition to prepare magnesium zinc oxide alloy thin films with significantly higher magnesium concentrations than those predicted from thermodynamic considerations. The pulsed laser deposition process produces ionic, atomic, and molecular species with kinetic energies on the order of 100-1000 kT.
(2.5-25 eV), whereas thermal processes (e.g., evaporation) generate species with energies on the order of kT (0.025 eV at ambient temperature). We have obtained bandgap values between 3.39 eV (x=0) and 4.42 eV (x=0.34) in hexagonal phase Mg_xZn_{1-x}O alloy films prepared using pulsed laser deposition. In addition, we used pulsed laser deposition to prepare a cubic phase Mg_{0.82}Zn_{0.18}O alloy, which exhibited a bandgap energy of 6.7 eV [5].

Ohtomo et al. recently demonstrated fabrication of Mg_xZn_{1-x}O/ZnO/Mg_xZn_{1-x}O superlattice structures [6]. One of the concerns related to fabrication of these structures is that magnesium diffusion at high temperatures (650-750 °C) can destroy the superlattice heterostructure. As such, processing temperature is an important parameter in the fabrication of Mg_xZn_{1-x}O-based optoelectronic devices. In this study, we evaluated the effect of deposition temperature on the structural and optical properties of Mg_{0.15}Zn_{0.85}O thin films prepared using pulsed laser deposition. Films were prepared at several deposition temperatures, including room temperature, 150 °C, 250 °C, 350 °C, 450 °C, 550 °C, 650 °C, and 750 °C. Film crystallinity and microstructure were examined using transmission electron microscopy and X-ray diffraction. Absorption and photoluminescence spectra were obtained in order to determine the optical properties of these materials. Determining the relationship between deposition temperature and optical behavior for magnesium zinc oxide thin films will facilitate the development of novel optoelectronic and microelectronic devices [7,8].

4.3 Experimental procedure

In this study, magnesium zinc oxide alloy films were grown on amorphous fused silica substrates (Alfa Aesar, Ward Hill, MA) using pulsed laser deposition. The magnesium oxide-zinc oxide composite target was prepared using a conventional calcine-sintering
method. 99.99% metals basis zinc oxide powder (Alfa Aesar, Ward Hill, MA) and >99% purity magnesium oxide powder (Honeywell Specialty Materials, Morristown, NJ) were mixed in methanol solution for one hour using a magnetic stirring plate. The mixture was subsequently evaporated on a hot plate for 48 hours to completely remove the methanol solvent. The mixture was then pressed into a one inch diameter die in order to form a pellet. The pellet was then sintered in air for twenty-four hours.

\( \text{Mg}_{0.15}\text{Zn}_{0.85}\text{O} \) thin films were deposited in a high vacuum chamber. The base pressure used in these studies was \( \sim 3 \times 10^{-6} \text{Torr} \). A KrF (\( \lambda = 248 \text{ nm} \)) excimer laser (Lambda Physik, Fort Lauderdale, FL) was used to ablate the magnesium oxide-zinc oxide composite target. The output laser pulse exhibited a frequency of 10 Hz and a pulse duration of 25 ns. The energy density used in these studies was 3.5 - 4.5 J/cm\(^2\). When laser radiation is absorbed by the target surface, electromagnetic energy is converted into electronic excitation, chemical energy, mechanical energy, and thermal energy to form a plasma plume. Immediately after ablation, the plasma plume expands with hydrodynamic flow from the target surface. The plume propagates in a forward-peaked manner towards the substrate. The deposition time was maintained at ten minutes for this study. Magnesium zinc oxide films were prepared at room temperature, 150 °C, 250 °C, 350 °C, 450 °C, 550 °C, 650 °C, and 750 °C. The film thickness is about 100 - 150nm.

\( \theta-2\theta \) scans were obtained by means of an X-ray diffractometer (Rigaku, The Woodlands, TX) using copper K\( \alpha \) radiation (\( \lambda = 0.154 \text{ nm} \)) and a nickel filter. Selected area electron diffraction and high resolution imaging of the \( \text{Mg}_{0.15}\text{Zn}_{0.85}\text{O} \) thin films were obtained using a 2010F analytical electron microscope (JEOL, Tokyo, Japan). Absorption spectra were
determined using a U-3010 ultraviolet-visible spectroscopy spectrometer (Hitachi, Tokyo, Japan). Photoluminescence spectra were measured using an F-2500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan). Both absorption and photoluminescence spectra were obtained at room temperature.

4.4 Results and discussion

The crystallinity of the Mg$_{0.15}$Zn$_{0.85}$O thin films was examined using X-ray diffraction (Figure 4.1). The films deposited at 150 °C, 250 °C, 350 °C, 450 °C, 550 °C, 650 °C, and 750 °C exhibited two reflection peaks, which were indexed as the (0002) and (0004) peaks of the wurtzite structure. No other peaks were identified, which indicated that phase separation did not occur. The (0002) and (0004) peaks were not observed in the X-ray diffraction pattern of the Mg$_{0.15}$Zn$_{0.85}$O thin film deposited at room temperature due to small grain size. Grain size in this material was confirmed using high resolution transmission electron microscopy (Figure 4.2). The Mg$_{0.15}$Zn$_{0.85}$O thin film deposited at room temperature exhibited a nanocrystalline structure, in which columnar grains with sizes under 5 nm were observed.
Figure 4.1 X-ray diffraction patterns for Mg$_{0.15}$Zn$_{0.85}$O thin films grown at several temperatures.
Figure 4.2 High resolution transmission electron micrograph of Mg$_{0.15}$Zn$_{0.85}$O thin film grown at room temperature.

Figure 4.3(a) contains the absorption spectra for Mg$_{0.15}$Zn$_{0.85}$O thin films deposited at room temperature and 150 °C. Excitonic peaks were not present in the films grown at room temperature and 150 °C. Bandgap values for these films did exhibit a blue shift, in which the film grown at the higher deposition temperature (150 °C) exhibited a larger bandgap energy.
than the film grown at the lower deposition temperature (room temperature). Figure 4.3(b) contains the absorption spectra for films deposited at 250 °C, 350 °C, 450 °C, 550 °C, 650 °C, and 750 °C. Excitonic peaks were observed in these films. In addition, a blue shift of excitonic peak was observed for these films. The possible reason is that the deposition temperature may affect the Mg concentration in the alloy. At low temperature, a considerable fraction of Mg atoms may not be in substitutional sites, thus the actual Mg concentration in the alloy may be lower than 15%.

Figure 4.3 (a) Absorption spectra for Mg$_{0.15}$Zn$_{0.85}$O thin films grown at room temperature and 150 °C. (b) Absorption spectra for Mg$_{0.15}$Zn$_{0.85}$O thin films grown 250 °C, 350 °C, 450 °C, 550 °C, 650 °C, and 750 °C.
The bandgap was determined using by fitting the absorption spectra near the absorption edge using the following equation [9]:

\[ \alpha(E) = \alpha_0 \exp\left(\frac{E - E_g}{E_u}\right) \]

for \( E < E_g \). In equation 1, \( \alpha_0 \) is a pre-exponential factor, \( E_g \) is the bandgap, and \( E_u \) is the Urbach energy.\(^\text{10}\) The bandgap and Urbach energy values for Mg\(_{0.15}\)Zn\(_{0.85}\)O thin films grown at room temperature, 150 °C, 250 °C, 350 °C, 450 °C, 650 °C, and 750 °C are listed in Table 1.

In Figure 4.4, fitting results are shown for Mg\(_{0.15}\)Zn\(_{0.85}\)O films deposited at room temperature, 350 °C, and 750 °C. In this figure, the fitting functions are shown as solid lines.

Table 4.1 Bandgap energy values and Urbach energy values for magnesium zinc oxide thin films grown at several temperatures.

<table>
<thead>
<tr>
<th>deposition temperature (°C)</th>
<th>bandgap (eV)</th>
<th>Urbach energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>room temperature</td>
<td>3.49</td>
<td>0.162</td>
</tr>
<tr>
<td>150</td>
<td>3.51</td>
<td>0.176</td>
</tr>
<tr>
<td>250</td>
<td>3.58</td>
<td>0.099</td>
</tr>
<tr>
<td>350</td>
<td>3.62</td>
<td>0.064</td>
</tr>
<tr>
<td>450</td>
<td>3.64</td>
<td>0.069</td>
</tr>
<tr>
<td>550</td>
<td>3.66</td>
<td>0.073</td>
</tr>
<tr>
<td>650</td>
<td>3.69</td>
<td>0.075</td>
</tr>
<tr>
<td>750</td>
<td>3.71</td>
<td>0.083</td>
</tr>
</tbody>
</table>
Figure 4.4 Absorption spectra for $\text{Mg}_{0.15}\text{Zn}_{0.85}\text{O}$ thin films grown at room temperature (red circles), 350 °C (green squares), and 750 °C (blue triangles). Simulation data are shown as solid lines.

Bandgap energy and Urbach energy are shown as a function of deposition temperature in Figure 5(a) and Figure 5(b), respectively. As seen in the absorption spectra, $\text{Mg}_{0.15}\text{Zn}_{0.85}\text{O}$ films grown at higher temperatures exhibited larger bandgap energy. The film deposited at 750 °C demonstrated a bandgap energy of 3.71 eV, which is similar to the value obtained from an epitaxial $\text{Mg}_{0.34}\text{Zn}_{0.66}\text{O}$ thin film grown on a c-plane sapphire substrate (3.73 eV) [11]. The $\text{Mg}_{0.15}\text{Zn}_{0.85}\text{O}$ films deposited at room temperature and 150 °C exhibited high Urbach energy. In these films, band-tail spreading may mask the excitonic peaks. On the other hand, films grown at temperatures greater than 250 °C did not exhibit significant band-tail effects.
Figure 4.5 (a) Bandgap energy values for $\text{Mg}_{0.15}\text{Zn}_{0.85}\text{O}$ thin films as a function of temperature. (b) Urbach energy values for $\text{Mg}_{0.15}\text{Zn}_{0.85}\text{O}$ thin films as a function of temperature.

Figure 4.6 contains photoluminescence spectra for $\text{Mg}_{0.15}\text{Zn}_{0.85}\text{O}$ thin films deposited at 250 °C, 350 °C, 450 °C, and 650 °C. Both excitonic emission and green band emission were observed in the photoluminescence spectra. In these films, the excitonic emission peak was observed at ~350 nm. The green band emission peak centered at ~480 nm was attributed to oxygen vacancies, donor-acceptor pairs, and other defects. The film deposited at 350 °C exhibited the highest excitonic emission intensity. On the other hand, the film grown at 250 °C showed the lowest excitonic emission intensity. $\text{Mg}_{0.15}\text{Zn}_{0.85}\text{O}$ films grown on amorphous fused silica substrates using pulsed laser deposition contain structural defects (e.g., voids and nodules) in addition to substitutional defects. These defects may result in band-tail spreading, which in turn may influence photoluminescence behavior.
Figure 4.6 Photoluminescence spectra for Mg$_{0.15}$Zn$_{0.85}$O thin films grown at 250 °C (blue lines), 350 °C (black lines), 450 °C (red lines), and 650 °C (green lines).

