ABSTRACT

TEMIZER, NAMIK KEMAL. Structure and Properties of Al and Ga-Doped ZnO. (Under the direction of Professor Jagdish Narayan).

Recently there is tremendous interest in Transparent conducting oxide (TCO) research due to the unlimited and exciting application areas. Current research is mostly focused on finding alternative low cost and sustainable materials in order to replace indium tin oxide (ITO), which caused serious concern due to the increasing cost of indium and chemical stability issues of ITO. The primary aim of this research is to develop alternative TCO materials with superior properties in order to increase the efficiency in optoelectronic applications, as well as to study the properties of these materials to fully characterize them. We have grown Al and Ga-doped ZnO films with an optimized composition under different deposition conditions in order to understand the effect of processing parameters on the film properties.

We report a detailed investigation on the structure-property correlations in Ga and Al codoped ZnO films on c-sapphire substrates where the thin film microstructure varies from nanocrystalline to single crystal. We have achieved highly epitaxial films with very high optical transmittance (close to 90%) and low resistivity (~110µΩ-cm) values. The films grown in an ambient oxygen partial pressure (P_{O_2}) of 50 mTorr and at growth temperatures from room temperature to 600°C showed semiconducting behavior, whereas samples grown at a P_{O_2} of 1 mTorr showed metallic nature. The most striking feature is the occurrence of resistivity minima at relatively high temperatures around 110 K in films deposited at high temperatures. The structure-property correlations reveal that point defects play an important role in modifying the structural, optical, electrical and magnetic properties and such changes in physical properties are controlled predominantly by the defect content.
To gain a better understanding of the conduction processes in doped ZnO thin films, we have studied the temperature variation of resistivity of some selected samples that showed some interesting behavior. Micro-structural, transport, optical and magnetic properties in ZnGa$_{0.002}$Al$_{0.02}$O films grown by pulsed laser deposition under different growth conditions was studied. In ZnO films grown at substrate temperatures of 600°C most interesting features are the concomitant occurrence of high temperature resistivity minima and room temperature ferromagnetism with a high saturation magnetic moment and considerable coercivivity. The temperature dependent resistivity data has been interpreted in the light of quantum corrections to conductivity in disordered systems, suggesting that the e-e interactions is the dominant mechanism in the weak-localization (WL) limit in the case of films showing resistivity minima. We propose that formation of oxygen vacancy-Zinc interstitial defect complex (V$_{O}$-I$_{Zn}$) is responsible for the enhancement in n-type conductivity, and zinc vacancies (V$_{Zn}$) for the observed room temperature ferromagnetism.

ZnO nanostructures are gaining importance in various applications, from gas sensing to thin film transistors (TFTs). We have studied the micro-structural, transport, optical and magnetic properties in ZnO nanostructured films grown by pulsed laser deposition under different ambient conditions. We have investigated the nanostructures in detail through x-ray diffraction, SEM and TEM techniques. We have achieved relatively low room temperature resistivity and the occurrence of room temperature ferromagnetism with significant saturation magnetic moment of 1000 A/m with coercivity in the range of 100-150 Oe. Photoluminescence measurements were conducted to get an insight about the types of defects that occur under different growth conditions. Correlations between transport, optical and magnetic properties has been established in terms of these defects and their complexes. These
nanostructured oxides with magnetic and optical properties are promising candidates in multifunctional spintronic and photonic devices.
DEDICATION

To My Family

Cevat Temizer, Guzide Temizer and Selim Temizer
BIOGRAPHY

Namik Kemal Temizer was born in Ankara, Turkey. After completing his high school in Ataturk Anadolu Lisesi, he joined Middle East Technical University to earn a BS degree in Electrical and Electronics Engineering in Ankara. He worked at Aselsan briefly. He got his MS degree in Electrical and Computer Engineering at NC State University. Then he joined PhD program at NCSU.
ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my thesis supervisor Prof. Jagdish (Jay) Narayan and MSE graduate secretary Ms. Edna Deas for their help, guidance, and support from the very beginning of my graduate study at NC State University. Working under a great scientist as well as a great person has been a great privilege and a learning experience for me. I am also indebted to Ms. Deas for her help and support whenever I most needed. I would like to thank Prof. John Prater and Prof. Lewis Reynolds for their guidance and helpful suggestions during my research. I would also like to thank Prof. Albena Ivanisevic for serving on my committee and providing suggestions during the course of my Ph.D.

I would like to give a special thanks to my colleagues and friends: Dr. Sid Mal, Dr. Titas Dutta, Dr. Pranav Gupta, Dr. Alok Gupta, Dr. Tsung-Han Yang, Dr. Sudhakar Nori, Dr. Srinivasa R. Singamaneni, Dr. Yi-Fang Lee, Dr. Sandhyarani Punugupati, Dr. Fan Wu, Dr. Reza Bayati, Dr. Roya Molaei, Gabrielle Mineo, Adele Moatti and Anagh Bhaumik. Their support throughout my doctoral research at NC State University has been invaluable and has made my stay an enjoyable experience. I want to thank from the bottom of my heart all my friends who have made my stay at NC State enjoyable and worthwhile.

I would like to thank my parents, Cevat Temizer and Guzide Temizer, and my brother Selim Temizer for their unconditional love, support and encouragement. Without their support, none of this would have been possible.
I acknowledge the contribution of Analytical Instrumentation Facility at NCSU and would like to thank the staff; Chuck Mooney, Roberto Garcia, Fred Stevie, Toby Tung and Elaine Zhou. I would also like to acknowledge the contribution of Shared Materials Instrumentation Facility (SMIF) at Duke University and SMIF Director Dr. Mark Walters.

This research was partially funded by the National Science Foundation (NSF) and the Army Research Office (ARO).
TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................... ix
LIST OF TABLES ............................................................................................................. xii

1. Introduction .................................................................................................................. 1
    1.1. References ............................................................................................................ 6

2. Background .................................................................................................................. 7
    2.1. Transparent Conducting Oxide (TCO) ................................................................. 7
        2.1.1 Figure of Merit for TCOs ............................................................................. 8
        2.1.2 Electrical Properties .................................................................................. 9
        2.1.3 Optical Properties .................................................................................... 10
        2.1.4 Work Function .......................................................................................... 14
    2.2. Thin Film Epitaxy ............................................................................................... 15
        2.2.1 Lattice Matching Epitaxy .......................................................................... 17
        2.2.2 Domain Matching Epitaxy .......................................................................... 17
    2.3. Zinc Oxide ........................................................................................................... 20
        2.3.1 Crystal Structure of ZnO ........................................................................... 21
        2.3.2 Electronic Structure of ZnO ..................................................................... 23
    2.4. Native Point Defects in ZnO ............................................................................. 23
        2.4.1 Oxygen Vacancies .................................................................................... 27
        2.4.2 Zinc Vacancies .......................................................................................... 28
        2.4.3 Zinc Interstitials ....................................................................................... 29

3. Experimental Techniques ......................................................................................... 31
    3.1. Substrate Preparation ....................................................................................... 31
    3.2. Pulsed Laser Deposition .................................................................................. 32
    3.3. X-Ray Diffraction ............................................................................................. 36
    3.4. Transmission Electron Microscopy .................................................................. 38
    3.5. Hall Effect Measurement ................................................................................. 40
    3.6. Four-Point Resistivity Measurement .................................................................. 42
    3.7. Photoluminescence Spectroscopy .................................................................... 43
    3.8. Absorption Spectroscopy ............................................................................... 45
References ..........................................................................................................................47
4. Ga and Al Doped Zinc Oxide Thin Films for Transparent Conducting Oxide Applications: Structure-Property Correlations .........................................................48
   4.1. Abstract ......................................................................................................................48
   4.2. Introduction .............................................................................................................49
   4.3. Experimental Details .............................................................................................51
   4.4. Results and Discussion .........................................................................................52
   4.5. Summary and Conclusions ....................................................................................59
   4.6. Acknowledgements ...............................................................................................60
   4.7. Tables ......................................................................................................................61
   4.8. Figures .....................................................................................................................62
   4.9. References ..............................................................................................................71
5. Defect Mediated Room Temperature Ferromagnetism and Resistance Minima Study in Epitaxial ZnGa\textsubscript{0.002}Al\textsubscript{0.02}O Transparent Conducting Oxide Films ..........73
   5.1. Abstract ......................................................................................................................73
   5.2. Introduction .............................................................................................................75
   5.3. Experimental Details .............................................................................................76
   5.4. Results and Discussion .........................................................................................78
   5.5. Summary and Conclusions ....................................................................................86
   5.6. Acknowledgements ...............................................................................................87
   5.7. Tables ......................................................................................................................88
   5.8. Figures .....................................................................................................................90
   5.9. References ..............................................................................................................96
6. Structure-Property Correlations and Room Temperature Ferromagnetism and in Nanostructured Zinc Oxide Thin Films ...............................................................99
   6.1. Abstract ......................................................................................................................99
   6.2. Introduction .............................................................................................................101
   6.3. Experimental Details .............................................................................................103
   6.4. Results and Discussion .........................................................................................104
   6.5. Summary and Conclusions ....................................................................................108
   6.6. Acknowledgements ...............................................................................................109
   6.7. Tables ......................................................................................................................110
   6.8. Figures .....................................................................................................................111
6.9. References ...................................................................................................................... 119
7. Conclusion .......................................................................................................................... 122
LIST OF FIGURES

Figure 2.1 (a) ZnO/Sapphire interface (b) Fourier filtered image showing epitaxial matching of planes according to DME (c) SAED pattern of ZnO/Sapphire interface (d) Schematic plan view of the epitaxy. ............................................19

Figure 2.2 Wurtzite crystal structure of ZnO. Zinc atoms are shown in white and oxygen atoms are shown in yellow. .................................................................22

Figure 2.3 Calculated energy values of defects in zinc oxide film. ..............................................24

Figure 3.1 Schematic diagram of the experimental pulsed laser deposition setup. ........33

Figure 3.2 A schematic diagram of Rigaku D-MAX/A diffractometer used in Bragg-Brentano setup. ..........................................................37

Figure 3.3 A schematic diagram of a 4-circle diffractometer setup. IBO: incident beam optics, DBO: diffracted beam optics. ..........................................................38

Figure 4.1 XRD spectra for all 0.2%Ga, 2%Al:ZnO films deposited at different temperatures RT-600°C. The oxygen partial pressure was maintained constant at 50 mTorr throughout the depositions. ...............................................62

Figure 4.2 XRD spectra for all 0.2%Ga, 2%Al:ZnO films deposited at different temperatures RT-600°C. The oxygen partial pressure was maintained constant at 1 mTorr throughout the depositions. ........................................63

Figure 4.3 Azimuthal (Φ) scan of ZnO/Al2O3 (0001) structure. Sapphire (11̅02) reflections at 2θ=25.58° and Ψ=57.61° and ZnO (101) reflections at 2θ=36.25° and Ψ=61.07°. ..............................................64

Figure 4.4 (a) HRTEM image shows highly epitaxial film with atomically sharp interface. (b) Selected area diffraction pattern of film-substrate interface. (c) Bright-field image showing the film thickness. (d) FF-HRTEM image showing epitaxial matching of planes...................................................65

Figure 4.5 UV-Vis transmission spectra of the films at different growth temperatures. Oxygen partial pressure during sample growth is held constant at (a) 50 mTorr and (b) 1 mTorr.................................................................66

Figure 4.6 Tauc plots for samples grown at different temperatures in the range from RT to 600°C. The oxygen partial pressure (PO2) during the growth was kept at (a) 50 mTorr and (b) 1 mTorr for the samples..................................................67
Figure 4.7 Variation of the electrical resistivity with temperature for the Ga,Al: doped ZnO samples grown at different temperatures in the range from 300-600°C. The oxygen partial pressure during the growth was kept at 50 mTorr for the samples (S1). The inset shows the metallic nature and the resistivity minimum occurring around 110K for the sample grown at 600°C. 

Figure 4.8 Temperature variation of the resistivity for the films grown at different deposition temperatures in the range of 100-600°C and at an oxygen partial pressure of 1x10^-3 Torr. The two insets show the variation of resistivity for the sample grown at 300°C (left inset) and the resistivity minimum occurring around 130K for the sample grown at 600°C (right inset).

Figure 4.9 Variation of carrier concentration and mobility with deposition temperature for the Ga,Al: doped ZnO samples grown at different temperatures in the range from RT to 600°C. The oxygen partial pressure during the growth was kept at (a) 50 mTorr and (b) 1 mTorr for the samples.

Figure 5.1 (a) 0-2θ XRD spectra for all three samples S1, S2 and S3 (b) φ-scan plot for S2.

Figure 5.2 TEM micrographs for sample S2 (a) Cross section HRTEM image shows highly epitaxial film with atomically sharp interface. FFT filtered HRTEM image (bottom) shows epitaxial matching of 6/7 and 5/6 domains to accommodate the 16% misfit between the film and the substrate. (b) SAED pattern of film-substrate interface. (c) Bright-field low magnification image showing film thickness of ~450 nm.

Figure 5.3 (a) UV-Vis optical transmittance spectra for all the three films (b) Corresponding Tauc plots to estimate the optical band gaps.

Figure 5.4 Variation of resistivity of AGZO films as a function of temperature for all the three films, S1 (right y-axis), S2 and S3 (left y-axis).

Figure 5.5 Resistivity vs. temperature plots of AGZO samples grown on c-plane sapphire. The solid red lines are the corresponding fits to experimental data to Eq. (5.1). It is evident that the fits to the data are excellent in all the three films, S1, S2 and S3.

Figure 5.6 Isothermal magnetic-field dependent magnetization curves for the AGZO (S1 and S2) films on sapphire substrates at 300 K. Plotted in the bottom inset are the low field M-H hysteresis loops between ± 400 Oe for S1 and S2 samples (at 10, 50, 100, 200 and 300 K) deciphering clearly the significant hysteresis shown by these films. S1 and S2 films exhibited RTFM with maximum saturation magnetization up to 28 emu/cc for the
case of S1, and about 61 emu/cc for S2. Top inset shows the M-H plot measured at several temperatures (10, 50, 100, 200 and 300 K) for S3. It is evident that this sample shows diamagnetic behavior at all the temperatures of measurement.