4.5 Conclusions

We have deposited Mg$_{0.15}$Zn$_{0.85}$O thin films on amorphous fused silica substrates at several temperatures using pulsed laser deposition. X-ray diffraction also showed that the films grown at temperatures between 250 °C and 750 °C exhibited similar degrees of crystallinity. Bandgap values were obtained from the absorption data, and larger bandgap values were observed in films grown at higher temperatures. The Mg$_{0.15}$Zn$_{0.85}$O film deposited at 750 °C exhibited a bandgap value similar to that for an epitaxial Mg$_{0.34}$Zn$_{0.66}$O thin film grown on a sapphire substrate. Photoluminescence values were in good agreement with Urbach energy values that were determined from absorption data. The highest photoluminescence properties were observed in the Mg$_{0.15}$Zn$_{0.85}$O film that was deposited at 350 °C. This film also exhibited the lowest amount of band-tail spreading. These results suggest that Mg$_{0.15}$Zn$_{0.85}$O
thin films grown using pulsed laser deposition have numerous potential optoelectronic applications, including use in ultraviolet-blue laser diodes, flat panel displays, and medical devices.
References


Chapter 5 Bandgap effect on optical and electrical properties of Ga-doped Mg_xZn_{1-x}O thin films

5.1 Abstract

The optical and electrical properties of heavily Ga-doped Mg_xZn_{1-x}O thin films were investigated. The films were grown epitaxially on c-plane sapphire using pulsed laser deposition. The film transparency is greater than 90% in the visible spectrum range. The absorption can be extended to lower wavelength range with higher magnesium concentration, which can improve the transparency in the ultraviolet wavelength range; however, conductivity is decreased. The optimal Ga concentration was found to be 0.5 at. %. At this Ga concentration, the film resistivity increased from $1.9 \times 10^{-3}$ to $3.62 \times 10^{-2}$ $\Omega$ cm, as the magnesium concentration increased from 5 at. % to 15 at. %.
5.2 Introduction

Transparent conducting oxides (TCOs) represent a class of materials used in opto-electronic devices such as flat panel displays and thin film solar cells [1]. At present, indium doped tin oxide (ITO) is the most widely used TCO material. However, there is a concern about the indium supply since indium has limited natural sources. In recently years, considerable research efforts have been devoted to developing possible alternative TCO materials. Zinc oxide doped with group III elements (e.g. aluminum and gallium) are considered to be the most promising candidates since zinc oxide is quite abundant and can have varying bandgap through alloying. The resistivity of doped zinc oxide is in the range of $10^{-5}$ to $10^{-4} \, \Omega \, \text{cm}$; and the transparency is improved in the ultraviolet (UV)-visible wavelength range compared with ITO [2].

Zinc oxide can be alloyed with magnesium oxide (Mg$_x$Zn$_{1-x}$O). The bandgap of Mg$_x$Zn$_{1-x}$O can be engineered between 3.3 eV (ZnO) to 7.8 eV (MgO). The crystalline structure can be either hexagonal or cubic when the magnesium concentration exceeds 40% [3]. The single crystalline hexagonal Mg$_x$Zn$_{1-x}$O film can contain magnesium concentration up to 36% by pulsed laser deposition (PLD) without phase separation. The corresponding bandgap was found to vary from 3.3 eV to 4.0 eV [4]. With increasing bandgap, the optical transparent window can be extended to UV wavelength range. This is desirable for opto-electronic devices working in UV range, e.g. thin film solar cells, since absorption will not occur to the transmitted UV light. The Mg$_x$Zn$_{1-x}$O thin film has been demonstrated as the transparent window layer for thin film solar cells and ITO was used as the electrode layer [5]. The Al and Ga can be doped in the Mg$_x$Zn$_{1-x}$O to enhance conductivity [6,7,8,9]. These conductive films
can be used as electrode layers whose transparency can be tuned as the bandgap is engineered by controlling magnesium oxide concentration in the alloy. There are several reports about the electrical and optical properties of aluminum-doped and Ga-doped Mg$_x$Zn$_{1-x}$O thin films. For example, Matsubara et. al. [6] demonstrated that aluminum-doped Mg$_x$Zn$_{1-x}$O, deposited on glass was a bandgap tunable TCO film. The reported resistivity varied between 3×10$^{-4}$ Ω cm and 1×10$^{-3}$ Ω cm as the bandgap was increased from 3.5 eV to 3.97 eV. The average transmittance was above 90% in visible wavelength region. Harada et. al. [7] deposited Ga-doped Mg$_x$Zn$_{1-x}$O by molecular beam epitaxy. However the phase separation occurred when the Ga concentration exceeded 1×10$^{18}$ cm$^{-3}$. Due to the low dopant concentration, the resistivity of single-phase Ga-doped Mg$_{0.1}$Zn$_{0.9}$ films were in the range of 1~10 Ω cm. In addition, the electrical and optical properties due to the bandgap engineering on doped Mg$_x$Zn$_{1-x}$O films were not studied in detail.

In this paper, we report our studies on the electrical and optical properties of heavily Ga-doped Mg$_x$Zn$_{1-x}$O thin films grown epitaxially on c-plane sapphire by PLD. The Ga concentration was varied from 0.5 at. %, 1 at. % to 3 at.%, and the magnesium concentration was varied from 5 at. %, 10 at. % to 15 at. %. The nonequilibrium nature of PLD enables growth of single-crystalline Mg$_x$Zn$_{1-x}$O thin films with Ga concentration exceeding thermodynamic equilibrium solubility limit [10].

5.3 Experiment

Ga-doped Mg$_x$Zn$_{1-x}$O thin films were grown on double sides polished sapphire by PLD. The substrate temperature was about 450 °C measured by a thermocouple welded in the heater. The film thickness was 500 nm. The target-to-substrate distance was 45 mm. The PLD
chamber was pumped to a base pressure of 2×10^{-6} torr. The oxygen partial pressure was kept at 2×10^{-5} torr during deposition. The multi-component ceramic targets were prepared using a conventional calcine-sintering method. Zinc oxide powder (purity: 99.99%, Alfa Aesar), magnesium oxide (purity: 99.99%, Alfa Aesar) and Ga_2O_3 (purity: 99.99%, Aldrich Chemical Company) were mixed in methanol solution using a magnetic stirring plate. The methanol solvent was subsequently removed by heating on a hot plate. The mixture was pressed into a 1 inch pellet target and sintered at 1000°C in air for 24 hours. A KrF excimer laser (COMPex 205, Lambda Physik) was used for target ablation. The laser wavelength was 248 nm and pulse duration was 25 ns. The energy density of laser spot was approximately 3.5-4.5 J/cm^2.

Samples were characterized by various techniques for its structural, chemical, electrical and optical properties. The crystalline structure was investigated by an X-ray diffraction (Rigaku, TX) using CuKα radiation and a nickel filter. The optical spectra were measured by a UV-Vis dual-beam spectrometer (U-3010, Hitachi). The Hall measurements (ECOPIA HMS-3000, Bridge Technology) were done by van der Pauw configuration at room temperature. Chemical analysis was performed by an X-ray photoelectron spectrometer (Kratos Analytical, NY), using a monochromatic aluminum Kα source. The sample was sputtered with Argon ions for two minutes to remove possible surface contamination.

5.4 Results and discussion

XRD 0-2θ curves for Mg_{0.1}Zn_{0.9}O thin films doped with 0.5 at. %, 1 at. % and 3 at. % Ga are shown in Figure 5.1. Two of the peaks in the spectra correspond to the (0002) and (0004) diffraction peaks of the wurtzite Mg_xZn_{1-x}O structure. The other two peaks in the spectra are
attributed to the (0006) and (00012) peaks of sapphire substrate. The split in the sapphire peaks was caused by the CuKα2 (λ = 0.15444 nm), which was not completely filtered from the CuKα1 (λ = 0.15406 nm). No evidence of phase separation or large size precipitates was observed in these films. The Ga-doped Mg,Zn_{1-x}O thin films are c-axis textured according to the θ-20 curves. Taking previous findings into account, these Ga-doped Mg,Zn_{1-x}O thin films were grown epitaxially on c-plane sapphire [11]. The epitaxial growth can be explained using domain matching epitaxy. The large misfit between Mg,Zn_{1-x}O and sapphire can be significantly reduced by matching five [0110] planes of Ga-doped Mg,Zn_{1-x}O with six [2110] planes of sapphire, reducing misfit from 37% to 0.24% [11].

![X-ray diffraction data](image)

Figure 5.1 X-ray diffraction data (θ-20 scan) for 0.5% Ga-doped Mg,Zn_{1-x}O thin films. Data for films with magnesium concentration (x) of 5%, 10% and 15% are shown.
Figure 5.2 shows the X-ray photoelectron spectrum of 0.5 at. % Ga-doped Mg$_{0.15}$Zn$_{0.85}$O thin film. Peaks at 1144.9 eV and 1117.9 eV were attributed to Ga 2p$_{1/2}$ and Ga 2p$_{3/2}$, respectively. The positions of Ga peaks are in good agreement with previous work and suggest that Ga is primarily found in the Ga$^{3+}$ state [12].

![X-ray photoelectron spectrum of 0.5% Ga-doped Mg$_{0.15}$Zn$_{0.85}$O thin film.](image)

The optical properties of Ga-doped Mg$_x$Zn$_{1-x}$O thin films were investigated in the ultraviolet-visible wavelength range using absorption and transmission spectra. Figure 5.3 (a) and (b) are transmission and absorption spectra of 1 at. % Ga-doped Mg$_x$Zn$_{1-x}$O with $x = 0.05$, 0.10 and 0.15, respectively. In the transmission spectrum, the transparency exhibited in all the samples was generally greater than 90% in the visible spectrum region (photon energy = 1.65
~ 3.1 eV, \( \lambda = 400 \sim 750 \) nm), which is comparable with reported values [6]. In the absorption spectra, the fundamental absorption edge shifts to lower wavelength region, which indicates an increase of bandgap, as the sample contains higher magnesium concentration. This shift improves optical transparency in the lower wavelength region. In Figure 3(a), the onset of absorption edge extends roughly from \( \lambda = 355 \) nm (3.49 eV) to \( \lambda = 340 \) nm (3.65 eV) when the magnesium concentration increases from 5 at. % to 15 at. %.
Figure 5.3 (a) Transmission spectra of 0.5% Ga-doped Mg$_x$Zn$_{1-x}$O thin films with fitting curves (solid lines). (b) Absorption spectra of 0.5% Ga-doped Mg$_x$Zn$_{1-x}$O thin films with fitting curves (solid lines).
The bandgap can be determined by fitting the absorption spectra with Urbach equation near the fundamental absorption edge. The Urbach equation is defined as below [14]:

\[
\alpha(E) = \alpha_0 \exp\left(\frac{E - E_g}{E_u}\right)
\]

(5.1)

In this equation, \( \alpha_0 \) is a pre-exponential factor and \( E_g \) is the bandgap. \( E_u \) is the Urbach energy, which is also known as band tail parameter. This equation is valid for \( E < E_g \) region, where the exponential band tail absorption dominates. The fitting curves are plotted as solid lines in Figure 5.3 (b). The \( E_g \) values extracted from the equation are 3.59 eV, 3.68 eV, and 3.78 eV, respectively. These values are slightly higher than that previously results for undoped Mg\(_x\)Zn\(_{1-x}\)O thin films [11]. This is known as Burstein-Moss effect caused by high carrier concentration in the conduction band [13].