**Figure 6.1** (a) XRD patterns of ZnO films grown at different ambient conditions on c-sapphire substrate (b) High resolution XRD shows different grain orientations present in the films.

**Figure 6.2** Cross section HRTEM micrographs for samples S1 and S2. a) Individual grains with varying orientations can be observed. Left inset shows bright-field low magnification image. SAED pattern confirms nano crystalline structure (right inset) of S1. b) S2 has larger columnar grains. Same grain structure can be observed in the low magnification image (left inset). Arcs in the SAED pattern are due to textured grain growth (right inset).

**Figure 6.3** SEM micrographs for all the samples a) S1, b) S2 and c) S3. Higher magnification images are shown in the insets.

**Figure 6.4** UV-Vis optical transmittance spectra for all the three films.

**Figure 6.5** Variation of resistivity of nanostructured ZnO films as a function of temperature for all the three films.

**Figure 6.6** Isothermal magnetic-field dependent magnetization curves for the ZnO films on sapphire substrates. Plotted in the top inset are the low field M-H hysteresis loops between ± 250 Oe for S1 deciphering clearly the significant hysteresis shown by this film. Bottom inset shows the M-H plot measured at several temperatures (10K, 100K, and 300K) for S2 and S3.

**Figure 6.7** Photoluminescence spectra for all three films obtained with HeCd laser source. Peaks at 325 nm and 650 nm correspond to line excitation and second order harmonics.

**Figure 6.8** Photoluminescence measurements of samples a) grown in oxygen (S3) b) grown in argon (S1). Best fits are obtained with a minimum number of four Gaussian peaks.
LIST OF TABLES

**Table 2.1** Figure of merit for some transparent conductors ................................................................. 8

**Table 2.2** Calculated formation energies at EF=0 for native point defects in ZnO under zinc-rich conditions ........................................................................................................................................ 26

**Table 4.1** The important parameters, such as the grain size, average percentage transmittance, resistivity values at 300 and 15 K, carrier concentration, mobility and band gap of films for both sets S1 and S2. ......................................................... 61

**Table 5.1** Average transmittance, resistivity values, carrier concentration, mobility, and optical band gaps of S1, S2, and S3 samples. .............................................................................................................. 88

**Table 5.2** All the important parameters extracted from the fits to the temperature dependent resistivity data to Equation (5.1). ........................................................................................................ 89

**Table 6.1** Average transmittance, film thicknesses, carrier concentration, and mobilities of S1, S2, and S3 samples. ......................................................................................................................... 110
1. Introduction

Transparent conducting oxides (TCOs) are electrically conductive materials with low absorption of electromagnetic waves within the visible region of the spectrum. Most TCOs are binary or ternary compound, containing one or two metallic elements. Basic requirements for TCO materials are an average transmittance of above 80% and resistivity below $10^{-3} \ \Omega \cdot \text{cm}$. This combination of conductivity and transparency is usually not possible in intrinsic stoichiometric oxides. Such conductivities are usually achieved in two ways: by producing the materials with a non-stoichiometric composition so the conductivity essentially is due to defects, or doping with appropriate dopants. Depending on the type of the carriers, TCOs can be classified into n- and p-type semiconductors, where the electrons and holes are the majority carriers, respectively.

There is a growing interest in the research on TCOs due to the numerous applications they have. Some of the actual and potential applications of TCO thin films include: flat panel displays, transparent electrodes for photovoltaic cells, transparent thin film transistors, light emitting diodes, semiconductor lasers, low emissivity windows, and window defrosters. The TCO material is chosen depending on the application needs, considering stability in operating environmental, compatibility with substrate, abrasion resistance, and electron work function as well as other factors. Other significant factors for choosing the appropriate TCO materials are the availability of the raw materials and the economics of the growth method.
Currently, the most widely used material for TCO applications is indium tin oxide (ITO). ITO is a solid solution of indium(III) oxide (In$_2$O$_3$), and tin(IV) oxide (SnO$_2$) with typically 3wt% to 10wt% SnO$_2$. ITO can be used both in crystalline and amorphous forms for display applications. Most common method for deposition is DC/RF magnetron sputter deposition. However, it seems to be difficult to maintain a constant stoichiometry of ITO, due to rapidly diminishing supply of indium. Abundance of indium in the continental crust is estimated to be approximately 0.05 parts per million, which prohibits direct mining of this element. Reserves of indium are obtained from either refining processes of zinc-sulfide ore mineral sphalerite or from recycling formerly used indium. The sputtering process in which ITO is deposited as a thin film is also highly inefficient. Approximately 30% of an ITO target material is deposited onto the substrate. The remaining 70% consists of spent ITO target material, and processing residue left on the walls of the sputtering chamber.

In addition to the high cost of indium, ITO suffers also from poor chemical stability in hydrogen atmospheres and shows poor diffusion barrier characteristics. Silicon based photovoltaic applications require a hydrogen passivation step in the solar cell fabrication, therefore, stability in hydrogen atmosphere is particularly important for process flow. Limited availability of indium along with these factors have motivated researchers to explore new and relatively inexpensive materials for TCO applications. It is also thought that these new materials can have technical advantages over ITO, especially in terms of processing and stability. At present, F-doped tin oxide, Nb-doped titanium dioxide, Al-doped zinc oxide and Ga-doped zinc oxide semiconductors are promising alternatives to ITO for thin film
transparent electrode applications. ZnO doped with Al or Ga is a promising candidate due to its superior stability in hydrogen environment, non-toxic nature, and relatively inexpensive supply. The doped ZnO films with conductivity and transmittance properties comparable to ITO can be grown on a variety of substrates, like sapphire, glass and flexible polymers.

The focus of this thesis is on determining the characteristics and properties of TCO films for possible applications in organic solar cells. For most photovoltaic applications, including solar cells, the basic requirements are transmittance above 80% and resistivity lower than $10^{-3}$ Ω-cm. In order to reach these requirements, carrier concentrations in the range of $10^{21}$ cm$^{-3}$ and mobilities around 50 cm$^2$/Vs need to be realized. The transmittance and conductivity are inversely related and a compromise is made between the two to achieve optimum TCO characteristics. The main limitation for the TCO films is the mobility, rather than a high carrier concentration. Mobility is usually limited by ionized impurity scattering in these systems. It is desirable to have mobilities exceeding 100 cm$^2$/Vs to reach a target resistivity of $5\times10^{-5}$ Ω-cm. One of the main objectives of this research was to design a TCO material with maximum conductivity and transmittance in the visible spectra.

Zinc oxide possesses some other unique properties that are key to future high performance devices. Conventional electronic devices rely on the transport of electrical charge carriers. However, shrinking transistor dimensions lead to challenges like gate leakage current and heat management. The industry is searching for new methods and materials to achieve performance improvements as an alternative to traditional techniques. Spin transport
electronics (spintronics) is a rapidly growing research field aimed at realizing new high performance devices that take advantage of the electron spin as well as of its charge. Combining both spin and charge functionalities could revolutionize the technology by providing improved efficiency, reduced power consumption and high boot-up speeds.

The best way to combine spin and charge is by synthesizing a material with both semiconducting as well as magnetic properties. However, it is necessary to find another way to integrate magnetic property with semiconducting property, since conventional semiconductors (Si, GaAs) are diamagnetic and they interact weakly with externally applied magnetic field. Transition metal doped ZnO thin films have generated special interest, since high temperature ferromagnetism with Curie temperature ($T_C$) above room temperature has been reported in these systems.9

Ferromagnetic properties of undoped and doped ZnO thin films have been studied in the second part of this thesis. Thin films have been grown by pulsed laser deposition technique with different growth parameters. Our primary scientific interests are, whether doping with non-magnetic dopants affects the observed ferromagnetism, how the microstructure changes the ferromagnetic properties of ZnO films and what is the role of intrinsic defects in tuning the magnetic properties.
The rest of this thesis is organized in the following chapters:

**Chapter 2:** In this chapter, background knowledge pertinent to the study is presented.

**Chapter 3:** A brief description of experimental techniques used for present work is given.

**Chapter 4:** Results of Ga and Al codoping in zinc oxide thin films for transparent conducting oxide applications is presented.

**Chapter 5:** The study of physics of the resistance minima occurring in doped ZnO films due to disorder is presented along with the results on the ferromagnetic behavior of these films.

**Chapter 6:** The growth and structure-property correlations of nanostructured pure ZnO thin films are discussed.

**Chapter 7:** A brief summary of the present work is presented. Scope for future work is discussed.
1.1. References


2. Background

2.1. Transparent Conducting Oxide (TCO)

In this section, the basic properties of TCOs and the several selection criteria will be discussed. TCOs are wide band-gap semiconductors that have high transmittance values with a relatively high concentration of free carriers. This carrier concentration may arise from defects that are intrinsic to the material, or from extrinsic dopants that have energy levels lying close to the conduction band edge. A TCO must necessarily represent a compromise between electrical conductivity and optical transmittance, since high electron carrier concentration causes absorption of electromagnetic radiation in both the visible and infrared portions of the spectrum. Main challenge in TCOs is achieving a careful balance between high optical transmittance and electrical conductivity. According to Boltzmann’s conductivity equation, a material’s conductivity is given by;

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

(2.1)

where \( \sigma \) is the electrical conductivity, \( n \) is the carrier concentration, \( |e| \) is electronic charge, and \( \mu \) is the carrier mobility. Increasing the mobility is probably the best direction to follow. Mobility is directly dependent on the relaxation time, and is inversely dependent on the effective mass of the carrier.
2.1.1 Figure of Merit for TCOs

An effective TCO should have high electrical conductivity combined with low absorption of visible light. An appropriate figure of merit for TCOs therefore is the ratio of the electrical conductivity $\sigma$ to the visible absorption coefficient $\alpha$:

$$\frac{\sigma}{\alpha} = -\left\{R_S \ln(T+R)\right\}^{-1}$$  \hspace{1cm} (2.2)

where $R_S$ is the sheet resistance in ohms/square, $T$ is the total visible transmission, and $R$ is the total visible reflectance. A larger value of $\sigma/\alpha$ indicates better performance of the TCO. Figures of merit for some transparent conductors are given in Table 2.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sheet Resistance ($\Omega/\square$)</th>
<th>Visible Absorption Coefficient ($\alpha$)</th>
<th>Figure of Merit ($\Omega^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:F</td>
<td>5</td>
<td>0.03</td>
<td>7</td>
</tr>
<tr>
<td>Cd$_2$SnO$_4$</td>
<td>7.2</td>
<td>0.02</td>
<td>7</td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>3.8</td>
<td>0.05</td>
<td>5</td>
</tr>
<tr>
<td>In$_2$O$_3$:Sn</td>
<td>6</td>
<td>0.04</td>
<td>4</td>
</tr>
<tr>
<td>SnO$_2$:F</td>
<td>8</td>
<td>0.04</td>
<td>3</td>
</tr>
<tr>
<td>ZnO:Ga</td>
<td>3</td>
<td>0.12</td>
<td>3</td>
</tr>
<tr>
<td>ZnO:B</td>
<td>8</td>
<td>0.06</td>
<td>2</td>
</tr>
<tr>
<td>SnO$_2$:Sb</td>
<td>20</td>
<td>0.12</td>
<td>0.4</td>
</tr>
<tr>
<td>ZnO:In</td>
<td>20</td>
<td>0.20</td>
<td>0.2</td>
</tr>
</tbody>
</table>
2.1.2 Electrical Properties

The conductivity is proportional to the product of the concentration of free carriers and the mobility. Carrier transport is limited primarily by ionized impurity scattering at high electron concentrations. Therefore, decreasing carrier mobility results in a decrease in the conductivity as well as the optical transmission at the near-IR edge. The resistivity reaches a lower limit with increasing dopant concentration and the optical window becomes narrower. The mobility and conductivity of TCOs are intrinsically limited by ionized impurity scattering for carrier concentrations exceeding $10^{20}$ cm$^{-3}$. However, the mobility is not only governed by ionized impurity scattering but also by lattice (phonon) scattering, neutral impurity scattering, electron-electron and electron-impurity scattering. In highly degenerate semiconductors, the contribution of ionized impurity scattering is given by,

\[ \mu_{\text{IIS}} = \frac{4e}{n} \left(\frac{\pi}{3}\right)^{1/3} n^{-2/3} \]  \hspace{1cm} (2.3)

In the case of polycrystalline TCOs, grain boundary scattering also becomes an important scattering mechanism. These boundaries contain fairly high densities of interface states, which trap free carriers from the bulk and scatter free carriers due to the inherent disorder and the presence of trapped charges. The interface states result in a space charge region in the grain boundaries. The contribution is given by,

\[ \mu_g = \mu_0 \exp\left(\frac{\phi_d}{kT}\right) \]  \hspace{1cm} (2.4)
where,

$$\mu_0 = \left( \frac{\mu^2 e^2}{2\pi m^* kT} \right)^{1/2} \quad (2.5)$$

in which, L is the grain size, \( \varphi_b \) is the grain boundary potential, \( m^* \) is the conduction band effective mass of electron.

Theoretical simulations show that the mobility decreases with decreasing grain size and increasing grain boundary potential. For a grain boundary potential value of \(~0.01\text{eV}\) and an average grain size of \(~100\ \text{nm}\), the calculated mobility was greater than \(200\ \text{cm}^2/\text{Vs}\). However, the mobility values reported in the literature are below \(100\ \text{cm}^2/\text{Vs}\).

Based on the discussion of various carrier scattering mechanisms, it can be assumed that the ionized impurity scattering sets the intrinsic limit for maximum value of mobility, and the maximum achievable conductivity of TCOs. The effect of other scattering mechanisms like scattering from defects and dislocations, electron-electron and electron-impurity interaction, and neutral impurity scattering also limit carrier mobility, but most of these tend to affect only at low temperatures.