The electrical properties of all samples, including Hall mobility, carrier concentration and resistivity are summarized in Table 5.1. At a given Ga concentration, Hall mobility (\( \mu \)) is found to decrease with higher Mg concentration, which is consistent with other reports [8,15]. This can be explained by increase of electron effective mass with higher magnesium concentration [8]. The mobility (\( \mu \)) can be defined using the following equation:

\[
\mu = \frac{q < \tau >}{m^*}
\]

(5.2)

\( < \tau > \) is electron average scattering time. \( q \) is the electron charge. At a given doping concentration, it is reasonable to assume \( < \tau > \) is a constant. Hence, the mobility is determined by electron effective mass. With higher magnesium concentration, the electron effective mass is increased, which in turn decreases the mobility. The highest mobility
achieved is $34 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, from the sample with 5 at. % Mg (Ga concentration is 0.5 at. %). This mobility value is in good agreement with the highest values ($40\text{~}50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) \cite{6,8,15}. The carrier concentration is also decreased with increasing magnesium concentration, which indicates that the addition of magnesium can lower Ga doping efficiency.

Table 5.1 Carrier concentration and mobility of Ga-doped Mg$_x$Zn$_{1-x}$O thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carrier concentration ($10^{20} \text{ cm}^{-3}$)</th>
<th>Mobility (cm$^2$/Vs)</th>
<th>Resistivity ($10^{-3} \text{ \Omega cm}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%Ga:Mg$<em>{0.05}$Zn$</em>{0.95}$O</td>
<td>0.93</td>
<td>34.0</td>
<td>1.9</td>
</tr>
<tr>
<td>1.0%Ga:Mg$<em>{0.05}$Zn$</em>{0.95}$O</td>
<td>1.12</td>
<td>23.2</td>
<td>2.4</td>
</tr>
<tr>
<td>3.0%Ga:Mg$<em>{0.05}$Zn$</em>{0.95}$O</td>
<td>0.27</td>
<td>6.3</td>
<td>36.2</td>
</tr>
<tr>
<td>0.5%Ga:Mg$<em>{0.10}$Zn$</em>{0.90}$O</td>
<td>0.51</td>
<td>21.8</td>
<td>3.1</td>
</tr>
<tr>
<td>1.0%Ga:Mg$<em>{0.10}$Zn$</em>{0.90}$O</td>
<td>0.92</td>
<td>14.8</td>
<td>9.5</td>
</tr>
<tr>
<td>3.0%Ga:Mg$<em>{0.10}$Zn$</em>{0.90}$O</td>
<td>0.13</td>
<td>4.9</td>
<td>324.8</td>
</tr>
<tr>
<td>0.5%Ga:Mg$<em>{0.15}$Zn$</em>{0.85}$O</td>
<td>0.34</td>
<td>21.0</td>
<td>8.3</td>
</tr>
<tr>
<td>1.0%Ga:Mg$<em>{0.15}$Zn$</em>{0.85}$O</td>
<td>0.21</td>
<td>11.8</td>
<td>25.0</td>
</tr>
<tr>
<td>3.0%Ga:Mg$<em>{0.15}$Zn$</em>{0.85}$O</td>
<td>0.03</td>
<td>1.3</td>
<td>1600.0</td>
</tr>
</tbody>
</table>

The film resistivity is generally increased with higher magnesium concentration. The lowest resistivity is $1.9\times10^{-3} \text{ \Omega cm}$, achieved from the sample with 5 at. % magnesium (Ga concentration is 0.5 at. %). This resistivity value is comparable with reported results \cite{8,9}. However, a low resistivity of $3\times10^{-4} \text{ \Omega cm}$ has been reported \cite{6}, which was obtained from polycrystalline Al-doped Mg$_x$Zn$_{1-x}$O grown at 200$^\circ$C. The relatively low substrate temperature may be the cause of low resistivity since the resistivity is increased as the substrate temperature is increased from 250$^\circ$C to 500$^\circ$C \cite{9}. Our studies (not shown here) also
indicate that low growth temperature can decrease the resistivity further, but it lowers optical transparency.

At 0.5 at. % Ga concentration, the film resistivity is increased from $1.9 \times 10^{-3} \Omega \text{ cm}$ to $3.62 \times 10^{-2} \Omega \text{ cm}$ as the magnesium concentration changes from 5 at. % to 15 at. %. Based on the optical and electrical data, the addition of Mg creates a tradeoff between optical transparency and resistivity in Ga-doped Mg$_{x}$Zn$_{1-x}$O films. Namely, with higher magnesium concentration, the film exhibits higher transparency in the ultraviolet region while it becomes more resistive. To optimize the resistivity, the Ga concentration is increased from 0.5 at. % to 3 at. %. However, the increase of Ga concentration does not lead to decrease of resistivity.

The resistivity $\rho$ is defined as $\rho = \frac{1}{\mu \cdot n \cdot e}$. The measured carrier concentration in Table 5.1 shows higher Ga concentration does not lead to higher carrier concentration. For example, in the samples with 5 at. % magnesium, the carrier concentration slightly increases from $9.3 \times 10^{19} \text{ cm}^{-3}$ to $1.12 \times 10^{20} \text{ cm}^{-3}$. However, it decreases significantly to $2.7 \times 10^{19} \text{ cm}^{-3}$ as Ga concentration is further increased from 1 at. % to 3 at. %. For the sample containing 15 at. % magnesium, the carrier concentration continuously decreases with increasing Ga concentration. This observation is very important for device applications. It shows that the decrease of conductivity caused by addition of magnesium may not be compensated by simply increasing Ga dopant concentration. The significant drop of carrier concentration at high Ga concentration indicates that a considerable fraction of Ga dopants are not electrically active, which is consistent with results from Cornelius et al.\[15\]. The optimum Ga
concentration is found to be about 0.5 at. % in this study, which seems reasonable since a solubility limit of 3 % aluminum in zinc oxide has been reported recently [16].

5.5 Summary

Heavily Ga-doped Mg$_x$Zn$_{1-x}$O thin films were epitaxially grown on sapphire substrates using pulsed laser deposition. The films were highly transparent (transparency $\geq$ 90%) in visible wavelength region. When the magnesium concentration was increased from 5 at. % to 15 at. %, the bandgap was increased from 3.59 eV to 3.78 eV, determined by fitting the absorption spectrum. The absorption edge extends roughly from $\lambda = 355$ nm to $\lambda = 340$ nm in transmission spectrum. At the same time, the resistivity was decreased from $1.9\times10^{-3}$ $\Omega$ cm to $3.62\times10^{-2}$ $\Omega$ cm. The resistivity was increased at higher Ga concentration, with an optimum Ga concentration of 0.5 at. %.
References


Chapter 6 Optical and electrical properties of Ga-doped Mg_xZn_{1-x}O

6.1 Abstract

In this study, the optical and electrical properties of epitaxial single crystal Ga-doped Mg_xZn_{1-x}O thin films grown on c-plane sapphire substrates by pulsed laser deposition were investigated. In these films, the Ga content was varied from 0.05 at.% to 7 at.% and the Mg content was varied from 5 at.% to 15 at.%. X-ray diffraction showed that the solid solubility limit of Ga in Mg_xZn_{1-x}O is less than 3 at.%. The absorption spectra were fitted to examine Ga doping effects on bandgap and band tail characteristics. Distinctive trends in fitted bandgap and band tail characteristics were determined in films with Ga content below 3 at.% and Ga content above 3 at.%. The effects of bandgap engineering on optical transparency were evaluated using transmission spectra. Carrier concentration and Hall mobility data were obtained as functions of Ga and Mg content. The electrical properties were significantly degraded when the Ga content exceeded 3 at.%. Correlations between conduction mechanisms and Ga doping of Mg_xZn_{1-x}O thin films were described. In addition, the effect of bandgap engineering on the electrical properties of epitaxial single crystal Ga-doped Mg_xZn_{1-x}O thin films was discussed.
6.2 Introduction

Transparent conducting oxides (TCOs) are used in a variety of opto-electronic devices, including flat panel displays and thin film solar cells [1]. Indium doped tin oxide (ITO) is the most widely used commercial TCO material. In recent years, a concern about the availability of indium has risen due to the fact that indium is a limited natural resource [1]. As a result, significant research efforts have been undertaken to develop alternative TCO materials, including Nb doped TiO$_2$ as well as ZnO-based materials [2]. Among alternative TCO materials, ZnO (bandgap=3.4 eV), ZnO doped with Al, and ZnO doped with Ga have received significant attention [3,4,5,6]. For example, Jin et al. deposited Al-doped ZnO thin films using dc magnetron sputtering of Al along with rf magnetron sputtering of ZnO; they prepared films with ~85% thermal infrared reflectance and ~% luminous absorbance [5]. ZnO also has several other advantages, including non-toxicity and cost-effectiveness [7].

Zinc oxide can be alloyed with various oxides, such as MgO [8], CdO [9] and BeO [10]. The bandgap of ZnO alloys can be tailored by varying the composition of these materials. For example, the bandgap of Mg$_x$Zn$_{1-x}$O alloy can be engineered between the bandgap values of ZnO (3.4 eV) and MgO (7.8 eV). The crystalline structure of Mg$_x$Zn$_{1-x}$O can change from hexagonal to cubic when the Mg content exceeds 40 at.% [11]. Single crystalline hexagonal Mg$_x$Zn$_{1-x}$O films containing magnesium content up to 36 at.% without phase separation have
been prepared using pulsed laser deposition (PLD); films with bandgap values up to 4.0 eV were prepared using this method [12]. Mimemoto et al. demonstrated use of MgₓZn₁₋ₓO thin films as transparent window layers for Cu(In,Ga)Se₂ (CIGS) solar cells [13]. The conduction band offset values of MgₓZn₁₋ₓO and Cu(In,Ga)Se₂ were controlled by changing the bandgap, enabling optimization of the Cu(In,Ga)Se₂ solar cell conversion efficiency.

As with ZnO, the bandgap of MgₓZn₁₋ₓO can be modified by doping this material with various elements. Several investigators have examined the electrical and optical properties of doped Al-doped MgₓZn₁₋ₓO [14, 15]. For example, Matsubara et al. [15] demonstrated use of Al-doped MgₓZn₁₋ₓO as a bandgap tunable TCO material. The reported resistivity increased from 3×10⁻⁴ Ω cm to 1×10⁻³ Ω cm as the bandgap increased from 3.5 eV to 3.97 eV. The average transmittance was above 90 at.% in visible wavelength region. Fewer studies have been performed on Ga-doped MgₓZn₁₋ₓO materials. For example, Harada et al. [16] has examined the electrical properties of Ga-doped MgₓZn₁₋ₓO thin films grown by molecular beam epitaxy. Phase separation was observed when the Ga content exceeded 1×10¹⁸ cm⁻³, which restricted their evaluation of the electrical properties of single crystal Ga-doped MgₓZn₁₋ₓO in the carrier concentration range lower than 2×10¹⁷ cm⁻³.

In this study, a systematic investigation of the optical and electrical properties of Ga-doped MgₓZn₁₋ₓO was performed, in which the Ga content was varied from 0.05 at.% to 7 at.% and
Mg content was varied from 5 at.% to 15 at.%. Absorption spectra and transmission spectra were obtained in order to determine the effect of Ga doping on optical properties. Carrier concentration and Hall mobility data were examined as functions of Ga and Mg content.

6.3 Experimental procedure

Ga-doped Mg$_x$Zn$_{1-x}$O thin films were grown on double-side polished c-sapphire by PLD at a substrate temperature of 650°C; films with thickness values of ~200 nm were obtained. The target-to-substrate distance was maintained at 45 mm during the deposition process. The oxygen partial pressure was maintained at 2×10$^{-5}$ torr during the deposition process. A COMPex 205 KrF excimer laser (Lambda Physik, Fort Lauderdale, FL, USA) was used for ablation of the Ga-doped Mg$_x$Zn$_{1-x}$O targets; this laser was performed using a wavelength and a pulse duration of 248 nm and 25 ns, respectively. A pulse repetition rate of 10 Hz was used in this study. The energy density of the laser beam was ~3.5 J/cm$^2$.

The multi-component targets were prepared by solid-state sintering method. 99.99 at.% purity ZnO powder (Alfa Aesar, Ward Hill, MA, USA), 99.99 at.% purity MgO (Alfa Aesar, Ward Hill, MA, USA) and 99.99 at.% purity Ga$_2$O$_3$ (Sigma Aldrich, St. Louis, MO, USA) were mixed in methanol solution using a magnetic stirring plate. The methanol solvent was subsequently removed by heating on a hot plate. The mixture was pressed into a one inch pellet. The pellet was the sintered at 1000°C in air for twenty-four hours. The crystalline
structure of the Ga-doped Mg$_x$Zn$_{1-x}$O thin films was investigated using X-ray diffraction (Rigaku, The Woodlands, TX) with CuKα radiation and a nickel filter. The optical spectra were measured with a U-3010 UV-Vis dual-beam spectrometer (Hitachi, Tokyo, Japan). The Hall measurements were obtained with an Ecopia HMS-3000 system (Bridge Technology, Chandler Heights AZ, USA) using the van der Pauw configuration at room temperature.

6.4 Results and discussion

6.4.1. X-ray diffraction studies of Ga-doped Mg$_x$Zn$_{1-x}$O thin films

Figure 6.1 shows the X-ray diffraction θ-2θ curves for Mg$_{0.05}$Zn$_{0.095}$O thin films with Ga contents ranging from 0.05 at.% to 7 at. %. (0006) diffraction of the c-sapphire substrate was assigned to the peak with a 2θ value of 41.6°. The peak shown at ~34.6° was attributed to (0002) diffraction of the wurtzite Mg$_x$Zn$_{1-x}$O structure. In films containing a Ga content of 3 at.% and higher, a small peak at 29.4° was observed; this feature was attributed to (220) diffraction of the ZnGa$_2$O$_4$ spinel structure [17]. The presence of the spinel phase indicates that the solid solubility for Ga in Mg$_x$Zn$_{1-x}$O is close to 3 at.%. This solubility limit is considerably higher than the reported thermodynamic solubility value (0.5 at.%), which was obtained from samples prepared by solid state reaction of Ga$_2$O$_3$ and ZnO powders [18]. The relatively high Ga concentration in PLD-deposited films was attributed to the nonequilibrium nature of excimer laser ablation. The average kinetic energy of depositing species produced
by excimer laser ablation is 100 - 1000 times higher than the thermodynamic equilibrium value (kT, in which k is the Boltzmann constant and T is the temperature). The X-ray diffraction data also revealed that Ga-doped Mg$_x$Zn$_{1-x}$O thin films were textured along the c-axis. Previous work by Jin et al. of Ga-doped Mg$_x$Zn$_{1-x}$O thin films grown on c plane sapphire indicates that film growth occurs by means of domain matching epitaxy [18,19].

Figure 6.1 X-ray diffraction profile for Ga-doped Mg$_{0.05}$Zn$_{0.95}$O. The Ga content in these films varies from 0.05 at.% to 7 at.%.
6.4.2. Optical properties of Ga-doped Mg$_x$Zn$_{1-x}$O thin films

Figure 6.2 shows optical transmission spectra of Mg$_{0.05}$Zn$_{0.95}$O thin films with Ga content between 0.05 at.% and 7 at.%. The overall transmission values varied in the range of ~80-95 % for wavelengths between ~370 nm and 800 nm, showing that all of the films were highly transparent in the visible wavelength range. The variation in transmittance was attributed to thin film interference. Figure 6.3 shows the absorption spectra of Mg$_{0.05}$Zn$_{0.95}$O thin films with Ga content between 0.05 at.% and 7 at.%. The absorption spectrum for the Mg$_{0.05}$Zn$_{0.95}$O thin film containing 0.05 at.% Ga showed two excitonic peaks near the fundamental optical absorption edge. Only one excitonic peak was observed as the Ga content increased to 0.1 at.%, which was attributed to broadening of excitonic states caused by dissociation of excitons by impurity atoms [20]. This dissociation process was continuously enhanced as the Ga content was increased from 0.1 at.% to 1 at.%. The exponential band tail (the Urbach tail) became prominent when the Ga content was further increased from 3 at.% to 7 at.%, which indicated that the films were highly disordered. Considering that the ZnGa$_2$O$_4$ spinel phase forms in films with Ga content greater than 3 at.%, the absorption spectra demonstrates very good agreement with XRD data.
Figure 6.2 Transmission spectra for Ga-doped Mg<sub>0.05</sub>ZnO<sub>0.95</sub>O. The Ga content in these films varies from 0.05 at.% to 7 at.%.

Figure 6.3 Absorption spectra for Ga-doped Mg<sub>0.05</sub>ZnO<sub>0.95</sub>O. The Ga content in these films varies from 0.05 at.% to 7 at.%.
The absorption spectra were fitted to examine bandgap and Urbach tail values in order to further investigate the effects of Ga doping on the optical properties of Mg$_x$Zn$_{1-x}$O films. The optical bandgap $E_g$ was determined using the following equation:

\[ \alpha(E) = C \cdot (E - E_g)^n \]  

(6.1)

in which C is a constant and n is a power factor. In this case, n=1/2 is used for the curve fitting since the Mg$_x$Zn$_{1-x}$O is a direct band semiconductor and the band to band direct allowed transition is dominant \cite{19}. The absorption coefficient can be determined from original absorption spectra using the following equation:

\[ I = I_0 \cdot \text{Exp}(-\alpha \cdot t) \]  

(6.2)

in which $\alpha$ is the absorption coefficient and t the thickness. Fitting was performed by plotting the square of the absorption coefficient as a function of the photon energy and extrapolating the linear region of the plotted curve to the photon energy axis. The bandgap values derived from this data fitting are listed in Table 6.1.
Table 6.1 The fitted values of bandgap and Urbach tail for Ga-doped Mg$_{0.05}$ZnO$_{0.95}$O

<table>
<thead>
<tr>
<th>Ga content (at %)</th>
<th>Bandgap (eV)</th>
<th>Urbach tail (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>3.45</td>
<td>100</td>
</tr>
<tr>
<td>0.1</td>
<td>3.44</td>
<td>109</td>
</tr>
<tr>
<td>0.5</td>
<td>3.47</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>3.48</td>
<td>91</td>
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<tr>
<td>3</td>
<td>3.39</td>
<td>134</td>
</tr>
<tr>
<td>5</td>
<td>3.38</td>
<td>155</td>
</tr>
<tr>
<td>7</td>
<td>3.35</td>
<td>164</td>
</tr>
</tbody>
</table>

The band tail was determined by fitting the absorption coefficient in the vicinity of the fundamental absorption edge using the Urbach equation:

\[
\alpha(E) = \alpha_0 \cdot \text{Exp} \left( \frac{E - E_g}{E_u} \right) \]

in which \(\alpha\) is the absorption coefficient, \(\alpha_0\) is the pre-exponential factor, and \(E_g\) is the optical bandgap, and \(E_u\) is the Urbach tail [21]. The Urbach tail \((E_u)\) is used to describe exponential dependence of the absorption coefficient at the optical absorption edge. The Urbach tail is caused by disorder in the materials, which leads to an extension of the parabolic density of states into the band edge. Disorder generally includes thermal disorder, which reflects thermal occupation of phonon states, or structural disorder, which is associated with impurities and defects in the material [22]. In this case, the Urbach tail was mainly attributed to the effects of Ga doping on the fundamental optical absorption. The Urbach tail values determined by fitting the absorption spectra in the wavelength range from 345 nm to 450 nm.
are listed in Table 6.1.

The bandgap and band tail values derived from curve fitting show two different types of correlations. Below a Ga content of 3 at.%, the bandgap showed a blue-shift and increased from 3.45 eV to 3.48 eV; the Urbach tail was approximately constant and the fitted value was ~100 meV. Above a Ga content of 3 at.%, the bandgap showed a red-shift and decreased from 3.48 eV to 3.35 eV; the fitted Urbach tail showed a continuous increase from 91 meV to 164 meV. This band gap narrowing can be understood by considering the widening of doping levels as a function of Ga content. Below a Ga content of 3 at.%, the Ga doping level was located below the conduction band and was separated from the conduction band. It should be noted that the doping level may have become broader as the Ga content was increased. In this case, there was no significant change in the density of states near the conduction band bottom, resulting in the almost constant Urbach tail values. The blueshift of bandgap was attributed to the Burstein-Moss effect since the electrons occupied the lower energy states in the conduction band and the band to band direct transition only occurred to higher energy states \(^{[23]}\). Above a Ga content of 3 at.%, the doping level became so broad that it was incorporated into the conduction band bottom. This incorporation of doping level as well as the formation of ZnGa\(_2\)O\(_4\) spinel caused an extension of density of states into the bandgap, resulting in the band tail at the band edge and the red-shift in the bandgap \(^{[24]}\). As additional
Ga dopants were incorporated in the Mg<sub>x</sub>Zn<sub>1-x</sub>O thin film, the Urbach tail became larger and the bandgap was reduced. Figure 6.4 shows the effects of Mg on the optical properties of Ga-doped Mg<sub>x</sub>Zn<sub>1-x</sub>O thin films. As the Mg content was increased, the fundamental absorption edge shifted to the lower wavelength region due to the increase in bandgap. This shift improved optical transparency in the shorter wavelength region. As shown in Figure 6.4, the onset of the absorption edge changed from λ=355 nm to λ=340 nm when the magnesium content was increased from 5 at. % to 15 at. %, respectively.