2.1.3 Optical Properties

As mentioned earlier, one of the important metrics for TCOs is that they must have very low absorption coefficients in the near UV – Visible – near IR region. Optically transparent
region (transparent window) is limited by the absorption edge in the near UV and the plasma edge in the near IR. The absorption edge is associated with the fundamental bandgap absorption and the plasma edge is determined by free electron plasma absorption.

The optical properties of TCOs transmission (T), reflection (R), and absorption (A) are determined by its band gap $E_g$, extinction coefficient $k$, refraction index $n$, and geometry. These parameters depend on the chemical composition and solid structure of the material. The geometry can be modulated by changing the film thickness, thickness uniformity and surface roughness.

In order to explain the transmittance and absorption, we need to consider the energy band diagram of the TCOs. The conduction band mainly consists of s electrons of the cations and the valance band is formed by 2p electrons of oxygen. The two bands are separated by a large bandgap greater than 3 eV, which leads to the transparency of TCOs in the visible spectrum. Electrons can absorb photons and jump from the valance band to conduction band upon radiation with energies higher than the bandgap. For the intrinsic semiconductors, the Fermi energy ($E_F$) lies in the middle of the bandgap ($E_g/2$). As the electron concentration increases, $E_F$ is shifted towards the conduction band. High concentration of electrons generated from the native defects and external dopants move $E_F$ inside the conduction band making it a degenerate semiconductor. This phenomenon is known as the Burstein-Moss effect, which is due to the filling up of lowest states by electrons in the conduction band. The increase in the optical bandgap leads to shift of the absorption edge towards shorter wavelength.
Under the assumption that the conduction band (CB) and valance band (VB) are parabolic, the dispersions of the CB and VB in the doped material are given by,

\[ E_v^0(k) = -\left(\frac{\hbar^2 k_F^2}{2m_c^*}\right) \]  \hspace{1cm} (2.6)

\[ E_c^0(k) = E_g - \left(\frac{\hbar^2 k_F^2}{2m_c^*}\right) \]  \hspace{1cm} (2.7)

then the measured band gap is,

\[ E_g^0(k) = E_g + \Delta E_{g}^{BM} \]  \hspace{1cm} (2.8)

where

\[ \Delta E_{g}^{BM} = \frac{\hbar^2 k_F^2}{2} \left(\frac{1}{m_v^*} - \frac{1}{m_c^*}\right) \]  \hspace{1cm} (2.9)

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

\[ k_F = (3\pi^2 n)^{1/3} \]  \hspace{1cm} (2.10)

Therefore,

\[ \Delta E_{g}^{BM} = (3\pi^2 n)^{2/3} \frac{\hbar^2}{2} \left(\frac{1}{m_v^*} - \frac{1}{m_c^*}\right) \]  \hspace{1cm} (2.11)

It can be seen that the measured optical band gap is proportional to \( n^{2/3} \).

In order to account for other scattering processes, a correction term can be added to the dispersion of energy bands,
\[ E_g = \Delta E_g^{BM} + W \]  \hspace{1cm} (2.12)

where, \( W \) represents a decrease of bandgap due to scattering terms.

Another important parameter for TCOs is the reflectivity. Like mobility, reflectivity is affected by the degenerate nature of a semiconductor. The plasma frequency (\( \omega_p \)) for the conduction electrons is the limiting parameter for the optical properties in a TCO. At frequencies below the plasma frequency, the TCO reflects and absorbs incident radiation. For most TCO materials, the plasma frequency falls in the near IR region of the spectrum. The plasma frequency of a conducting material is defined from Drude model,

\[ \omega_p = \left( \frac{ne^2}{\varepsilon_\infty \varepsilon_0 m^*} \right)^{1/2} \]  \hspace{1cm} (2.13)

which is valid for the case when \( \omega < \omega_p \) the conductor is highly reflective and \( \varepsilon_1 < 0 \). This has been obtained by considering limit of electron density (\( n > 10^{21} \text{ cm}^{-3} \)) and high mobility (\( > 20 \text{ cm}^2/\text{Vs} \)) for indium tin oxide. This means that for a film to be non-reflective to light of free space wavelength \( \lambda_0 \), the electron density must satisfy,

\[ n < \frac{4\pi^2 \varepsilon_\infty m^*}{\mu_0 e^2 \lambda_0^2} \]  \hspace{1cm} (2.14)
For the case of ITO, for efficient transmission of the whole visible spectrum, the electron density should not exceed $2.6 \times 10^{21} \text{ cm}^{-3}$.

These calculations show that the requirement for transparency gives an absolute lower limit on the resistivity of about $4 \times 10^{-5} \ \Omega\text{-cm}$. These calculations do not take into account the dependence of effective mass on the increase in carrier concentration. The effective mass increases with increasing carrier concentration, hence the limit for the resistivity is around $3 \times 10^{-5} \ \Omega\text{-cm}$ and the corresponding carrier concentration is $9 \times 10^{21} \text{ cm}^{-3}$ with effective mass correction.

### 2.1.4 Work Function

Work function ($\phi$) of a TCO is defined as the energy difference between the Fermi level and the ionization potential. In most n-type TCOs the Fermi level lies in the conduction band due to the degenerate nature of these films. Therefore, the work function is essentially the energy required to remove the electron from the conduction band. The work function has two contributions, the chemical affinity ($\chi$) and the value of $(E_F - E_c)$. The value of work function is given by:

$$\phi = \chi + (E_F + E_c) \quad (2.15)$$
Work function is extremely sensitive to the surface characteristics as it affects the value of $\chi$.

$\phi$ is also a function of the carrier concentration because the value of $(E_F - E_c)$ is mainly determined by the carrier concentration. Although, $\chi$ is a material property, it has been found that it also exhibits a slight dependence on the carrier concentration. In general the higher the carrier concentration, the lower is the work function of a given sample. Pure zinc oxide has a work function value of 4.5 eV with a carrier concentration of $7 \times 10^{19}$ cm$^{-3}$.

In organic devices the work function of the electrode materials is very important since it determines together with the lowest unoccupied molecular orbital (LUMO) / highest occupied molecular orbital (HOMO) and Fermi-level of the semiconductor whether the electrode forms an ohmic or a blocking contact for the respective charge carrier (holes in VB, electrons in CB). Moreover a large difference in work function of the electrode materials can increase the open circuit voltage $V_{oc}$ considerably. The variability of work function poses a similar situation as balancing the optical properties ($%T$ and R) and the electrical properties. However, optimization of the work function does not always assure the highest efficiency, because the carrier injection is also dependent on the chemical and structural characteristics of the heterojunction interface.

2.2. Thin Film Epitaxy

The term epitaxy comes from two Greek words $\varepsilon\pi\alpha$ (epi - placed or resting upon) and $\tau\alpha\zeta\iota\varsigma$ (taxis - arrangement). It was first introduced by Royer to describe the phenomenon of the
oriented growth of crystals of one substance on the crystal surface of another substance. The term has since been generalized to thin crystalline films grown with one or more well-defined orientations on a single-crystal substrate. In the strict sense epitaxy refers to formation of single crystalline film on a substrate such that the film has a fixed orientation relationship with the substrate. The single crystalline epitaxy is not possible when the substrate and the film have different crystal symmetries in the growth plane. In such instances of thin film epitaxy, film may have more than one orientation relationship with the substrate.

Epitaxy can be further classified as homoepitaxy or heteroepitaxy. Homoepitaxy refers to the case where the film and substrate are the same material. Growth of epitaxial Si on Si wafers in the fabrication of bipolar and some MOS transistors by vapor phase epitaxy is the most significant example of homoepitaxy. The second type of epitaxy is known as heteroepitaxy and refers to films and substrates composed of different materials, e.g., ZnO deposited on Al$_2$O$_3$ substrates. Optoelectronic devices such as light-emitting diodes and lasers are based on compound semiconductor heteroepitaxial film structures. Since the film and the substrate materials are different in heteroepitaxy, the properties of heteroepitaxial films are influenced by crystallographic properties of the substrate and the film, the difference in film and substrate chemistry, and the difference in film and substrate thermal expansion coefficients. The most relevant crystallographic properties to epitaxy are crystal symmetry and in-plane lattice constants which decide lattice misfit. The lattice misfit between substrate and film is key parameter which controls growth, morphology and properties of the film. The lattice misfit is defined as,
\[ f = \frac{a_{film} - a_{subs}}{a_{subs}} \]  

(2.16)

2.2.1 Lattice Matching Epitaxy

In lattice matching epitaxy, one to one matching of lattice parameters across the film substrate interface is considered. This matching of lattice parameters occurs by means of strain in the film and the substrate, and the growth is pseudomorphic. The growth continues until a critical thickness is reached where the strain energy becomes large enough to trigger nucleation of dislocations. The critical thickness for dislocation is directly related to the misfit. In low misfit systems the critical thickness for dislocation nucleation may be quite large and dislocation nucleation and strain relaxation may not be possible. Also, these dislocations are nucleated at the film surface and must glide to the interface to relieve the strain. The obstacles to the glide of dislocations may result in a high threading dislocation density in the film, which is detrimental for devices.

2.2.2 Domain Matching Epitaxy

Lattice matching epitaxy is possible as long as the lattice misfit between the film and the substrate is less than 7–8%. Above this misfit, it was presumed that the film will grow textured or largely polycrystalline. The epitaxial growth in high misfits systems can be explained by domain matching epitaxy (DME), proposed by Narayan et al. In the domain matching epitaxy, matching of lattice planes is considered, which could be different in
different directions of the film–substrate interface. This is in contrast to LME in which there is one-to-one matching of lattice constants across the film–substrate interface. An important feature of the domain epitaxy concept is that most of the strain is relieved quickly within a couple of monolayers, so that the misfit strain and dislocations can be engineered and confined near the interface. The rest of the film then grows free of defects and lattice strains.

In DME misfit is accommodated by matching of integral multiples of lattice planes, and there is one extra half plane (dislocation) corresponding to each domain. If the misfit falls in between the perfect matching ratios of planes, then the size of the domain can vary in a systematic way to accommodate the additional misfit.

The residual strain after the matching of m planes of film with n planes of substrate is given by,

\[ \varepsilon_r = \frac{m \times d_f}{n \times d_s} \]  \hspace{1cm} (2.17)

where m and n are simple integers and \(d_f\) and \(d_s\) are the interplanar spacing of film and substrate, respectively. If the matching is perfect, residual strain is zero and \(md_f = nd_s\). For the case of nonzero \(\varepsilon_r\), then two domains alternate with certain frequency (\(\alpha\)) to accommodate for perfect matching,

\[ (m + \alpha)d_f = (n + \alpha)d_s \]  \hspace{1cm} (2.18)
Since the concept of DME was first proposed, it has been shown to be important for growing thin heterostructures with large lattice misfit. Some typical examples for the DME growth are TiN/Si(100) heterostructures, III-nitride epitaxy on Si(111), and ZnO and III-nitrides on sapphire (0001). In the case of ZnO, growth of high quality films on sapphire poses a great challenge. The epitaxial growth of high quality ZnO has been accomplished by DME. Figure 2.1 shows how the epitaxial growth of ZnO on a c-plane sapphire substrate was accomplished by DME.

Figure 2.1 (a) ZnO/Sapphire interface (b) Fourier filtered image showing epitaxial matching of planes according to DME (c) SAED pattern of ZnO/Sapphire interface (d) Schematic plan view of the epitaxy.
The planar misfit of 15.4 % corresponds to 5/6 and 6/7 plane matching. More detailed analysis on ZnO epitaxy is given in Chapter 4.

2.3. Zinc Oxide

Zinc oxide is a wide and direct band gap semiconductor with a band gap of ~3.37 eV at room temperature. Recently, there has been great interest in ZnO thin films and nanostructures due to the emerging applications in optoelectronics, transparent electronics, and spintronics. This thesis mostly focuses on developing ZnO as an alternative material for blue and ultraviolet optoelectronic devices, which are currently based on gallium nitride (GaN). One of the main advantages of ZnO over GaN is its high excitonic binding energy, 60meV compared to 30meV for GaN. The high excitonic energy leads to an intense near-band-edge excitonic emission above room temperature that makes ZnO a potential candidate for exciton recombination-based lasing devices. Undoped ZnO is inherently n-type. This behavior has been attributed to the presence of intrinsic defects like oxygen vacancies and zinc interstitials. Doping with Ga or Al makes zinc oxide highly conductive. This has stimulated research to develop ZnO as a transparent conducting oxide (TCO), as a cheaper alternative to indium tin oxide (ITO). Zinc oxide also has large piezoelectric, which makes it useful material for transducers and actuators. Room temperature ferromagnetism in transition metal (e.g., Fe, Mn, Co, and Ni) doped ZnO, makes it a potential candidate for next generation spintronic devices. The electrical conductivity of ZnO thin films is very sensitive to the adsorbed species like hydrogen and oxygen. This high surface sensitivity makes zinc oxide a
promising material for gas sensors. Strong non-linear resistance of polycrystalline ZnO is the basis of commercially available ZnO varistors. Zinc oxide exhibits strong luminescence in green-white range of the spectrum. The other properties of ZnO which make it preferable over other wide-band-gap materials are its high energy radiation stability and amenability to wet chemical etching. Several experiments confirmed that ZnO is very resistive to high-energy radiation making it a very suitable candidate for space applications. ZnO is easily etched in all acids and alkalis, and this provides an opportunity for fabrication and patterning of small-size devices.

2.3.1 Crystal Structure of ZnO

ZnO crystallizes in three different forms: wurtzite (hexagonal), zinc blende, and rock salt structures. Wurtzite is thermodynamically the most stable structure under ambient conditions. Other two structures are also observed to appear 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 Wurtzitic structure belongs to point group 6mm and the space group P63mc. This structure is composed of two interpenetrating hexagonal-close-packed (hcp) sublattices of Zn and O atoms (Figure 2.2). These two sublattices are displaced from each other by 0.375 c along c-axis. This displacement of Zn and O sublattices makes this structure non-centrosymmetric and imparts a polarity to ZnO along c-axis. In this structure each zinc ion is tetrahedrally coordinated by four oxygen ions and vice versa.
Though the tetrahedral coordination is indicative of sp3 covalent bonding, ZnO has substantial ionic character.