![Transmission spectra for 1 at.% Ga-doped Mg<sub>x</sub>Zn<sub>1-x</sub>O. The magnesium content in these films varies from 5 at.% to 15 at.%.](image)

Figure 6.4. Transmission spectra for 1 at.% Ga-doped Mg<sub>x</sub>Zn<sub>1-x</sub>O. The magnesium content in these films varies from 5 at.% to 15 at.%.
6.4.3. Electrical properties of Ga-doped Mg₅Zn₁ₓO thin films

Figure 6.5 shows the carrier concentrations of Ga-doped MgₓZn₁₋ₓO thin films as a function of Ga content. For films with Mg content of 5 at.% and 10 at.%, the carrier concentration generally increased as the Ga content was continuously increased from 0.05 at.% to 1 at.%. At 5 at.% Mg, the carrier concentration increased from $8.2 \times 10^{18}$ cm⁻³ to $1.1 \times 10^{20}$ cm⁻³. For films with 10 at.% Mg, the carrier concentration increased from $5.2 \times 10^{18}$ cm⁻³ to $9.2 \times 10^{19}$ cm⁻³. It should be noted that the carrier concentration became significantly lower when the Ga content was increased from 3 at.% At 5 at.% Mg, the carrier concentration decreased to $2.1 \times 10^{19}$ cm⁻³. At 10 at.% Mg, the carrier concentration decreased to $1.4 \times 10^{19}$ cm⁻³. As the Ga content was increased from 3 at.% to 7 at.%, the carrier concentration showed a very small increase, indicating that Ga doping of Mg₅Zn₁₋ₓO was saturated in this doping content range. For samples with 15 at.% Mg, the maximum carrier concentration ($3 \times 10^{18}$ cm⁻³) was achieved at 0.5 at.% Ga. The carrier concentration continuously decreased as the Ga content was further increased. For MgₓZn₁₋ₓO films with 5 at.% and 7 at.% Ga content, the carrier concentration exceeded the measurement capabilities of the Hall measurement system. The significant reduction of carrier concentration in MgₓZn₁₋ₓO films with high Ga content region indicated that a considerable fraction of Ga dopants were not electrically active. This was mainly attributed to the formation of the ZnGa₂O₄ spinel phase when the Ga content
Figure 6.5 Carrier concentration data for Ga-doped Mg$_{0.05}$ZnO$_{0.95}$O.

Figure 6.6 shows Hall mobility data for Ga-doped Mg$_x$Zn$_{1-x}$O thin films as a function of Ga content. Hall mobility values increased as the Ga content was increased from 0.05 at.% to 0.5 at.%. The highest Hall mobility value (34 cm$^2$ V$^{-1}$ s$^{-1}$) was obtained from the 0.5 at.% Ga-doped Mg$_{0.05}$Zn$_{0.95}$O thin film. The measured Hall mobility data shows very good agreement with Hall mobility values for doped ZnO that have been described in the literature [$^{25}$]. The tendency of the Hall mobility values to increase with increasing Ga content indicates that the dominant scattering mechanism below a Ga content of 3 at.% is grain boundary scattering [$^{26}$]. For electron transport by thermionic emission across the grain
boundary region, the effective mobility $\mu_{\text{eff}}$ is determined by the grain barrier with potential energy $E_b$:

$$
\mu_{\text{eff}} = \frac{eL}{\sqrt{2\pi n^* kT}} \cdot \exp\left(-\frac{E_b}{kT}\right) \tag{6.4}
$$

In this equation, $L$ is the grain size, $m^*$ is the effective mass, $T$ is the sample temperature, and $k$ is the Boltzmann constant. This model has been applied to epitaxially grown Al- or Ga-doped ZnO thin films in the $\leq 10^{19}$ cm$^{-3}$ carrier concentration range [27]. The Hall mobility continuously decreased as the Ga content further was increased from 0.5 at.% to 7 at.%. For Mg$_{0.05}$Zn$_{0.95}$O thin films, the Hall mobility dramatically decreased from 34 cm$^2$ V$^{-1}$ s$^{-1}$ to 0.84 cm$^2$ V$^{-1}$ s$^{-1}$. The rapid decrease of Hall mobility in the heavy doping region cannot be explained by the well-known theoretical models (e.g., Conwell-Weisskopf and Brooks-Herring-Dingle models), in which substitutional dopant atoms are assumed to be distributed homogeneously as scattering centers. It should be noted that this assumption is not valid due to the existence of the ZnGa$_2$O$_4$ spinel phase. It is more likely that the ZnGa$_2$O$_4$ spinel phase can form clusters that are distributed throughout the films. These clusters may play a critical role in the scattering process, which causes the rapid decrease in Hall mobility values. Lu et al. also reported a similar decrease in Hall mobility values for heavily Al-doped (up to 10 at.%.) ZnO, which was attributed to formation of Al-Al and Al-O clusters in the intragrain region; an intragrain cluster scattering mechanism was proposed [28]. Our
experimental results suggest that structural inhomogeneity is an important factor in determining electron mobility in heavily doped semiconductors, particularly in the ZnO-based TCO materials since ZnO can easily form spinel phases with Al₂O₃ and Ga₂O₃ [17]. Masetti et al. proposed an empirical basis for modeling mobility as a function of doping content [29]. Theoretical models are needed to describe explain the dramatic decrease of electron mobility to very low values for heavily doped ZnO.

![Figure 6.6 Hall mobility data for Ga-doped Mg₀.₀₅ZnO₀.₉₅O.](image)

Figure 6.6 Hall mobility data for Ga-doped Mg₀.₀₅ZnO₀.₉₅O.

The Mg content has a significant influence on the electrical properties of MgₓZn₁₋ₓO thin films [30]. At a given Ga content, higher carrier concentration values were observed in
Mg\textsubscript{x}Zn\textsubscript{1-x}O thin films with lower Mg content. In 1 at.% Ga-doped Mg\textsubscript{x}Zn\textsubscript{1-x}O, the carrier concentration dropped significantly from $1.1 \times 10^{20}$ cm\textsuperscript{-3} to $2.1 \times 10^{19}$ cm\textsuperscript{-3}. At a given Ga concentration, Hall mobility (\(\mu\)) values were shown to decrease in Mg\textsubscript{x}Zn\textsubscript{1-x}O thin films with higher magnesium concentration values. These results can be attributed to several factors. The electron effective mass can affect mobility, which can be defined using the following equation:

$$\mu = \frac{q < \tau >}{m^*}$$

In this equation, \(< \tau >\) is electron average scattering time and q is the electron charge. In films with higher magnesium content, electron effective mass is increased, which in turn decreases the mobility \([^{31}]\). In addition, the incorporation of magnesium in the Mg\textsubscript{x}Zn\textsubscript{1-x}O film introduces an alloy scattering mechanism, which decreases the electron mobility \([^{14}]\). The carrier concentration is also decreased with increasing magnesium concentration, which indicates that the addition of magnesium can lower the Ga doping efficiency.

6.5 Conclusions

Ga-doped Mg\textsubscript{x}Zn\textsubscript{1-x}O thin films, in which the Ga content was varied from 0.05 at.% to 7 at.% and Mg content was varied from 5 at.% to 15 at.%, have been grown epitaxially on sapphire by pulsed laser deposition. XRD \(\theta-\theta\) data revealed that the solid solubility of Ga in Mg\textsubscript{x}Zn\textsubscript{1-x}O is less than 3 at.%. In order to evaluate the effect of Ga doping and Mg doping on
the optical properties of Mg$_x$Zn$_{1-x}$O, absorption spectra were fitted to determine bandgap and Urbach tail values. When the Ga content is lower than 3 at.\%, the bandgap showed a blue-shift and Urbach tail remained approximately constant with an increase in Ga content. When the Ga content was higher than 3 at.\%, the bandgap showed a red-shift and Urbach tail continuously increased with an increase in Ga content. The transmittance values for these films is in the range of 80 % to 95 % in the wavelength range from $\lambda=\sim370$ nm to $\lambda=800$ nm for Mg$_{0.05}$Zn$_{0.95}$O. This optical transparent window can be extended to shorter wavelength region through modulation of the Mg content. The onset of the absorption edge extended from approximately $\lambda=320$ nm to $\lambda=340$ nm as the Mg content was increased from 5 at.\% to 15 at.\%. However, the carrier concentration and Hall mobility values were decreased in films with high Mg content. These results suggest that optical transparency and conductivity values are compromised due to bandgap engineering in Ga-doped Mg$_x$Zn$_{1-x}$O thin films. The carrier concentration and Hall mobility values were significantly degraded in films with a Ga content greater than 3 at.\%. These results provide a systematic evaluation of the electrical and optical properties of Ga-doped Mg$_x$Zn$_{1-x}$O thin films, which provide support for use of this material in TCO applications.
References


Chapter 7 Mott transition in Ga-doped Mg$_x$Zn$_{1-x}$O

7.1 Abstract

This paper reports the direct evidence for Mott transition in Ga-doped Mg$_x$Zn$_{1-x}$O thin films. Highly transparent Ga-doped Mg$_x$Zn$_{1-x}$O thin films were grown on c-plane sapphire substrates using pulsed laser deposition. 0.1 at.% 0.5 at.% and 1 at.% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O films were selected for resistivity measurements in the temperature range from 250 K to 40 mK. The 0.1 at.% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O thin film showed typical insulator-like behavior and the 1 at.% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O thin film showed typical metal-like behavior. The 0.5 at.% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O film showed increasing resistivity with decreasing temperature; resistivity was saturated with a value of $1.15 \times 10^{-2}$ Ω·cm at 40 mK, which is characteristic of the metal-insulator transition region. Temperature dependent conductivity $\sigma(T)$ in the low temperature range revealed that the electron-electron scattering is the dominant dephasing mechanism.
7.2 Introduction

Transparent conducting oxide (TCO) materials are utilized in a variety of opto-electronic devices, including flat panel displays, light-emitting diodes, and photovoltaic cells \[^{1, 2}\]. Indium-doped tin oxide (ITO) is the most widely used TCO material at this time. Significant research efforts are underway to create alternative TCO materials due to concerns regarding the availability of indium \[^{3}\]. For example, ZnO, Mg\(_{x}\)Zn\(_{1-x}\)O doped with Al, and Mg\(_{x}\)Zn\(_{1-x}\)O doped with Ga have received attention due to their high transmission and high conductivity \[^{3, 4, 5}\]. The electrical properties of ZnO-based materials have been examined in order to develop a better understanding regarding conduction mechanisms, such as carrier generation and electron scattering mechanisms, in these materials \[^{6}\]. The electrical transport properties of impurity-doped ZnO materials, including Ga-doped \[^{7, 8}\], Al-doped \[^{9}\] and B-doped \[^{10}\] ZnO, have been recently investigated. With sufficiently high doping concentration, these doped ZnO films were n-type degenerated, with resistivity values on the order of 10\(^{-4}\) Ω.cm. In temperature-dependent resistivity measurements, these films were observed to exhibit metal-like conductivity in the high temperature range and semiconductor-like conductivity in the low temperature range. The metal-like conductivity was indicated by a positive temperature coefficient of resistivity (TCR) while the semiconductor-like conductivity was indicated by a negative TCR.