The lattice constants of ZnO hexagonal unit cell are $a=3.2499$ Å and $c=5.2066$ Å. The ratio $c/a$ of the elementary translation vectors, with values around 1.602, deviates slightly from the ideal value of $c/a=1.633$ for hexagonal close packed structure. The four most common face terminations are the polar Zn terminated (0002) and O terminated (000$\bar{2}$) faces (c-plane), and the non-polar (11$\bar{2}$0) a-plane and (10$\bar{1}$0) m-plane faces, which both contain an equal number of Zn and O atoms. One of the most important semi-polar planes in ZnO is the (10$\bar{1}$2) r-plane.

![Figure 2.2 Wurtzite crystal structure of ZnO. Zinc atoms are shown in white and oxygen atoms are shown in yellow.](image)
2.3.2 Electronic Structure of ZnO

ZnO is a direct-gap semiconductor with the global maxima of the valence band (VB) and the minima of the conduction band (CB) at the same point in the Brillouin zone, namely at k=0. The lowest unoccupied orbital (LUMO), or the bottom of the conduction band is formed from the 4s levels of Zn$^{2+}$. The top of the valence band, or highest occupied molecular orbital (HOMO), is formed from the 2p levels of O$^{2-}$. The band gap at room temperature is ~3.37 eV. The effective electron mass in is quite isotropic, with a value around $m_e = 0.28m_o$. The hole masses are similar for the A, B and C valence bands, with typical values of $m_{h\perp,A,B} = 0.59m_o$, $m_{h\parallel,C} = 0.31m_o$, and $m_{h\perp,C} = 0.55m_o$.

2.4 Native Point Defects in ZnO

There are a number of intrinsic defects in ZnO with different ionization energies: O vacancy ($V_O$), Zn vacancy ($V_{Zn}$), Zn interstitial ($Zn_i$), O interstitial ($O_i$) and antisite Zn ($ZnO$). Zn interstitials, oxygen and zinc vacancies are known to be the predominant ionic defect types. The calculated energy levels of the native defects in ZnO film are shown in Figure 2.3.
Figure 2.3 Calculated energy values of defects in zinc oxide film.

The atomic and electronic structures of the native defects in ZnO have been extensively investigated, both theoretically and experimentally. However, there is no one widely accepted model to understand them. To better understand behaviors in intrinsic ZnO materials and self-compensation in undoped and doped ZnO materials, Janotti et al. calculated the formation energy of native defects in ZnO based on the density functional theory within the local density approximation (LDA) as well as the LDA + U approach for overcoming the band-gap problem. In this theory, the concentration of a defect in a crystal depends on its formation energy ($E_{\text{form}}$) that is given as,

$$c = N \left( \frac{-E_{\text{form}}}{k_B T} \right)$$  \hspace{1cm} (2.19)

where $E_{\text{form}}$ is the defect formation energy, and $N$ is the number of sites that the defect can be incorporated. It can be seen that low formation energy implies a high equilibrium
concentration, and high formation energy means that defect is unlikely to form. The formation energy of a defect in a charge state q can be calculated by,

$$E_{\text{form}}(q) = E_{\text{total}}(q) - n_{Zn} \mu_{Zn} + n_{o} \mu_{o} - q E_{F} \quad (2.20)$$

where $E_{\text{total}}(q)$ is the total energy of the system, which contains $n_{Zn}$ and $n_{o}$ number of zinc and oxygen atoms, $\mu_{Zn}$ and $\mu_{o}$ are the chemical potentials for zinc and oxygen, respectively, and $E_{F}$ is the Fermi energy. The growth parameters control the chemical potentials. For the zinc-rich case, $\mu_{Zn} = \mu_{Zn}(\text{bulk})$ and for the oxygen-rich case $\mu_{o} = \mu_{o}(O_{2})$. The formation energies of native defects in ZnO under zinc-rich conditions are given in Table 2.1.
Table 2.2 Calculated formation energies at $E_F=0$ for native point defects in ZnO under zinc-rich conditions

<table>
<thead>
<tr>
<th>Defect</th>
<th>$q$</th>
<th>$n$</th>
<th>$E^{\text{LDA}}$</th>
<th>$E^{\text{LDA+U}}$</th>
<th>$E'$</th>
<th>(CB/VB) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_o$</td>
<td>2+</td>
<td>0</td>
<td>-0.37</td>
<td>-0.60</td>
<td>-0.60</td>
<td>62/38</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>1</td>
<td>0.64</td>
<td>0.81</td>
<td>1.91</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>2</td>
<td>0.09</td>
<td>1.34</td>
<td>3.72</td>
<td></td>
</tr>
<tr>
<td>$V_{Zn}$</td>
<td>0</td>
<td>4</td>
<td>5.94</td>
<td>6.39</td>
<td>7.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>5</td>
<td>6.02</td>
<td>6.49</td>
<td>7.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2+</td>
<td>6</td>
<td>6.31</td>
<td>6.94</td>
<td>8.43</td>
<td></td>
</tr>
<tr>
<td>$Zn_i$</td>
<td>2+</td>
<td>0</td>
<td>-0.10</td>
<td>-0.45</td>
<td>-0.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>1</td>
<td>1.32</td>
<td>1.56</td>
<td>3.20</td>
<td>87/13</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>2</td>
<td>2.76</td>
<td>3.62</td>
<td>6.95</td>
<td></td>
</tr>
<tr>
<td>O(oct)</td>
<td>0</td>
<td>4</td>
<td>6.36</td>
<td>6.83</td>
<td>8.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>5</td>
<td>6.63</td>
<td>7.22</td>
<td>9.26</td>
<td>23/77</td>
</tr>
<tr>
<td></td>
<td>2-</td>
<td>6</td>
<td>7.49</td>
<td>8.28</td>
<td>10.86</td>
<td></td>
</tr>
<tr>
<td>O(split)</td>
<td>2+</td>
<td>2</td>
<td>5.13</td>
<td>5.12</td>
<td>5.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>3</td>
<td>5.01</td>
<td>5.02</td>
<td>5.24</td>
<td>03/97</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>4</td>
<td>4.93</td>
<td>4.97</td>
<td>5.24</td>
<td></td>
</tr>
<tr>
<td>$Zn_o$</td>
<td>4+</td>
<td>0</td>
<td>0.14</td>
<td>-0.31</td>
<td>-0.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3+</td>
<td>1</td>
<td>0.48</td>
<td>0.44</td>
<td>1.57</td>
<td>54/46</td>
</tr>
<tr>
<td></td>
<td>2+</td>
<td>2</td>
<td>0.22</td>
<td>0.33</td>
<td>2.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>3</td>
<td>1.81</td>
<td>2.74</td>
<td>6.49</td>
<td>89/11</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>4</td>
<td>3.43</td>
<td>4.98</td>
<td>10.47</td>
<td></td>
</tr>
<tr>
<td>$O_{Zn}$</td>
<td>0</td>
<td>4</td>
<td>9.94</td>
<td>10.04</td>
<td>13.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>5</td>
<td>10.53</td>
<td>10.88</td>
<td>14.68</td>
<td>41/59</td>
</tr>
<tr>
<td></td>
<td>2-</td>
<td>6</td>
<td>11.08</td>
<td>11.76</td>
<td>16.45</td>
<td></td>
</tr>
</tbody>
</table>

There are two possible interstitial sites in the wurtzite ZnO: one is tetrahedrally coordinated and the other is octahedrally coordinated. It is generally agreed that the two most common defects in ZnO are likely to be oxygen and zinc vacancies. Analysis of the formation energy for the native defects in ZnO shows that the dominant native defects in ZnO should be vacancies: anion vacancies in n-type material (when the Fermi level is close to the conduction band) and cation vacancies in p-type material (when the Fermi level is close to the valence band). Some of the native defects (with the formation energy of several electron volts), have extremely low probability of being formed during the growth, such as zinc interstitials. However, we should note that these formation energies are calculated at
thermodynamic equilibrium and may not represent the conditions attained during real growth atmosphere, especially with non-equilibrium processes, such as pulsed laser deposition.

2.4.1 Oxygen Vacancies

$V_O$ may be thought of as a host oxygen atom, in the −2 oxidation state, being removed from the lattice. The electrons that would normally be bound to the missing O atom can be viewed as coming from the four neighboring Zn sites, half an electron from each. These electrons are still present, at least for an uncharged defect, so the two additional electrons that would have been at the O site mean that $V_O$ is expected to act as a (double) donor. In the neutral charge state the four neighboring Zn atoms shift inwards by around 10%, forming a pair of Zn–Zn bonds. In the case of the +1 and +2 charge states, the four neighboring Zn atoms shift in the opposite direction, outwards by 3% and 23%, respectively. The origin of the different structures may be viewed as a chemical reconstruction in the neutral charge state, and this large geometric effect has an impact upon the electrical properties. The charge-dependent formation energies indicate a (0/+2) level around $E_v + 1.0 \text{ eV}$, too deep to be the cause of n-type conductivity in ZnO. The oxygen vacancy is a deep, negative-U donor, where the 1+ charge state is never thermodynamically the most stable charge state for any value of the electron chemical potential. When the Fermi energy is above the (0/ + 2) level, the defect is in the neutral charge state. When the Fermi energy is below the (0/ + 2) level, the defect has a charge of +2e. The negative-U nature of this center is a result of the chemical reconstruction in the neutral charge state: indeed, negative-U centers are typically characterized by large
structural changes with charge state. Based on theoretical calculations, the neutral $V_O$ has relatively low formation energy of $\sim 1$ eV under Zn-rich conditions. It is worth noting that $V_O$ has relatively high migration barrier of 2.4 eV. This implies that $V_O$ undergoes very little diffusion at room temperature, but that annealing to higher temperatures may result in the movement of these double donors, and possibly their direct interaction with other defects in the lattice.

2.4.2 Zinc Vacancies

The oxygen atoms around the zinc vacancy shift outward by about 3% with respect to the equilibrium ZnO bond length. There is a similar relaxation for the singly charged state, however relaxation is substantial in the doubly charged state. Zinc vacancies are double acceptors in ZnO. Neutral $V_{\text{Zn}}$ centers have very high formation energy, being about 3.5 eV in the neutral charge state even under O-rich conditions. In n-type material the formation energy is lower. The 0/1- and 1/-2- acceptor levels are calculated to be 0.1-0.2 and 0.9-1.2 eV above the valance band maximum. The zinc vacancy has a spin $S=1/2$ and an anisotropic g-tensor in the 1- charge state. In the neutral charge state, two holes are trapped on different nonaxial O sites, resulting in a spin $S=1$.

Zinc vacancies may originate the green luminescence in some ZnO samples. Janotti et. al. showed that the transition from a shallow donor level to the 1–2– acceptor level could give rise to photoluminescence signal around 2.5 eV. Also, green band intensity is reduced by
exposure of ZnO samples to H plasma, which is consistent with the passivation of Zn vacancies. However, green band intensity decreases upon electron irradiation, even though defects such as Zn vacancies are created. Zn vacancies produced by electron irradiation can be annealed at 200-300°C. Concentration of vacancy defects decreases with increasing sintering temperature in ZnO.

2.4.3 Zinc Interstitials

Zinc interstitials might be another of the sources of the common, unintentional n-type conductivity in as-grown ZnO. It was mentioned earlier that there are two main sites for zinc interstitials in the wurtzite structure: the tetrahedral interstitials site, and the octahedral interstitial site. The difference between the tetrahedral and octahedral interstitial sites is that Zn interstitials at the octahedral sites are more stable than Zn interstitials at the tetrahedral sites. Placing the zinc interstitial at an octahedral site induces a noticeable local lattice relaxation, particularly in terms of a strong interaction between the Zn atom and three of the nearest neighbor O atoms. Zn interstitials have relatively high formation energies in n-type material and are expected to rapidly diffuse with a low migration barrier of about 0.57 eV. It has been found that the Zn interstitial behaves as a shallow donor, although thermodynamically not stable. Based on the calculated energy of formation and low migration barrier, Zn interstitials are not expected to be stable at room temperature and are unlikely to be responsible for the unintentional n-type conductivity of ZnO. However, due to the low migration barrier, Zn interstitials can diffuse relatively freely and they may find other
sites such as O vacancies to form Zn antisites, or they may act as defect complexes to play a role in the n-type conductivity in ZnO.
3. Experimental Techniques

The main technique employed in this thesis work for thin film growth had been Pulsed Laser Deposition (PLD). Major steps followed for deposition and the analysis thereafter could be listed as substrate preparation, pulsed laser deposition, x-ray diffraction, transmission electron microscopy, Hall Effect measurement, four-point resistivity measurement, photoluminescence spectroscopy and absorption spectroscopy. Each of the listed steps is briefly described in the following sections.

3.1. Substrate Preparation

Preparing the substrate of choice and placement of the substrate on the substrate heater inside the PLD chamber is the first step in PLD thin film growth process. An important and necessary task in substrate preparation is cleaning the substrates before the deposition, because dust particles and organic impurities on substrate surfaces may have adverse effects on nucleation and epitaxial growth of thin films. After cleaning, the substrates should quickly be loaded into the PLD chamber.

Sapphire (0001) substrates had been used for thin film deposition in this study. The following steps were applied for cleaning the substrates:

- Substrates were placed in acetone bath and heated to ~ 200°C for 10 minutes.
- Substrates in the bath were agitated ultrasonically for 5 minutes to remove particulates.
- To remove the acetone, substrates were then cleaned ultrasonically in methanol bath.
- Substrates were blow-dried using high purity nitrogen.

Substrates were immediately loaded into the PLD chamber and a fast-drying silver paste was used to promote heat conduction and even heating of the substrates.

3.2. **Pulsed Laser Deposition**

The main technique employed in this study for thin film growth had been Pulsed Laser Deposition (PLD), which is a versatile non-equilibrium growth technique based on physical vapor deposition. In the PLD technique, the material to be deposited, referred to as target, and the substrate are placed in the same PLD chamber, and high-energy laser beams are focused and shot on the target material. As a result of the interaction between the laser and the target material, a highly energetic plasma forms due to localized vaporization of the target, a phenomenon usually called as *laser ablation*. The ablated material moves in a direction that is normal to the surface of the target material, in a *plume* form. As a result of the PLD technique, the material from the plume is deposited on the substrate, which is usually heated.
Excimer lasers can provide the very high energy densities that are required for the ablation of most target materials. Therefore excimer lasers are most commonly used in PLD processes. The emission wavelength of excimer lasers depend on the composition of the gas used in the laser cavity, and ArF (193 nm) and KrF (248 nm) excimer lasers are most commonly used for PLD.

The laser-solid (target material) interaction at energy densities above the vaporization threshold had been analyzed and a model had been proposed\textsuperscript{3} that divides the laser ablation process into the following important regimes:
• An evaporation regime that results from the interaction of the laser with the bulk target, causing the evaporation of the surface layers.

• A high-temperature isothermal expanding plasma formed as a result of the interaction of the laser with the evaporated material. This regime becomes effective as the target starts to evaporate, and it continues until the end of the pulse.

• An anisotropic three-dimensional adiabatic expansion of the plume that starts after the laser pulse terminates. This regime gives rise to the characteristic forward directed nature of the deposition.

Laser ablation of target materials occurs when the laser fluence (energy per unit area) exceeds a minimum threshold value. This threshold value is a function of both the laser properties (such as emission wavelength and pulse width) and the target material properties (optical properties such as absorption coefficient and thermal properties such as thermal diffusivity). Hence coupling of the laser and the target material is important for the efficiency of ablation process. The ablated material from the surface of the target also interacts further with the laser and gets heated by the laser beam. It is estimated that the plasma temperatures may reach up to 10000 K.

One of the biggest advantages of PLD is the stoichiometric transfer of material from target to the film, making PLD suitable for deposition of multi-elemental complex materials (such as YBCO). In PLD, the kinetic energy of the pulse laser ablated species is in the range of 10 to 100 eV in contrast to the thermal evaporation processes where the kinetic energy of the
species is around 100 meV. This feature enables high surface mobility in the growing film, and hence film growth could be achieved at lower temperatures than the thermal evaporation processes. Another advantage of PLD is the effective controllability of the film thickness, since each ablation pulse only provides enough material for the growth of a sub-monolayer.

On the other hand, PLD technique has limited application for large area thin film depositions. This is due to the non-uniformity of the thickness as a result of the plume profile. Generation and deposition of particulates during laser ablation is another important issue related with the PLD process. Among the important parameters to be managed carefully during PLD are the laser wavelength, pulse duration, pulse frequency, energy fluence, laser spot size, target-substrate distance, substrate temperature and background gas and pressure.

In this study, a Lambda LPX 210 KrF Excimer Laser was used with the following experimental configuration:

- Wavelength : 248 nm
- Pulse width : 25 ns
- Laser spot size : $\sim 2 \text{ mm} \times 3 \text{ mm}$
- Pulse frequency : 10 Hz
- Energy density : 3-4 J/cm$^2$
- Target-substrate distance : 4.5 cm
- Substrate temperature : 27 – 600 °C
Also the PLD chamber was evacuated to \(\sim 10^{-6}\) Torr before heating the substrate for thin film deposition and in many cases oxygen and argon were introduced into the chamber during deposition.

### 3.3. X-Ray Diffraction

X-ray diffraction is a nondestructive method for thin film characterization. It can be employed to obtain the lattice parameter value, phase identification and determination of crystallographic orientation and texture. In x-ray diffraction a material is probed with x-rays having wavelength close to lattice spacing. The conditions for diffraction are given by Bragg’s law\(^4\),

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

In this work, \(\theta-2\theta\) scans were performed using Rigaku D-MAX/A diffractometer with Cu-K\(\alpha\) radiation. This instrument is a two-circle diffractometer in which sample can be rotated along one of the axis (\(\theta\)-axis) and also the detector can be rotated independently (2\(\theta\)-axis). A schematic diagram for the diffractometer is given in Figure 3.2. This diffractometer is based on Bragg-Brentano diffraction geometry. In this geometry, the diffracted beam always lies in the plane containing the incident beam and the plane normal\(^5\). Due to the restricted rotation of the sample only along \(\theta\)-axis, this diffractometer can only be used to obtain diffraction information from the planes which are parallel to the surface of the sample (out-of-plane orientation). The in-plane orientation of the films can be accessed by a four circle
diffractometer. In this setup, the sample can be tilted with respect to the incident beam and also can be rotated 360° around the surface normal.

![Diagram of Rigaku D-MAX/A diffractometer used in Bragg-Brentano setup.](image)

Figure 3.2 A schematic diagram of Rigaku D-MAX/A diffractometer used in Bragg-Brentano setup.

The in-plane epitaxial information can be obtained by φ-scans. To perform a φ-scan an appropriate crystallographic plane (hkl), which is inclined to the growth plane (sample surface) is identified. The θ and 2θ angles are set to corresponding to Bragg angle for the identified plane. The sample tilt, ψ is set equal to the crystallographic angle between the growth plane (sample surface) and the (hkl) plane identified for the φ-scan. The diffraction intensity is then recorded as a function of sample rotation along φ-axis. If the film is epitaxial then φ-scan exhibits sharp peaks at certain φ-angles. On the other hand if the in-plane orientation of the film is random, there is no appreciable variation in the diffraction intensity.
in the \( \phi \)-scan. In the present study Philips X’Pert system and Rigaku Smartlab was used to perform \( \phi \)-scans.

![Figure 3.3 A schematic diagram of a 4-circle diffractometer setup. IBO: incident beam optics, DBO: diffracted beam optics.](image)

3.4. **Transmission Electron Microscopy**

Transmission electron microscope (TEM) utilizes electrons to image materials. Due to very small de Broglie wavelength of electrons (e.g., \( \lambda = 0.0251 \) Å for electrons accelerated through 200 keV), resolutions of the order of 1 Å can be achieved which makes possible to get images with atomic resolution.\(^6\) In this study TEM characterization was done to get atomic scale details of interfaces, misfit dislocations, crystalline defects, grain boundaries and other microstructural features in the deposited films. Selected area electron diffraction (SAED) patterns were also acquired to establish the epitaxial details. Unlike \( \theta-2\theta \) x-ray diffraction scans, SAED patterns can give information about in-plane crystallographic orientation of textured thin films. In-plane orientation of the deposited thin films was established by indexing SAED patterns.
The TEM operates in two modes; imaging and diffraction. In TEM images, the contrast arises because of the scattering of the incident beam of electrons when it passes through the sample. The electron beam can change both its amplitude and its phase as it traverses the specimen and both types of change can give rise to image contrast. Thus a fundamental distinction that can be made in the TEM is between amplitude contrast and phase contrast. In many situations both types of contrast may contribute to the image. Two types of amplitude contrast are possible: mass-thickness contrast and diffraction contrast. Mass-thickness contrast occurs due to the incoherent elastic scattering of electrons. This type of contrast is important if non-crystalline sample is observed. Diffraction contrast occurs due to the coherent elastic scattering at Bragg angles. The latter is the basis of forming bright field (BF) and dark field (DF) images. The BF images are formed by selecting the direct beam while DF images are formed by selecting only one of the diffracted beams.

The high resolution TEM (HRTEM) imaging is based on phase contrast and relies on the difference in phase among the electron waves scattered through a thin sample. In contrast to BF or DF imaging, in which a single electron beam is used to form the image, phase-contrast image requires the selection of more than one beam. In HRTEM the objective astigmatism has to be minimized to achieve atomic resolution. Other main requirement for a HRTEM is highly coherent and monochromatic electron beam. The interpretation of contrast in HRTEM images is not easy to interpret as it is sensitive to many factors: the appearance of the image
varies with small changes in the thickness, orientation, or scattering factor of the specimen, and variations in the focus or astigmatism of the objective lens.

In the present study, a JEOL 2000 FX TEM was used for bright/dark field imaging and electron diffraction. This microscope is equipped with a LaB$_6$ filament and was operated at 200 kV. The high resolution TEM characterization was done using a JEOL 2010F microscope operated at 200 kV. This microscope is equipped with a field emission gun which provides highly coherent electron beam. This microscope can also be operated in STEM, STEM-Z contrast and EELS spectroscopy modes. All of the TEM samples were cross section samples. The electron transparent TEM samples were prepared by mechanical grinding, dimpling and ion milling. Focused ion beam (FIB) milling is also used to prepare some of the samples.

3.5. Hall Effect Measurement

Hall measurement technique is based on the Lorentz force acting on moving electrons in the presence of a magnetic field$^7$, and is a simple and quick method for determining carrier concentration, carrier type and mobility. The Lorentz force results in a Hall voltage in a direction that is perpendicular to both the applied current and the magnetic fields.

In this study, a combination of resistivity and Hall measurements were taken using van der Pauw technique in order to determine both the mobility (denoted by $\mu$) and the sheet density
Thin film samples were first cut in the shape of ~1 x 1 cm squares, and electrical contacts were created on four corners of the samples using gold wires and indium pads in the van der Pauw configuration. After measuring the two resistance values, $R_A$ and $R_B$, the Hall voltage (denoted as $V_H$) was measured when a magnetic field perpendicular to the substrate surface was applied. Using those interim values, the sheet resistance ($R_s$), carrier density ($n_s$) and mobility ($\mu$) were calculated as follows:

\[
\exp\left(-\frac{\pi R_A}{R_s}\right) + \exp\left(-\frac{\pi R_B}{R_s}\right) = 1
\]

\[
n_s = \frac{IB}{q|V_H|}
\]

\[
\mu = \frac{|V_H|}{R_sIB} = \frac{1}{qn_sR_s}
\]

The following checklist should generally be observed when Hall measurements are under way:

- The contacts to the sample are ohmic and small in size.
- The lateral dimensions of the sample should be large when compared to film thickness and contact sizes.
- The sample should be uniform.
- Sample thickness should be known accurately to estimate carrier concentration.
• The sample should be enclosed in a dark environment to minimize photoconductive and photovoltaic effects.

3.6. Four-Point Resistivity Measurement

In this study, four-point probing technique was used to measure the electrical resistivity of the thin film samples. The four-point probe method is a standard technique for measuring electrical resistivity, and it can be used for both bulk and thin film samples. In the four-point probe method, the specimen is contacted by four probes, one pair of which is used to apply a current and the other pair is used to measure the voltage drop. The distances between the probes are assumed to be known or measured easily. The usage of four probes increases the robustness in the measurement process by eliminating errors due to the probe resistance, the spreading resistance under each probe, and the contact resistance between each probe and the specimen. For a thin film where the film thickness is much less than the spacing between the probes (denoted by $s$), the current profile from the probes could be considered to be rings. In that case, the resistance could be computed as:

$$dR = \rho \frac{dl}{A}, \text{ where } dl = dx, \text{ and } A = 2\pi xt$$

The total resistance can be computed as an integration from $s$ to $2s$, and becomes:
\[ R = \rho \frac{\ln 2}{2\pi t} \]

Equating the above to the resistance \( R = V/2I \) assuming that the applied current is \( I \) and the measured voltage is \( V \), the sheet resistivity of the thin film is computed as:

\[ \rho = \frac{\pi t}{\ln 2} \times \frac{V}{I} \]

Sheet resistance is expressed as \( R_s = \rho/t \), therefore, \( \rho = R_st \), giving the sheet resistivity of the thin film material.

The four-point probe measurements in this study were conducted in a temperature range of 15 – 350 K using a close cycle helium refrigerator set-up. The probe contacts to the film were constructed using gold wires attached to the film by indium pads. Electrical measurements were taken using an Keithley 2400 Series SourceMeter.

3.7. Photoluminescence Spectroscopy

When a sample is irradiated with an external source of light with a suitable wavelength, the electrons in the sample are excited to higher energy levels, and then the radiative transition from high energy levels back to lower energy levels causes light emission from the sample, or *luminescence*. This phenomenon is known as photoluminescence.
Photoluminescence spectroscopic measurements usually entail the recording and the interpretation of the following two types of spectra:

- **Photoluminescence Spectrum (PL):** In order to record the PL spectrum, a specific wavelength of light is used to illuminate the sample and the variation of luminescence intensity as a function of luminescence wavelength is measured. PL spectrum content is informative about the radiative energy levels in the sample.

- **Photoluminescence Excitation Spectrum (PLE):** This measurement is obtained by recording the intensity of specific luminescence wavelength as a function of the wavelength of the illuminating light. PLE spectrum contains information about the energy transformation among the energy levels in the sample.\(^9,10\)

A Horiba Jobin Yvon Labram Aramis system and a HeCd laser line as the excitation source were used at room temperature for taking the PL measurements in this study. Excitation wavelengths in the range 220 nm to 800 nm were available for selection by a diffraction grating on the incident beam side. In the experimental setup, the light emitted by the sample went to a photomultiplier through another diffraction grating, and was recorded by a computer.
3.8. Absorption Spectroscopy

A sample exposed to an incident beam will reflect one part of the beam, transmit another part of the beam, and finally absorb the remaining part of the beam due to the transition of electrons from lower energy levels to higher energy levels by the absorption of photons. The intensity change of a monochromatic light beam per unit distance travelled in a uniform medium gives the absorption coefficient, \( \alpha \), for that uniform medium and the beam intensity as a function of the travelled distance, \( x \), could be written as:

\[
I(\lambda) = I_0(\lambda) e^{-\alpha(\lambda)x}
\]

According to classical electromagnetic theory, the absorption coefficient is related to the imaginary part of the complex index of refraction (which is also referred to as the extinction coefficient) \( n_c = n - ik \), with \( \alpha = 4\pi\nu/c \), where \( \nu \) is the frequency of light. Hence the absorption coefficient is a function of frequency (wavelength) and a measurement of the variation of absorption coefficient with wavelength provides the absorption spectrum of the material under examination, which can be obtained by measuring transmission spectrum or by measuring reflectance spectrum.