According to Mott’s theory of impurity conduction \[^{11}\], the transition from insulator behavior to metal behavior in extrinsic semiconductors occurs as a function of doping content. At low doping content, the distance between doping atoms is so large that the hydrogenic wave functions of the outer electrons of the doping atoms have negligible overlap. As a result,
electron transports by hopping from the host doping atom to another. At sufficiently low temperatures, the material exhibits insulator behavior since the hopping electron cannot be thermally activated to overcome the electron-electron repulsion barrier on the target doping atom. At high doping content, the overlap of wave functions enables the electron to overcome the electron-electron repulsion and the material exhibits metal behavior. The metallic conduction should hold, by definition, even at the temperature of zero K, since electrons can transport in the impurity band generated by highly concentrated doping atoms. Therefore, a sufficiently low temperature is critical at practice for the direct observation of Mott transition in extrinsic semiconductors.

In this study, the Mott transition in Ga-doped Mg$_x$Zn$_{1-x}$O films was directly observed in temperature dependent resistivity measurements from 250 K to 40 mK. Ga-doped Mg$_x$Zn$_{1-x}$O thin films were grown on double-side polished c-sapphire substrates using pulsed laser deposition. Details of multi-component target preparation and thin film growth parameters can be found in Wei et al [12]. Although the thermodynamic equilibrium solubility of Ga$_2$O$_3$ in ZnO is 0.5 at.% [13], pulsed laser deposition is a nonequilibrium film deposition process that enables epitaxial Mg$_x$Zn$_{1-x}$O thin films with Ga content greater than 0.5 at% to be prepared.

**7.3 Experiment**

The crystalline structure of Ga-doped Mg$_{0.1}$Zn$_{0.9}$O films was investigated with X-ray diffraction (Rigaku, Woodlands, TX) using CuKα radiation and a nickel filter. Optical spectra were recorded using a U-3010 UV-Vis spectrometer (Hitachi, Tokyo, Japan). Electrical resistivity measurements were obtained using an AVS-47B resistance bridge.
(Picowatt (RV-Elektroniikka Oy), Vantaa, Finland), employing the four-probe technique in the temperature range 300 K to 40 mK. The measurements were carried out at a frequency of 15 Hz; no detectable dependence on frequency was noted. A completely cryogen-free dilution refrigerator (Leiden Cryogenics B.V., Leiden, the Netherlands) was pre-cooled using a PT 415 two-stage pulse tube cryocooler (Cryomech Inc. Syracuse, NY) in order to reach the milli-Kelvin temperature range. The Ga-doped Mg$_{0.1}$Zn$_{0.9}$O films were cooled from room temperature to a base temperature below 20 mK in less than thirty hours; the cooling power is ~300 μW at 100 mK. During measurement cycles, no detectable sample heating (Joule heating) was observed down to cryostat base temperature with an applied power below 12 fW. The temperature of the Ga-doped Mg$_{0.1}$Zn$_{0.9}$O films was measured with a calibrated resistance thermometer. Sample contacts were made using freshly cleaved indium.

### 7.4 Results and discussion

Figure 7.1 shows XRD patterns of 0.1 at.%, 0.5 at.% and 1 at.% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O films. The two peaks at 2θ values of 41.6° and 90.7° were indexed as the (0006) and (00012) peaks of c-sapphire, respectively. The two peaks at 2θ values of 34.6° and 72.7° were attributed to the (0002) and (0004) peaks of wurtzite Mg$_{0.1}$Zn$_{0.9}$O, respectively. The XRD patterns showed that the 0.1 at.%, 0.5 at.% and 1 at.% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O films were highly c-axis textured. No other phases or precipitates observed in the XRD data, indicating that all of the Ga-doped Mg$_{0.1}$Zn$_{0.9}$O films were homogeneously grown on the c-sapphire substrates.
Figure 7.1 X-ray diffraction profiles for 0.1 at.%., 0.5 at.% and 1 at.% Ga-doped Mg_{0.1}ZnO_{0.9}O thin films.

Figure 7.2(a) shows optical transmission spectra of 0.1 at.%., 0.5 at.% and 1 at.% Ga-doped Mg_{0.1}ZnO_{0.9}O films. The overall transmittance values of the Ga-doped Mg_{0.1}ZnO_{0.9}O films varied between 85-95 % in the wavelength range $\lambda=250$ nm to $\lambda=750$ nm, indicating that the films were highly transparent in the visible wavelength range. The variation of transmittance was caused by thin film interference. Figure 2(b) shows absorption spectra of the 0.1 at.%, 0.5 at.% and 1 at.% Ga-doped Mg_{0.1}ZnO_{0.9}O films in wavelength range between $\lambda=250$ nm and $\lambda=400$ nm. The fundamental absorption edge was observed to shift to shorter wavelength
region as the doping content was increased from 0.1 at.% to 1 at.%. This was attributed to Burstein-Moss effect caused by electrons occupation of energy states near the bottom of the conduction band [1]. The absorption spectrum of 0.1 at.% Ga-doped Mg_{0.1}Zn_{0.9}O showed a clear excitonic peak near the absorption edge. The excitonic peak was observed to decrease as the Ga concentration was increased from 0.1 at.% to 1 at.%, which was attributed to broadening of excitonic states caused by dissociation of excitons by impurity atoms at higher concentrations [14]. Detailed information regarding analysis of absorption and transmission spectra can be found in Wei et al. [12]

Figure 7.2 Transmission and absorption spectra for 0.1 at.%, 0.5 at.% and 1 at.% Ga-doped Mg_{0.1}ZnO_{0.9}O thin films.

Figure 7.3 shows resistivity of 0.1 at.%, 0.5 at.% and 1 at.% Ga-doped Mg_{0.1}Zn_{0.9}O films in the temperature range from 250 K to 40 mK. 1 at.% Ga-doped Mg_{0.1}Zn_{0.9}O showed clear metal-like conduction over the nearly four order of magnitude of change in temperature. The
resistivity at 250 K (2.49×10^{-3} \, \Omega \cdot \text{cm}) was only decreased by 6% compared with the resistivity at 40 mK (2.34×10^{-3} \, \Omega \cdot \text{cm}). For the 0.5 at.% Ga-doped Mg_{0.1}Zn_{0.9}O film, the resistivity at 40 mK was three times higher than that at 250 K. It should be noted that the resistivity was saturated with a value of 1.15 × 10^{-2} \, \Omega \cdot \text{cm} at 40 mK. Details on 0.5 at.% Ga-doped Mg_{0.1}Zn_{0.9}O film resistivity in the temperature range between 40 mK to 0.55 K can be found in Figure 7.4. Saturation of resistivity for this dopant concentration is characteristic of the metal-insulator transition (MIT) region. The 0.1 at.% Ga-doped Mg_{0.1}Zn_{0.9}O film showed typical insulator-like conduction. At ~29 K, the sample resistance exceeded the measurement limit (2 \, \text{M}\Omega). The exponential increase of resistivity in the low temperature range indicated that the resistivity would infinitely increase as the temperature approached 0 K. To confirm the insulator behavior of the 1.0 at.% Ga-doped Mg_{0.1}Zn_{0.9}O at low temperature, the film was evaluated in another two-probe setup, in which resistance up to 1 \, \text{G}\Omega can be measured. Resistivity data in the temperature range between 100 and 7 K shown in Figure 7.3 (inset) indicates that this material exhibits insulator behavior. The change in resistivity behavior at different Ga doping contents clearly demonstrates the Mott transition in the Ga-doped Mg_{0.1}Zn_{0.9}O system.
Figure 7.3 Temperature-dependent resistivity for 0.1 at.%, 0.5 at.% and 1 at.% Ga-doped Mg$_{0.1}$ZnO$_{0.9}$ thin films from 250 K to 40 mK.

In order to further understand the nature of the MIT, 0.5 at.% Ga-doped Mg$_{0.1}$ZnO$_{0.9}$, which is in the transition region, was selected for data analysis in the light of scaling theory. For the convenience of data analysis, the resistivity data was converted to conductivity. Figure 7.4 shows the variation of the conductivity (open circle) between 40 mK and 550 mK and the best fitting curve to Eq. (1) (solid green line). The inset shows the log-log plot of conductivity versus temperature in the entire temperature range. In disordered metal systems, the scaling theory predicts important corrections to electrical transport including electron-
electron interactions and localization effect. These inelastic scattering mechanisms are characterized by scattering times $\tau_{e-e}$ and $\tau_i$, respectively \cite{11, 16, 17}. As a result, the temperature variation of conductivity $\sigma(T)$ is given by \cite{16}:

$$\sigma = \sigma(0) + m\sqrt{T} + BT^{p/2} \quad \cdots \quad (7.1)$$

$\sigma(0)$ is the zero temperature conductivity. The $\sqrt{T}$--dependent term in equation (7.1) arises due to the electron-electron interaction and the last term corresponds to the correction of localization effect. The coefficients $m$ and $B$ appearing in equation (7.1) are given as \cite{16},

$$m = \frac{e^2}{4\pi^2\hbar\sqrt{2}} \left( \frac{4}{3} - 3F \right) \sqrt{k_B} \quad \cdots \quad (7.2)$$

$$B = \frac{e^2}{2\pi^2\hbar\sqrt{\tau_i}} \alpha \quad \cdots \quad (7.3)$$

where $\alpha$ is a constant and $F$ is the screening parameter. The conductivity data was fitted using Eq. (7.1) with $p$ value of 3/2. Similar fitting process has been performed by Liu et al \cite{10} in B doped ZnO films grown by MOCVD. The fitted values of $\sigma(0)$, $m$ and $B$ are $90.86 \Omega^{-1}\cdot\text{cm}^{-1}$, $-1.22 \Omega^{-1}\cdot\text{cm}^{-1}K^{-1/2}$ and $0.268 \Omega^{-1}\cdot\text{cm}^{-1}K^{-3/4}$, respectively. The fitting curve (green line) was in very good agreement with the experimental data, indicating that the inelastic electron-electron scattering is the dominant phase breaker in Ga-doped Mg$_{0.1}$Zn$_{0.9}$O. The inelastic scattering time determined from the fitting process is $T^{-3/2}$. 