A Hitachi U3031 Visible-UV Spectrometer with two continuous light sources (a tungsten lamp for measuring transmittance in the visible range from 1000 nm to 320 nm, and a deuterium lamp for measurements in the ultraviolet range from 320 nm to 200 nm) was used
for absorption spectroscopic measurements in this study. Based on the optical system arrangement, the pre-monochromator first splits the light beam into a monochromatic beam, and then the beam is redirected onto the sample. The intensity of the beam after it passes through the main monochromator is measured by the photomultiplier and recorded by a computer. Also, as reflectivity is not always negligible, the final data should also account for the contribution from reflection.
References


5 XRD user manual, Department of Materials Science and Engineering, North Carolina State University.


4. Ga and Al Doped Zinc Oxide Thin Films for Transparent Conducting Oxide Applications: Structure-Property Correlations

Namik K. Temizer¹, Sudhakar Nori and Jagdish Narayan

NSF Center for Advanced Materials and Smart Structures, Department of Materials Science and Engineering, North Carolina State University Raleigh, NC 27695

4.1. Abstract

We report a detailed investigation on the structure-property correlations in Ga and Al codoped ZnO films on c-sapphire substrates where the thin film microstructure varies from nanocrystalline to single crystal. We have achieved highly epitaxial films with very high optical transmittance (close to 90%) and low resistivity (~110µΩ-cm) values. The films grown in an ambient oxygen partial pressure (P_{O_2}) of 5x10^{-2} Torr and at growth temperatures from room temperature to 600°C show semiconducting behavior, whereas samples grown at a P_{O_2} of 1x10^{-3} Torr show metallic nature. The most striking feature is the occurrence of resistivity minima at relatively high temperatures around 110 K in films deposited at high temperatures. The measured optical and transport properties were found to be a strong function of growth conditions implying that the drastic changes are brought about essentially by native point

¹ Corresponding author’s email: nktemize@ncsu.edu
defects. The structure-property correlations reveal that point defects play an important role in modifying the structural, optical, electrical and magnetic properties and such changes in physical properties are controlled predominantly by the defect content.

**Keywords:** Point defects; Optical transmittance; Transparent conducting oxides; Doped semiconductors; Electrical resistivity; Transmission electron microscopy; Epitaxial thin films; Zinc oxide

### 4.2. Introduction

There has been a growing and intense interest in the recent years for new, efficient and inexpensive materials to cater the needs of optoelectronic device applications.\(^1\)\(^2\) Recently, zinc oxide based transparent conducting oxide (TCO) films have received considerable attention and emerged as commercially viable alternatives to indium tin oxide (ITO) due to the high cost of indium metal.\(^3\)\(^-\)\(^6\) The optoelectronic properties of ZnO thin films depend highly on the deposition and growth conditions as these properties change significantly with nature and concentration of dopants, the oxygen flux during film deposition, deposition temperature and desorption during annealing treatment in a reducing atmosphere.\(^7\)\(^,\)\(^8\) ZnO compounds doped with group III elements (Al, Ga, In) which are n-type dopants, have shown promising results when used as anode in organic solar cells.\(^9\) These n-type dopants can effectively decrease the electrical resistivity of pure undoped zinc oxide to less than 200 $\mu\Omega$-cm.\(^10\)\(^,\)\(^11\) Ga and Al codoped ZnO based thin films are the ideal materials that match the stringent requirements of high transparency and low resistivity for next generation of optoelectronic smart devices for TCO applications.
Our research group has previously investigated\textsuperscript{[12-15]} the properties and metal-semiconductor transition characteristics observed in transparent and conducting Ga doped ZnO films grown by pulsed laser deposition. In the present work, we focus on partial substitution of Ga by Al, and microstructure and electrical property correlations in Al and Ga codoped ZnO films (henceforth referred to as AGZO). Al doped ZnO has definite advantages such as low cost, low toxicity, enhancing chemical stability in reducing atmosphere\textsuperscript{[16]} and diffusion barrier characteristics\textsuperscript{[17]}, while Ga doping enhances humidity resistance and the conductivity.\textsuperscript{[18,19]} Doping with two donors is highly advantageous and expected to increase doping efficiency and activation, and achieve higher crystal quality without the need for high temperature deposition and subsequent annealing.\textsuperscript{[20]}

With respect to Al-doping of ZnO, recent synchrotron x-ray absorption near edge structures (XANES) studies on Al-doped ZnO have shown that Al prefers to be substitutional on Zn site and forms $\text{Al}_\text{Zn}$ donor over an interstitial site (Al\textsubscript{i}) state.\textsuperscript{[21]} These XANES measurements were found to be in agreement with theoretical first-principles calculations. Thus, the majority of Al can go into substitutional Zn sites and act as donors. However, a small fraction of $\text{Al}_\text{Zn}$ can combine with $\text{V}_{\text{Zn}}$, forming $\text{Al}_\text{Zn}$-$\text{V}_{\text{Zn}}$ and 2$\text{Al}_\text{Zn}$-$\text{V}_{\text{Zn}}$ complexes, which result in reduced carrier concentration and mobility.
In this work, we have identified 2% Al and 0.2% Ga as our optimum composition, resulting in a Ga/Al ratio of 0.1. The motivation behind the present study is to achieve high quality films with as high optical transmittance as possible (~90%) and with lowest possible resistivity on the order of 100 μΩ-cm.

4.3. Experimental Details

ZnO thin films doped with Al (2%) and Ga (0.2%) have been deposited on single crystal c-plane sapphire substrates using pulsed laser deposition (PLD). This composition was found to be optimum based upon our initial work. Powder targets of fixed compositions used in the current study were prepared by the conventional solid-state reaction technique. The films were deposited on to the sapphire substrates using a KrF excimer laser (λ = 248 nm, τ = 25 ns). A pulse energy density of 2-3 J/cm² with a repetition rate of 10 Hz was used to deposit the thin films. The target-substrate distance was maintained at 4.5 cm during the film deposition. Nonmagnetic plastic tweezers were used throughout the sample growth and characterization processes to avoid any external contamination. Sapphire (0001) substrates were initially cleaned ultrasonically in acetone followed by cleaning in methanol before being transferred to the deposition chamber. Two different series of thin films were deposited for 5000 pulses (~10 minutes) at (i) several substrate temperatures (T_{dep}) in the range of room temperature (RT) to 600°C, and (ii) under two different oxygen partial pressure (P_{O2}) of 5 x 10⁻² Torr (S1) and 1 x 10⁻³ Torr (S2). The deposition chamber was evacuated to a base pressure of less than 5×10⁻⁷ Torr prior to deposition. The structure of these films was
characterized by x-ray diffraction (XRD) using a Rigaku X-ray diffractometer with Cu $K_{\alpha}$ radiation ($\lambda$=0.154 nm) and a Ni filter and a JEOL 2010F field emission transmission electron microscope. X-ray Φ-scans were carried out using a Panalytical X’Pert PRO MRD HR X-Ray Diffraction System. Temperature variation of electrical resistivity was measured in the range of 15-300 K in a Van-der-Pauw configuration using gold wires and fresh cleaved indium to make contacts onto the sample surface. Hall Effect measurements were performed using an Ecopia HMS-3000 Hall Effect Measurement System. Optical measurements (absorption/transmission) were made using a Hitachi U-3010 UV-Visible, Scanning Spectrophotometer.

4.4. Results and Discussion

X-ray diffraction patterns (θ-2θ scan) in Figures 1 and 2 show the effect of substrate temperature on the crystallinity of the samples. In both sets, the (0002) and (0004) peaks are predominant, which indicate that the ZnO film has c-axis direction parallel to c-direction of sapphire. In both sets, the films grown below 200°C are nanocrystalline, though not completely amorphous. Room temperature grown samples are observed to be nanocrystalline with an average grain size around 25 nm for S1 and 6 nm for S2, as calculated using Scherrer’s formula. At higher substrate temperatures, the intensity and sharpness of (006) peaks are found to increase.
Figure 3 shows the typical Φ-scan data performed on 300°C grown film to get information about the in-plane orientation and establish the growth of ZnO film on the sapphire substrate. The plot shows a six-fold symmetry of ZnO reflection, i.e. (101) ZnO planes, which are inclined at $\Psi=61.07^\circ$ from the (0001) planes, with $2\theta=36.25^\circ$. The θ-2θ and Φ-scan data show that the ZnO grows epitaxially on [0001] $\alpha$-Al$_2$O$_3$ above 200°C with the following out-of-plane and in-plane orientation relationships, respectively:

\[
[0001]_{\text{GAZO}} \parallel [0001]_{\text{Al}_2\text{O}_3}
\]

\[
[2\bar{1}10]_{\text{GAZO}} \parallel [10\bar{1}0]_{\text{Al}_2\text{O}_3} \text{ and } [10\bar{1}0]_{\text{GAZO}} \parallel [2\bar{1}10]_{\text{Al}_2\text{O}_3}
\]

According to the above epitaxial relationships, the ZnO rotates by 30° with respect to the basal c-plane of Al$_2$O$_3$. Epitaxy in such a large (16%) misfit system can be explained by the domain matching epitaxy (DME) paradigm [22], where integral multiples of planes match across the film/substrate interface. In this particular case, six (10\bar{1}0) planes of ZnO match with seven (2\bar{1}10) planes of sapphire substrate (6/7 domains).

Figure 4 shows the TEM micrographs for the sample grown at 400°C and $P_{O_2} = 1\times10^{-3}$Torr. The high resolution image reveals the highly epitaxial nature of the film Fig.4(a). The interface is atomically sharp with no evidence of any interfacial reaction or intermixing. The
selected area diffraction pattern obtained at the interface Fig.4(b) shows sharp diffraction spots confirming good crystallinity. The alignment of ZnO diffraction spots with the underlying sapphire substrate shows epitaxial nature of the film with a $30^\circ$ in-plane rotation. The low magnification bright-field image Fig.4(c) shows good crystalline quality without any precipitates or clustering. The film thickness for this particular sample was determined to be around 780-800 nm. The fast Fourier transform (FFT) filtered HRTEM micrograph shows matching of planes across the interface Fig.4(d). It is observed, in accordance with the DME paradigm, that 6/7 domains alternate with 5/6 domains to accommodate the misfit. \cite{22}

Figure 5 shows the transmission spectra of the ZnO films for both sets S1 and S2. The S1 shows an average transmittance around 90% in the visible range, whereas the average transmittance for S2 is about 85% for growth temperatures above 300°C. In concurrence with the X-ray diffraction data, this further explains the improved crystallinity at higher growth temperatures. The decrease in transparency between the two sets is due to the increased defect content in the films, which results from growth in oxygen deficient atmosphere.

Optical transmittance data yields important information about the band gap ($E_g$) values in these films. The band gap can be determined from the transmittance data using Tauc plots. The relationship between the absorption coefficient ($\alpha$) and the photon energy ($h\nu$) for direct allowed transition is given as;
\[
(ahv)^2 = A(hv - E_g)
\]

where, \(A\) is a function of the index of refraction and hole/electron effective masses, and \(E_g\) is the band gap. The absorption coefficient \(\alpha\) is obtained by the relation \(\alpha = -(1/d) \ln(T)\), where \(T\) is the transmittance and \(d\) is the thickness of the film. The Tauc plots for both sets are shown in Figure 6. The band gap is determined by extrapolating the linear portion of the curve on to the energy axis at \(\alpha=0\). In the case of undoped ZnO, the band gap is around 3.37 eV.\(^{23,24}\) The observed optical properties are best interpreted and can be understood with the aid of some of the existing formalisms in the literature. Broadening of the band gap is well described by the Burstein-Moss effect.\(^{25,26}\) Enhancement in the carrier concentration results in the shift in the Fermi level well into the conduction band. Reduction in the linear part of the slope is due to defect states within the band gap. Thus the shift can be interpreted as merging of an impurity band into the conduction band, shrinking the band gap. Broadening due to the Burstein-Moss effect is compensated by the formation of such donor band. It can also be seen from the absorption spectrum that the band gap narrowing (BGN) effect is present in the films grown at different temperatures. Furthermore, BGN often appears in addition to the Burstein-Moss shift in semiconductors with high carrier concentration. This is the phenomenon where the band edge shifts to the longer wavelength side of the spectrum due to the many-body effects of the electrons, as a result of high carrier concentration. Essentially, the width of the energy gap decreases because the repulsive electron-electron
interaction and the localization of the electronic wave function is weakened by the screening potential arising due to the presence of many electrons. Consequently, the bandgap is reduced by the BGN effect with the increase of the carrier concentration. The extracted values of the $E_g$ from Tauc plots (see Fig. 6) for S1 increases from 3.26 eV for the samples deposited at 100°C to 3.39 eV for the sample deposited at 600°C growth temperature. Similarly, for S2 the band gap varies from 3.36 eV to about 3.65 eV. The above discussion clearly emphasizes the role played by the defects in engineering the band gap and opto-electronic properties of the Ga,Al:ZnO films, which in turn has important consequences.

In order to investigate the role of defects and their influence on electronic properties of the films, we have measured the electrical resistivity of all the 14 different films in the temperature range from 15-300 K. We have plotted the temperature variation of the resistivity for all the samples of sets S1 and S2, and the same is shown in Figures 7 and 8. Figure 7 clearly illustrates a gradual transition from semiconducting behavior to metallic nature as the growth temperature was increased from 300°C to 600°C. While the film grown at 300°C shows a semiconducting behavior in the entire temperature range, the films deposited at higher growth temperatures showed a systematic and gradual change in the trend of $\rho$ vs. T curves from a semiconducting to metal nature that clearly signifies the semiconducting to metal transition (SMT). The resistance of the film that was grown at 400°C increases by nearly a factor of 1.5 with decreasing temperature, again typical of a semiconducting behavior, with its resistivity changing from 89 mΩ-cm at 300 K to about 120
mΩ-cm at 15 K. The resistivity of the film grown at 500°C also changes in a similar semiconductor type of behavior, but with less variation in its absolute resistivity values compared to the 400°C grown film. Here, for the 500°C grown film the absolute value of resistivity changes from 32 mΩ-cm at 300 K to about 72 mΩ-cm at low temperatures, a two-fold increase. The sample grown at 600°C shows metallic behavior and also the resistance minimum at 110 K, which is plotted in the inset of Figure 7 for clarity. All the important parameters, such as grain size, average % transmittance, resistivity values at 15K and 300K, carrier concentrations, mobility and the band gap of all the films are summarized in Table 1. For the sake of brevity, S1 and S2 in Table 1 represent the samples grown at 5 x 10^{-2} Torr and 1 x 10^{-3} Torr, respectively.