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Figure 7.4 Temperature-dependent conductivity for 0.5 at.% Ga-doped Mg$_{0.1}$ZnO$_{0.9}$O thin film with both conductivity and temperature plotted in log scale. The saturated conductivity is showed in the low temperature range. The inset shows the fitted conductivity (open circles) in the temperature range from 40 mK to 550 mK. The green line corresponds to the fitting curve using equation (1).

7.5 Summary

The Mott transition has been demonstrated for the first time using temperature-dependent resistivity measurements in the Ga-doped Mg$_x$Zn$_{1-x}$O system for films in which the Ga doping content was varied from 0.1 at% to 1 at%. These studies revealed that the 0.1 at.% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O thin film exhibited typical insulator-like behavior while the 1 at.% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O thin film exhibited a typical metal-like behavior. Resistivity increased
with decreasing temperature in the 0.5 at% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O thin film; this film showed saturated resistivity with a value of $1.15 \times 10^{-2}$ $\Omega \cdot$cm at 40 mK. The conductivity in the low temperature range can be well described by scaling theory. The fitting process showed that the inelastic electron-electron scattering is the dominant dephasing of coherent backscattering.
References


Chapter 8 Epitaxial growth and ohmic contacts in Mg$_x$Zn$_{1-x}$O/TiN/Si(111) heterostructures

8.1 Abstract

In this work, Mg$_{0.1}$Zn$_{0.9}$O/TiN/Si(111) heterostructures were processed using krypton fluoride excimer pulsed laser deposition. X-ray diffraction and transmission electron microscopy studies demonstrated epitaxial growth of the titanium nitride interlayer and the Mg$_{0.1}$Zn$_{0.9}$O thin film. Two epitaxial relationships were observed: (a) along the [111]-direction of the silicon substrate and the titanium nitride interlayer parallel to the [0001]-direction of the Mg$_{0.1}$Zn$_{0.9}$O thin film in the growth direction and (b) along the [011]-direction of the silicon substrate and the titanium nitride interlayer parallel to the [2110]-direction of the Mg$_{0.1}$Zn$_{0.9}$O thin film in the in-plane direction. Transmission electron microscopy demonstrated a thin (~5 nm) spinel layer along the magnesium zinc oxide/titanium nitride interface. Current-voltage measurements revealed ohmic contact behavior through the magnesium zinc oxide/titanium nitride interface. These results suggest that the titanium nitride interlayer in the Mg$_x$Zn$_{1-x}$O/TiN/Si(111) heterostructure provides a buffer layer for integrating magnesium zinc oxide thin films with silicon substrates, which both enables epitaxial growth and serves as an ohmic electrode for the magnesium zinc oxide thin film. These efforts will facilitate the development of zinc oxide-based surface acoustic wave devices, electro-optic modulators, ultraviolet-blue light emitting diodes, ultraviolet-blue light laser diodes, and other advanced devices.
8.2 Introduction

Zinc oxide (ZnO) and magnesium zinc oxide (Mg$_x$Zn$_{1-x}$O) are wide-bandgap II-VI semiconductors, which have numerous optoelectronic and piezoelectric applications. Possible applications for these materials include use as transparent conducting oxides [1]; window materials for solar cells and displays [2]; surface acoustic wave devices [3]; electro-optic modulators [4]; ultraviolet-blue light emitting diodes; and ultraviolet-blue light laser diodes [5,6,7]. There are two challenges that have limited the development of high performance optoelectronic devices using zinc oxide-based materials. One challenge is the growth of a high quality, epitaxial zinc oxide film on a silicon substrate, which will enable integration of zinc oxide with conventional silicon electronics. Another challenge is the creation of a high-quality ohmic contact on zinc oxide, because device failure may result from the high resistance of the ohmic contact between semiconductors and metals [5,8]. It is currently difficult to obtain epitaxial growth of zinc oxide thin films on silicon substrates because oxidation of silicon occurs at temperatures required for zinc oxide film growth; it is not possible to grow epitaxial zinc oxide films due to the amorphous nature of silicon dioxide. Buffer layers are commonly used to integrate zinc oxide films with silicon substrates. For example, aluminum nitride (AlN) and gallium nitride (GaN) have previously been used as buffer layers for integrating zinc oxide thin films with silicon substrates [8,9]. Another potential buffer material is titanium nitride. Titanium nitride is a hard, thermally stable, wear resistant, and corrosion resistant material that is commonly used as a coating on machine tools and medical devices, including electrodes, artificial heart valves, and left ventricular assist devices [10,11]. Due to its high electrical conductivity, titanium nitride is commonly
used as conductive barrier in copper-based chips; the conductive barrier permits the flow of electrical current but prevents undesirable intermixing between the copper film and the silicon substrate. Titanium nitride films can be epitaxially grown on silicon substrates by means of cube-on-cube domain-matching epitaxy, in which four lattice planes of titanium nitride match three lattice planes of silicon with less than 4% misfit [12]. For example, Sharma et al. have demonstrated that epitaxial titanium nitride can serve as buffer layer for the epitaxial growth of Pb(Zr_{0.52}Ti_{0.48})O_{3} films on silicon substrates [13]. In previous studies, we have developed epitaxial zinc oxide films on silicon (111) substrates using titanium nitride and magnesium oxide as buffer layers; these films demonstrated high crystallinity and excellent exciton emission [9].

8.3 Experiment

In this work, we have developed magnesium zinc oxide/titanium nitride/silicon (111) heterostructures. Magnesium zinc oxide may be doped with Group III elements such as gallium to enhance conductivity, which is a very desirable feature for transparent electrode (e.g., thin film solar cell) applications [14,15]. One of the goals in this work is to integrate the magnesium zinc oxide thin film with the silicon substrate using conductive titanium nitride as a buffer layer. Another goal of this work is to develop an ohmic contact between the metallic titanium nitride buffer layer and the magnesium zinc oxide thin film.

Silicon (111) wafers (Virginia Semiconductor, Fredricksburg, VA, USA) were used as substrate materials in this study. Substrates were cleaned with acetone and methanol for ten minutes in ultrasonic bath. They were subsequently immersed in 25 % hydrofluoric acid solution for 30 seconds to remove the native silicon dioxide layer. Mg_{0.1}Zn_{0.9}O/TiN/Si(111)
heterostructures were prepared using krypton fluoride excimer pulsed laser deposition. A Compex 205 krypton fluoride excimer laser (Coherent, Fort Lauderdale, FL, USA) operated at $\lambda=248$ nm (pulse duration=20 nanoseconds, repetition rate=10 Hertz) was used to ablate the target materials. The laser energy density utilized in this study was $\sim2.3$ J/cm$^2$. The films were grown in a high vacuum chamber; depositions were performed under a background pressure of $\sim2\times10^{-7}$ Torr. The titanium nitride target was commercially obtained (Alfa Aesar, Ward Hill, MA, USA). The Mg$_{0.1}$Zn$_{0.9}$O target was prepared using standard calcine-sintering methods, in which the powders of the component materials in desired stoichiometry were first calcined at 400 °C for four hours, pressed in round pellets, and sintered for twelve hours at 900 °C. The titanium nitride buffer layer was grown at 650 °C for ten minutes. The substrate temperature was reduced to 450 °C for growth of Mg$_{0.1}$Zn$_{0.9}$O thin films; these films were also grown for ten minutes.

8.4 Results and discussion

The crystalline structure of the Mg$_{0.1}$Zn$_{0.9}$O/TiN/Si(111) heterostructure was examined using X-ray diffraction and transmission electron microscopy. $\theta$-20 scans were obtained with an X-ray diffractometer (Rigaku, Woodlands, TX, USA) using Cu Kα radiation and a nickel filter. A 2010F analytical electron microscope (JEOL, Tokyo, Japan) was used to examine the structure and crystallinity of the Mg$_{0.1}$Zn$_{0.9}$O/TiN/Si(111) heterostructures. Current-voltage measurements were obtained using a 4155B Semiconductor Parameter Analyzer (Agilent, Santa Clara, CA, USA). The two-probe contacts used in this study were fabricated out of indium. A gold wire made contact with the Mg$_{0.1}$Zn$_{0.9}$O/TiN/Si(111) heterostructure via
indium contacts. One contact was made to the titanium nitride interlayer. Another contact was made to the Mg$_{0.1}$Zn$_{0.9}$O doped with 1 atomic percent gallium thin film. The distance between the two contacts was maintained at ~1 cm.

Figure 8.1 shows the X-ray diffraction pattern obtained from the Mg$_{0.1}$Zn$_{0.9}$O/TiN/Si(111) heterostructure. Reflections from the (111) planes of the silicon substrate, the (111) planes of the titanium nitride buffer layer, and the (0001) planes of the Mg$_{0.1}$Zn$_{0.9}$O film were observed. The X-ray diffraction pattern indicates the titanium nitride interlayer and the Mg$_{0.1}$Zn$_{0.9}$O films were either grown epitaxially on the silicon (111) substrate or formed a textured structure, in which the [111] direction of titanium nitride and the [0001] direction of Mg$_{0.1}$Zn$_{0.9}$O were parallel to the [111] direction of silicon substrate. The thickness of titanium nitride buffer layer measured from TEM image was ~70 nm and the thickness of Mg$_{0.1}$Zn$_{0.9}$O thin film in the Mg$_{0.1}$Zn$_{0.9}$O/TiN/Si(111) heterostructure was ~200 nm.

![Figure 8.1 X-ray diffraction pattern of the Mg$_{0.1}$Zn$_{0.9}$O/TiN/Si(111) heterostructure.](image)
Figure 8.2a shows the selected area electron diffraction pattern obtained from a region of a cross-section \( \text{Mg}_{0.1}\text{Zn}_{0.9}\text{O/TiN/Si}(111) \) heterostructure sample that included the silicon substrate, titanium nitride interlayer, and \( \text{Mg}_{0.1}\text{Zn}_{0.9}\text{O} \) thin film. The diffraction patterns of silicon substrate and titanium nitride buffer result from the \([\bar{1}12]\)-zone axis. The zone-axis for \( \text{Mg}_{0.1}\text{Zn}_{0.9}\text{O} \) film is \([01\bar{1}]\). Epitaxial growth of the \( \text{Mg}_{0.1}\text{Zn}_{0.9}\text{O/TiN/Si}(111) \) heterostructures was confirmed by the selected area electron diffraction pattern. Two epitaxial relationships were observed: (a) along the \([11\bar{1}]\)-direction of the silicon substrate and the titanium nitride interlayer parallel to the \([0001]\)-direction of the \( \text{Mg}_{0.1}\text{Zn}_{0.9}\text{O} \) thin film in the growth direction and (b) along the \([01\bar{1}]\)-direction of the silicon substrate and the titanium nitride interlayer parallel to the \( [\bar{2}1\bar{1}0]\)-direction of the \( \text{Mg}_{0.1}\text{Zn}_{0.9}\text{O} \) thin film in the in-plane direction. The epitaxial relationship between the titanium nitride interlayer and the silicon (111) substrate results from cube-on-cube domain-matching epitaxy. The in-plane epitaxial relation between the titanium nitride interlayer and the \( \text{Mg}_{0.1}\text{Zn}_{0.9}\text{O} \) thin film is illustrated in Figure 8.2b. Magnesium zinc oxide \( (\text{Mg}_x\text{Zn}_{1-x}\text{O}) \) remains the hexagonal wurtzite structure of zinc oxide with lattice parameters close to that of zinc oxide. The hexagonal structure of magnesium zinc oxide could be realized with magnesium contents as high as 32 at.% when the films were grown using pulsed laser deposition.\(^{16}\) The in-plane epitaxial relationship corresponds to a plane misfit of 8.4% between the TiN interlayer and the \( \text{Mg}_{0.1}\text{Zn}_{0.9}\text{O} \) film. Figure 3a is the high-resolution transmission electron micrograph obtained from the interfacial area between the TiN interlayer and the \( \text{Mg}_{0.1}\text{Zn}_{0.9}\text{O} \) film.
Figure 3b is the inverse Fast Fourier Transformation (FFT) pattern of the image shown in Figure 3a. A 5-7 nm thick reaction layer was observed between the TiN interlayer and the Mg$_{0.1}$Zn$_{0.9}$O film interface. This thin reaction layer was attributed to the spinel structure of Mg$_{2-x}$Zn$_x$TiO$_4$ (lattice constant is 8.44 Å), which has a lattice constant that is approximately twice that of titanium nitride. The formation of the spinel layer was attributed to interdiffusion reaction between the TiN interlayer and the Mg$_{0.1}$Zn$_{0.9}$O film interface. Figure 3b is the inverse Fast Fourier Transform image obtained by masking the reflexes from the (011) plane of the titanium nitride layer, the (011) plane of the spinel layer, and the (2110) plane of the Mg$_{0.1}$Zn$_{0.9}$O film in the Fourier transform of the image shown in Figure 3a. The inverse Fast Fourier Transformation image, which contains information from the (011) plane of the titanium nitride layer, the (011) plane of the spinel layer, and the (2110) plane of the Mg$_{0.1}$Zn$_{0.9}$O film, demonstrates two-one plane matching along the TiN/spinel interface and the spinel/Mg$_{0.1}$Zn$_{0.9}$O interface.
Figure 8.2 (a) Selected area electron diffraction pattern of Mg$_{0.1}$Zn$_{0.9}$O/TiN/Si(111) heterostructure. (b) Schematic illustration of the in-plane epitaxial relationship between titanium nitride interlayer and magnesium zinc oxide thin film.

Figure 8.3 (a) High resolution transmission electron micrograph obtained from the titanium nitride-magnesium zinc oxide interface. The inset is the corresponding Fast Fourier
Transform pattern. (b) The inverse Fast Fourier Transform image of the titanium nitride-magnesium zinc oxide interface, showing the 2:1 plane matching on each side of the spinel layer.

The current-voltage characteristics were examined for a Mg$_{0.1}$Zn$_{0.9}$O /TiN/Si(111) heterostructure. Room temperature Hall measurements indicate Mg$_{0.1}$Zn$_{0.9}$O film has a carrier concentration of $\sim$5.8×10$^{18}$/cm$^3$ and a mobility of 9.8 cm$^2$/Vs. I-V data was obtained at room temperature. As shown in Figure 8.4, linear I-V characteristics were observed at all the three temperatures, indicating that an ohmic contact was obtained between the titanium nitride interlayer and the Mg$_{0.1}$Zn$_{0.9}$O film. The through layer resistance is $\sim$8.9 $\Omega$ at room temperature. A linear I-V characteristic or an ohmic contact implies that a small Schottky barrier, $\Phi_B$, exists between the metal and the semiconductor:

$$\Phi_B = \Phi_M - \chi_{SC} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (8.1)$$

In this equation, $\Phi_M$ is the work function of the metal and the $\chi_{SC}$ is the electron affinity of the semiconductor. Depending on stoichiometry, the work function value of titanium nitride is in range of 4.25 eV to 4.65 eV.$^{18}$ These work function values are very similar to those of zinc oxide ($\sim$ 4.45-4.5 eV).$^{19}$ The thin spinel layer at the titanium nitride-magnesium zinc oxide interface did not alter the current-voltage contact characteristics; this result is attributed to high tunneling efficiency and low thickness of the spinel layer.
Figure 8.4 The current-voltage curves of Mg_{0.1}Zn_{0.9}O/TiN/Si(111) heterostructure, measured at room temperature. The linear current-voltage characteristics show that an ohmic contact exists between the titanium nitride interlayer and the Mg_{0.1}Zn_{0.9}O.

8.5 Summaries

Magnesium zinc oxide/titanium nitride/silicon (111) heterostructures with unusual structural and electrical properties were developed using excimer laser pulsed laser deposition. Epitaxial growth of the titanium nitride interlayer and the magnesium zinc oxide thin film was confirmed using X-ray diffraction and transmission electron microscopy. Current-voltage measurements for the Mg_{0.1}Zn_{0.9}O/TiN/Si(111) heterostructure demonstrated that an ohmic contact existed between the titanium nitride layer and the magnesium zinc oxide layer. These results suggest that a titanium nitride interlayer in a zinc oxide-based heterostructure may both integrate the magnesium zinc oxide thin film with the silicon substrate and serve as an ohmic electrode. These efforts will facilitate the development of zinc oxide-based electronic and opto-electronic devices.
References


Chapter 9 Summaries

Undoped Mg\textsubscript{x}Zn\textsubscript{1-x}O

Undoped Mg\textsubscript{x}Zn\textsubscript{1-x}O thin films have been grown on amorphous fused silica substrates at several temperatures using pulsed laser deposition. X-ray diffraction also showed that the films grown at temperatures between 250 °C and 750 °C exhibited similar degrees of crystallinity. Bandgap values were obtained from the absorption data, and larger bandgap values were observed in films grown at higher temperatures. The Mg\textsubscript{0.15}Zn\textsubscript{0.85}O film deposited at 750°C exhibited a bandgap value similar to that for an epitaxial Mg\textsubscript{0.34}Zn\textsubscript{0.66}O thin film grown on a sapphire substrate. Photoluminescence values were in good agreement with Urbach energy values that were determined from absorption data. The highest photoluminescence properties were observed in the Mg\textsubscript{0.15}Zn\textsubscript{0.85}O film that was deposited at 350 °C. This film also exhibited the lowest amount of band-tail spreading. These results suggest that Mg\textsubscript{0.15}Zn\textsubscript{0.85}O thin films grown using pulsed laser deposition have numerous potential optoelectronic applications such as ultraviolet-blue laser diodes, flat panel displays, and medical devices.

Ga-doped Mg\textsubscript{x}Zn\textsubscript{1-x}O

Ga-doped Mg\textsubscript{x}Zn\textsubscript{1-x}O thin films have been grown epitaxially on sapphire by pulsed laser deposition. The Ga content was varied from 0.05 at.% to 7 at.% and Mg content was varied from 5 at.% to 15 at.%. XRD θ-2θ data revealed that the solid solubility of Ga in Mg\textsubscript{x}Zn\textsubscript{1-x}O is less than 3 at.% In order to evaluate the effect of Ga doping on the optical properties of Mg\textsubscript{x}Zn\textsubscript{1-x}O, absorption spectra were fitted to determine bandgap and Urbach tail values. When the Ga content is lower than 3 at.%, the bandgap showed a blue-shift and Urbach tail
remained approximately constant with an increase in Ga content. When the Ga content was higher than 3 at.%, the bandgap showed a red-shift and Urbach tail continuously increased with an increase in Ga content. The transmittance values for these films are in the range of 80% to 95% in the wavelength range from about 370 nm to 800 nm for Mg$_{0.05}$Zn$_{0.95}$O. This optical transparent window can be extended to shorter wavelength region through modulation of the Mg content. The onset of the absorption edge extended from approximately 320 nm to 340 nm as the Mg content was increased from 5 at.% to 15 at.%. However, the carrier concentration and Hall mobility values were decreased in films with high Mg content. These results suggest that optical transparency and conductivity values are compromised due to bandgap engineering in Ga-doped Mg$_x$Zn$_{1-x}$O thin films. The carrier concentration and Hall mobility values were significantly degraded in films with a Ga content greater than 3 at.%. These results provide a systematic evaluation of the electrical and optical properties of Ga-doped Mg$_x$Zn$_{1-x}$O thin films, which provide support for use of this material in TCO applications.

**Low temperature transport properties in Ga-doped Mg$_x$Zn$_{1-x}$O**

The low temperature transport properties have been studied in Ga-doped Mg$_x$Zn$_{1-x}$O. The Mott transition has been demonstrated for the first time using temperature-dependent resistivity measurements in the films in which the Ga doping content was varied from 0.1 at% to 1 at.%. These studies revealed that the 0.1 at.% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O thin film exhibited typical insulator-like behavior while the 1 at.% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O thin film exhibited a typical metal-like behavior. Resistivity increased with decreasing temperature in the 0.5 at% Ga-doped Mg$_{0.1}$Zn$_{0.9}$O thin film; this film showed saturated resistivity with a
value of $1.15 \times 10^2 \, \Omega \cdot \text{cm}$ at 40 mK. The conductivity in the low temperature range can be well described by scaling theory. The fitting process showed that the inelastic electron-electron scattering is the dominant dephasing of coherent backscattering.

**Integration of Ga-doped Mg$_{x}$Zn$_{1-x}$O on Silicon**

Ga-doped Mg$_{x}$Zn$_{1-x}$O/TiN/Si (111) heterostructures with structural and electrical properties were developed using pulsed laser deposition. Epitaxial growth of the TiN buffer layer and the Ga-doped Mg$_{x}$Zn$_{1-x}$O thin film was confirmed using X-ray diffraction and transmission electron microscopy. Current-voltage measurements for the Mg$_{0.1}$Zn$_{0.9}$O/TiN/Si(111) heterostructure demonstrated that an ohmic contact existed between the titanium nitride layer and the magnesium zinc oxide layer. These results suggest that a TiN buffer layer in a ZnO-based heterostructure may both integrate the magnesium zinc oxide thin film with the silicon substrate and can be used as an ohmic electrode. These efforts will facilitate the development of ZnO-based electronic and opto-electronic devices.