Figure 8 shows the curves of ρ vs T for the samples grown at 1x10^{-3} Torr for the AGZO films deposited at different growth temperatures form 100 to 600°C. In contrast to S1, here, all the samples show metallic behavior with a monotonic decrease in resistivity with the decrease in temperature. The values of the resistivities are in the μΩ-cm range typical of those of metallic or metal-like systems. The resistivity variation for the samples grown at 300°C and 600°C are plotted and shown as left (300°C) and right (600°C) insets of Figure 8. The lowest resistivity that we have achieved here was about 110 μΩ-cm for the sample grown at 300°C. In fact, a closer look into some of the samples plots reveals that they undergo resistivity minima, an interesting phenomenon in itself. In contrast to the sample grown at 600°C in S1 (see inset of Figure 7), the minimum in resistivity has shifted by about 20 degrees and now
occurs at 130 K (right inset of Figure 8). The resistivity minima, especially at low temperatures, occur when there are competing interactions among electrons and phonons, and the electronic scattering processes with other electrons leading to localization processes.\[14\]

Changes in carrier concentration and mobility with respect to growth temperature are shown in Figure 9 for both sets. It is observed that for both sets, carrier concentration values are higher at lower deposition temperatures. This fact confirms that the conductivity in our samples is mainly defect driven. In S2, carrier concentration value reaches a maximum at 200°C. However, lowest resistivity is observed at 300°C, where carrier concentration starts to decrease, but the mobility is almost three times the value observed at 200°C due to improved crystallinity. Further increase in growth temperature results in reduced carrier concentration, while the mobility is somewhat improved. It is also worth mentioning that the carrier concentration values at higher growth temperatures are very close to each other. Although the oxygen partial pressures are different in both sets, the effect of higher substrate temperatures results in annealing of defects, and the conductivity is caused mainly by the dopants.

Both the interesting and striking features in our study, viz., observation very low resistivity and very high transmittance ought to have their origin in the intrinsic oxygen and zinc defects. We propose a phenomenological model that explains our experimental findings in a consistent manner. A large concentration of vacancies and interstitials are formed in oxygen and zinc sub-lattices during the film growth due to the highly energetic and non-equilibrium
nature of pulsed laser ablation process. Zinc vacancies are deep acceptors and contribute little to cause p-type conductivity. On the other hand, oxygen interstitials with low migration energy depending upon where in the lattice they are located (either in tetrahedral or octahedral sites), anneal out rather quickly. The above mechanism leads to the formation of oxygen vacancy-Zinc interstitial defect complex \((V_O-I_{Zn})\).\(^{[27]}\) We propose that this defect complex \(V_O-I_{Zn}\) is responsible, and acts as a source for the significant concurrent enhancements in n-type conductivity and in optical transparency. Our experimental observation is, in fact, in direct agreement with the \textit{ab-initio} calculations based on the first principles study by Kim and Park.\(^{[28]}\) The low migration energy of the Zinc interstitials (\(~0.5\) eV) facilitates a rapid diffusion in the lattice and can quickly pair with the available oxygen vacancies thereby forming shallow donor levels, leading to the \(n\)-type conductivity in ZnO films. We also observed defect induced room temperature ferromagnetism (RTFM), which we believe to be caused by Zn vacancies in close proximity with substitutional oxygen. The data on RTFM in Al- and Ga-doped ZnO will be reported shortly.

4.5. **Summary and Conclusions**

Highly transparent Ga (0.2\%) and Al (2\%) ZnO thin films were grown on c-plane sapphire substrates using pulsed laser deposition. Samples grown at \(P_{O_2}=5\times10^{-2}\) Torr show semiconducting behavior, whereas samples grown at \(P_{O_2}=1\times10^{-3}\) Torr show mostly metallic behavior. The films deposited under \(5\times10^{-2}\) Torr showed increasing resistivity with decreasing temperature; resistivity was saturated with values in the range 3.0-375 m\(\Omega\)-cm at
low temperatures, 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 that resulted in the interesting resistivity minimum. The structure-property correlations reveal that the oxygen vacancies or point defects play an important role in the structural, optical and electrical properties and that the electrical and optical characteristics stemmed out are essentially defect driven. We were able to achieve the lowest resistivity of $\sim110 \ \mu\Omega\text{-cm}$ and a resistivity minimum at relatively high temperatures 110-130 K with high transmittance values $\sim90\%$ making the samples well suited for TCO based devices. Optical and electrical properties were found to be a strong function of growth conditions implying that the drastic changes are brought about essentially by native point defects.

4.6. Acknowledgements

The authors acknowledge Dr. J. Prater, ARO, for useful discussions during the course of this work, S. Punugupati for her help in sample preparation, and the use of the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina. Part of this research was supported by the National Science Foundation.
### 4.7. Tables

Table 4.1 The important parameters, such as the grain size, average percentage transmittance, resistivity values at 300 and 15 K, carrier concentration, mobility and band gap of films for both sets S1 and S2.

<table>
<thead>
<tr>
<th></th>
<th>Grain Size (nm)</th>
<th>Avg %T</th>
<th>$\rho_{300K}$ (mΩ-cm)</th>
<th>$\rho_{15K}$ (mΩ-cm)</th>
<th>$n_e$ ($cm^{-3} x 10^{20}$)</th>
<th>$\mu$ (cm$^2$/V.s)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>S1 26</td>
<td>81</td>
<td>&gt;MΩ</td>
<td>&gt;MΩ</td>
<td>-</td>
<td>-</td>
<td>3.28</td>
</tr>
<tr>
<td></td>
<td>S2 6</td>
<td>26</td>
<td>0.79</td>
<td>0.98</td>
<td>4.25</td>
<td>13.99</td>
<td>3.49</td>
</tr>
<tr>
<td>100°C</td>
<td>S1 32</td>
<td>89</td>
<td>16.3</td>
<td>18.1</td>
<td>1.53</td>
<td>3.08</td>
<td>3.32</td>
</tr>
<tr>
<td></td>
<td>S2 6</td>
<td>64</td>
<td>0.67</td>
<td>0.63</td>
<td>4.96</td>
<td>12.85</td>
<td>3.57</td>
</tr>
<tr>
<td>200°C</td>
<td>S1 37</td>
<td>90</td>
<td>3.88</td>
<td>4.01</td>
<td>1.57</td>
<td>9.4</td>
<td>3.39</td>
</tr>
<tr>
<td></td>
<td>S2 25</td>
<td>32</td>
<td>0.65</td>
<td>0.6</td>
<td>9.07</td>
<td>14.25</td>
<td>3.57</td>
</tr>
<tr>
<td>300°C</td>
<td>S1 36</td>
<td>85</td>
<td>209.73</td>
<td>375.72</td>
<td>0.44</td>
<td>10.08</td>
<td>3.26</td>
</tr>
<tr>
<td></td>
<td>S2 47</td>
<td>83</td>
<td>0.11</td>
<td>0.1</td>
<td>6.73</td>
<td>41.62</td>
<td>3.59</td>
</tr>
<tr>
<td>400°C</td>
<td>S1 29</td>
<td>91</td>
<td>88.53</td>
<td>122.45</td>
<td>0.12</td>
<td>8.52</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>S2 43</td>
<td>88</td>
<td>0.4</td>
<td>0.33</td>
<td>4.98</td>
<td>47.67</td>
<td>3.63</td>
</tr>
<tr>
<td>500°C</td>
<td>S1 43</td>
<td>86</td>
<td>32.36</td>
<td>72.17</td>
<td>0.24</td>
<td>10.3</td>
<td>3.28</td>
</tr>
<tr>
<td></td>
<td>S2 47</td>
<td>89</td>
<td>0.63</td>
<td>0.54</td>
<td>1.64</td>
<td>50.77</td>
<td>3.42</td>
</tr>
<tr>
<td>600°C</td>
<td>S1 44</td>
<td>91</td>
<td>3.5</td>
<td>3.3</td>
<td>0.84</td>
<td>9.9</td>
<td>3.32</td>
</tr>
<tr>
<td></td>
<td>S2 49</td>
<td>88</td>
<td>4.0</td>
<td>3.79</td>
<td>0.61</td>
<td>34.79</td>
<td>3.34</td>
</tr>
</tbody>
</table>
4.8. Figures

Figure 4.1 XRD spectra for all 0.2% Ga, 2% Al:ZnO films deposited at different temperatures RT- 600°C. The oxygen partial pressure was maintained constant at 50 mTorr throughout the depositions.
Figure 4.2 XRD spectra for all 0.2% Ga, 2% Al:ZnO films deposited at different temperatures RT - 600°C. The oxygen partial pressure was maintained constant at 1 mTorr throughout the depositions.
Figure 4.3 Azimuthal (Φ) scan of ZnO/Al2O3 (0001) structure. Sapphire (11̅02) reflections at 2θ=25.58° and Ψ=57.61° and ZnO (101) reflections at 2θ=36.25° and Ψ=61.07°.
Figure 4.4 (a) HRTEM image shows highly epitaxial film with atomically sharp interface. (b) Selected area diffraction pattern of film-substrate interface. (c) Bright-field image showing the film thickness. (d) FF-HRTEM image showing epitaxial matching of planes.
Figure 4.5 UV-Vis transmission spectra of the films at different growth temperatures. Oxygen partial pressure during sample growth is held constant at (a) 50 mTorr and (b) 1 mTorr.
Figure 4.6 Tauc plots for samples grown at different temperatures in the range from RT to 600°C. The oxygen partial pressure ($P_{O_2}$) during the growth was kept at (a) 50 mTorr and (b) 1 mTorr for the samples.
Figure 4.7 Variation of the electrical resistivity with temperature for the Ga,Al: doped ZnO samples grown at different temperatures in the range from 300-600°C. The oxygen partial pressure during the growth was kept at 50 mTorr for the samples (S1). The inset shows the metallic nature and the resistivity minimum occurring around 110K for the sample grown at 600°C.
Figure 4.8 Temperature variation of the resistivity for the films grown at different deposition temperatures in the range of 100-600°C and at an oxygen partial pressure of 1x10^{-3} Torr. The two insets show the variation of resistivity for the sample grown at 300°C (left inset) and the resistivity minimum occurring around 130K for the sample grown at 600°C (right inset).
Figure 4.9 Variation of carrier concentration and mobility with deposition temperature for the Ga,Al: doped ZnO samples grown at different temperatures in the range from RT to 600°C. The oxygen partial pressure during the growth was kept at (a) 50 mTorr and (b) 1 mTorr for the samples.
4.9. References


5. Defect Mediated Room Temperature Ferromagnetism and Resistance Minima
Study in Epitaxial ZnGa₀.₀₁₂Al₀.₀₁₂O Transparent Conducting Oxide Films

Namik K. Temizer¹, Sudhakar Nori¹, D. Kumar² and Jagdish Narayan¹

¹NSF Center for Advanced Materials and Smart Structures, Department of Materials Science and Engineering, North Carolina State University Raleigh, NC 27695
²Department of Mechanical Engineering, North Carolina A & T State University Greensboro, NC 27411

5.1. Abstract

We report on the micro-structural, transport, optical and magnetic properties in ZnGa₀.₀₁₂Al₀.₀₁₂O films grown by pulsed laser deposition under different growth conditions. ZnO films grown at substrate temperatures of 600°C show metal-like behavior with a resistivity minima at lower temperatures, whereas films grown at 300°C and ambient oxygen partial pressure of 1 mTorr show metallic nature with resistivity values on the order of 100 µΩ·cm at room temperature. The most interesting features are the concomitant occurrence of high temperature resistivity minima and room temperature ferromagnetism with a high saturation magnetic moment of 61 emu/cc and with coercivity in the range 100 to 240 Oe. The temperature dependent resistivity data has been interpreted in the light of quantum corrections to conductivity in disordered systems, suggesting that the e-e interactions is the
dominant mechanism in the weak-localization (WL) limit in the case of films showing resistivity minima. The simultaneous ferromagnetic ordering coupled with the enhancements in both optical transmittance (~90%) and electrical conductivity in Ga and Al doped ZnO system should have their origin in native point defects in the form of oxygen and zinc vacancies and interstitials and their complexes. We propose that formation of oxygen vacancy-Zinc interstitial defect complex (VO-IZn) is responsible for the enhancement in n-type conductivity, and zinc vacancies (VZn) for the observed room temperature ferromagnetism.

*Keywords:* A. Zinc oxide; B. Epitaxial films; C. Ferromagnetism; D. Electrical transport; E. Transparent conducting oxides; F. Metal to Semiconductor transition

1 Corresponding author’s email: nktemize@ncsu.edu
5.2. Introduction

Zinc oxide based transparent conducting oxide (TCO) films have recently received considerable attention due to their excellent physical properties and potential technological applications.\textsuperscript{1,2} ZnO is regarded as one of the alternatives to indium tin oxide because of the high cost as well as diminishing reserves of indium.\textsuperscript{3–6} Group III elements such as Al, Ga, In and B have mainly been used as n-type dopants in ZnO in order to obtain highly conductive and transparent films.\textsuperscript{7–11} It has been found that the growth conditions, such as, oxygen partial pressure, deposition temperature, dopant concentration and post growth annealing treatments significantly affect the optical and transport properties of ZnO thin films.\textsuperscript{12} An important effect that has been observed and studied in detail in ZnO thin films is the semiconductor-metal transition (SMT).\textsuperscript{13–15} Detailed investigation of the SMT phenomenon in doped ZnO films in the light of quantum corrections to conductivity can be used to understand the basic interaction processes involved in the conduction especially at lower temperatures. Our research group has earlier investigated\textsuperscript{16,17} on the properties of transparent and conducting Ga doped ZnO films grown by pulsed laser deposition, focusing on the effect of the doping level on SMT. Mott transition in Ga doped Mg$_x$Zn$_{1-x}$O as a function of Ga doping level was carefully investigated based on the electrical conductivity measurements down to 40 mK and associated features with such an SMT were found to be due to dominant dephasing mechanism arising out of electron-electron scattering and the inelastic scattering time was found to vary as $T^{-3/2}$.\textsuperscript{18} We now have observed similar SMT in Al and Ga codoped ZnO (AGZO) films.
The motivation behind the present study is to achieve high quality epitaxial doped zinc oxide films on sapphire substrates and to introduce native point defects such as oxygen vacancies in a controlled manner and further investigate the defect mediated ferromagnetism. Our group has made extensive studies in epitaxial zinc oxide films (both doped and undoped) that correlate structural and magnetic properties. \(^{19,20}\) We hitherto strongly believe that zinc oxide has tremendous potential to be considered as a next generation \textit{multifunctional} candidate, not only in the field of optoelectronics, but also in spintronic related applications. We also intend to get an insight into the associated electron transport mechanisms causing the resistivity minima occurring at relatively high temperatures and correlate them with the ferromagnetic properties.

In this work, we report the presence of metallic conductivity at room temperature and semiconducting behavior at lower temperatures as well as a SMT. We also focus on electrical and the room temperature ferromagnetic (RTFM) properties and their correlations with the microstructure in AGZO films.

\subsection*{5.3. Experimental Details}

ZnO thin films doped with Al (2\%) and Ga (0.2\%) have been deposited on single crystal c-plane sapphire substrates using pulsed laser deposition (PLD). Recently, we have studied systematically the structure-property correlations of AGZO thin films with respect to growth
temperature and oxygen partial pressure. Details about the sample preparation and growth conditions can be found elsewhere.\textsuperscript{21} Solid sintered targets were prepared from high purity ZnO, Al\textsubscript{2}O\textsubscript{3} and Ga\textsubscript{2}O\textsubscript{3} powders by the conventional solid-state reaction technique. Thin films were deposited using a KrF excimer laser source ($\lambda = 248$ nm, $\tau = 25$ ns), with a pulse energy density of 2-3 J/cm\textsuperscript{2}, and a repetition rate of 10 Hz. Target to substrate distance was maintained at 4.5 cm during the film deposition. The c-plane (0001) sapphire substrates were cleaned in an ultrasonic bath in acetone, followed by cleaning in methanol before being transferred to the deposition chamber. Three samples were deposited using 5000 pulses at varying oxygen partial pressures ($P_{O_2}$) and substrate temperatures ($T_g$): 1 mTorr, 300°C (S1), 1 mTorr, 600°C (S2) and 50 mTorr, 600°C (S3). The deposition chamber was evacuated to a base pressure of less than 10\textsuperscript{-6} Torr prior to deposition. The structure of these films was characterized by x-ray diffraction (XRD) using a Rigaku X-ray diffractometer with Cu $K_\alpha$ radiation ($\lambda=0.154$ nm) and a JEOL 2010F field emission transmission electron microscope. X-ray and $\Phi$-scans were carried out using a Rigaku Smartlab X-Ray Diffractometer equipped with a 4-circle sample stage. Temperature variation of electrical resistivity was measured in the range of 15-300 K by employing a Van-der-Pauw configuration using thin gold wires and freshly cleaved indium to make very fine contacts onto the sample surface. Hall Effect measurements were performed using an Ecopia HMS-3000 Hall Effect Measurement System. Optical measurements (absorption/transmission) were recorded using a Hitachi U-3010 UV-Visible Scanning Spectrophotometer. Field dependent magnetization (M-H) measurements were carried out using a physical property measurement system (PPMS) in conjunction with an Evercool-2 vibrating sample magnetometer (VSM) attachment.
(Quantum Design). All the magnetization measurements were carried out on rectangular sample strips of 5 mm x 3 mm. Hysteresis measurements were performed by sweeping the magnetic fields from -10 to +10 kOe at several temperatures; viz., 10, 50, 100, 200 and 300K. The magnetic field was applied parallel to the surface of the films. Great care was exercised to keep the samples in a dust-free environment and not to contaminate the samples during growth and measurement by handling the samples with non-magnetic plastic tweezers.

5.4. Results and Discussion

Figure 1 shows θ-2θ and Φ-scan XRD results for all the three samples. The (0002) and (0004) peaks are predominant in all the films, which indicate that the ZnO films are highly textured or epitaxial with c-axis as their preferred orientation. The intensities of (000l) peaks are observed to be higher in S2, and S3, indicating better crystalline quality of ZnO films grown at higher substrate temperatures. A Φ-scan was performed to get information about the in-plane orientation and establish the growth of ZnO film on the sapphire substrate. The following orientation relation was established between the film and the substrate: [0001]f || [0001]s, [2110]f || [1010]s and [1010]f || [2110]s. This corresponds to a 30° or 90° rotation of ZnO with respect to the basal c-plane of Al₂O₃.

Further structural details were obtained using high-resolution TEM and selective area diffraction patterns. Figure 2 shows the cross-section HRTEM micrographs for S2. It can be
seen that the ZnO film has grown epitaxially on sapphire. The interface is atomically sharp with no evidence of any interfacial reaction or nanosized clusters, which might have been difficult to detect by XRD. The selected area diffraction pattern obtained at the film-substrate interface. Fig.2(b) shows sharp diffraction spots confirming good crystallinity. The alignment of ZnO diffraction spots with the underlying sapphire corresponds to a 30° or 90° rotation in the basal plane of sapphire substrate. The epitaxy in such a large (16%) misfit system occurs as a result of domain matching epitaxy, where integral multiple of film planes $6\{10\bar{1}0\}_f$ match with $7\{2\bar{1}\bar{1}0\}_s$ of substrate planes. It is observed that 6/7 domains alternate with 5/6 domains to accommodate the misfit. \(^{22}\) Fast Fourier transform (FFT) filtered HRTEM micrograph shows matching of planes across the interface. The low magnification bright-field image Fig.2(c) shows good crystalline quality without any precipitates or clustering. The film thickness for this particular sample (S2) was determined to be around 450 nm.

The transmission spectra of the AGZO films is shown in Fig.3(a). Samples S1 and S2 show an average transmittance around 90% in the visible range, whereas the average transmittance for S3 is just above 80%. The decrease in transparency between samples is due to the increased defect content in the films, which results from growth in oxygen deficient atmosphere.
The optical band gap can be determined from the transmittance data using Tauc plots. The Tauc plots for all three samples are shown in Figure 3(b). The relationship between the absorption coefficient ($\alpha$) and the photon energy ($h\nu$) for direct allowed transition is given as 

$$(ah\nu)^2 = A(h\nu - E_g),$$

where $A$ is a function of the index of refraction and hole/electron effective masses and $E_g$ is the band gap. The absorption coefficient $\alpha$ is given by the relation $\alpha = -(1/d) \ln(T)$, where $T$ is the transmittance and $d$ is the thickness of the film. The band gap is determined by extrapolating the linear portion of the curve on to the energy axis at $\alpha=0$.

In the case of undoped ZnO, the band gap is around 3.37 eV.$^{23,24}$ It can be observed that the band gap of S1 is larger (3.59 eV), while the band gaps of S2 (3.34 eV) and S3 (3.32 eV) are smaller than the band gap for undoped ZnO. Broadening of the band gap for S1 can be explained by Burstein-Moss effect$^{25,26}$, where Fermi level shifts into the conduction band due to the enhancement in the carrier concentration. The absorption edge shifts toward higher energy due to filled energy levels below the Fermi level. Reduction in the linear part of the slope is due to defect states within the band gap. It can also be seen from the absorption spectrum that the band gap narrowing (BGN) effect is present in S2 and S3 samples. The BGN often appears in addition to the Burstein-Moss shift in semiconductors, where the band edge shifts to the longer wavelength side of the spectrum due to the many-body effects of the electrons, as a result of high carrier concentration. Essentially, the width of the energy gap decreases because the repulsive electron-electron interaction and the localization of the electronic wave function is weakened by the screening potential arising due to the presence
of many electrons. Consequently, the bandgap is reduced by the BGN effect with the increase of the carrier concentration.

In an attempt to understand the combined role of defects and disorder and its influence on electronic transport as well as on other physical properties of the films, we have measured the electrical resistivity of all the films in the temperature range from 15-300 K. Some of other important parameters, such as growth conditions, ρ values at 15 and 300 K, carrier concentrations (nₑ), mobility (μ) and the band gap (Eₔ) of the films are given in Table 1. Figure 4 shows the temperature dependence of electrical resistivity (ρ) for samples S1, S2 and S3. The S1 shows a monotonic decrease in its resistivity as the temperature decreases with its resistivity decreasing from 111.5 μΩ-cm at 300 K to 95 μΩ-cm at 15 K. Whereas S2 and S3 also show positive temperature coefficients of resistivity (TCR) until about 120-150 K, below which the samples show a negative TCR with an upturn as the temperature was further reduced. These two samples show the resistance minima at 145 K (S2) and 115 K (S3) respectively. The resistivities of S2 and S3 increase by nearly a factor of 1.5 with the increase in temperature, from their respective minima with their ρ values changing from 3.79 mΩ-cm at 15 K to about 4.0 mΩ-cm at 300 K for S2 and 3.3 mΩ-cm at 15 K to about 3.5 mΩ-cm at 300 K in case of S3. In our earlier work, we had reported systematic changes from semiconducting to metallic type behavior with the increase in the growth temperature in AGZO thin films.²¹ We have also observed Mott transition in Ga-MgₐZnₙ₋ₐ-O thin films as a
function of Ga doping level and the important features associated with such a semiconducting to metal transition were essentially due to electron-electron scattering.\textsuperscript{18}

The resistivity minima, typically at low temperatures, occur when there are competing interactions among electrons and phonons and the other scattering processes involving defects or disorder.\textsuperscript{14,18,27} The interesting features such as metallic resistivity and the occurrence of resistivity minima at somewhat elevated or high temperatures observed in the present study are better understood in the light of scaling theory\textsuperscript{14}, by fitting the resistivity data to different equations\textsuperscript{13,15,27} which capture most of the important processes of electron transport at low temperatures. Electron-electron (\textit{e-e}) interactions and localization effects constitute as important quantum corrections to the electrical conductivity predicted by scaling theory. Such corrections are well analyzed by the scattering times for \textit{e-e} interactions and due to localization effect\textsuperscript{13,14,28,29} and as a result the temperature dependent resistivity can written as,

\begin{equation}
\rho(T) = \frac{1}{\left(\sigma_0 + \alpha_1 T^{\beta/2} + \alpha_2 \sqrt{T}\right)} + \beta T^2
\end{equation}

\textbf{(5.1)}
where, $\sigma_0$ is the reciprocal of the residual resistivity ($1/\rho_0$), the coefficients, $\alpha_1 = \frac{e^2}{2\pi^2 h \sqrt{\frac{\tau}{\hbar}}}$

and $\alpha_2 = \frac{e^2}{4\pi^2 h} \sqrt{\frac{3}{2}} \frac{\dot{F}_\sigma}{d\sigma} \left( \frac{k_B}{d\sigma} \right)$. Here, $\dot{F}_\sigma$ is the Hartree screening parameter and $\alpha$ is a constant. The second term, $\alpha_1 T^{p/2}$, in the denominator corresponds to the weak localization (WL) effect due to the self-interference of quantum wave functions backscattered on impurities and the $\alpha_2 \sqrt{T}$ term arises from the modification of the density of states at the Fermi energy due to renormalization of the Coulomb $e-e$ interactions. The $\beta T^2$ term represents the high temperature phonon scattering contribution. One can notice that if the constants $\sigma_1$ and $\sigma_2$ are zero, i.e. in the absence of quantum corrections, the expression reduces to the classical Boltzmann formula. It should be noted that the $\alpha_2$ can change sign as a function of disorder. We have analyzed our resistivity data for S1, S2 and S3 according to the above Eqn. (5.1) and the results are plotted in Figure 5. The solid red lines are the best fits of the data to this equation. It is clear that our data fits very well, and the merit of the fit is reflected in the $R^2$ parameter (Goodness parameter) which is very close to unity in all the samples. The corresponding fit parameters are tabulated in Table 5.2. The exponent values extracted from the fitting are $p=3$ for the case of S1, and $p=2$ for S2 and S3. The value of $p$ in the term $\alpha_1 T^{p/2}$ in Eqn. (5.1), which is due to the WL, depends on the type of interactions present in the system. For $e-e$ interactions, $p$ assumes a value 2, and corresponding to the presence of electron-phonon ($e-ph$) interactions its value is 3. In the case of S1, the best fit yields a value of 3 for $p$ suggesting that the electron-phonon ($e-ph$) interactions dominate at low temperatures. On the other hand, for S2 and S3 $e-e$ interactions is the dominant mechanism in the WL limit, that is in the clean-limit or the pure regime. A comparison of all
the coefficients and the fit parameters indicates that the essential contributions to quantum corrections to the conductivity are due to the presence of e-e interactions. It should be mentioned that this approach is considered to be valid if the contribution from quantum corrections are much smaller than the Boltzmann conductivity\textsuperscript{31} i.e., $\sigma_0 \gg \alpha_1 T^{p/2} + \alpha_2 \sqrt{T}$.

For all our samples, the sizes of the quantum corrections are below 8\% of $\sigma_0$ in the 10-180K range, meaning that the contributions of quantum corrections to the conductivity are small with respect to the residual conductivity.

In order to understand the role of defects and disorder and their mediation in our films, we have measured the magnetic properties of our samples. The Field-dependent magnetization curves for all the three samples of ZnO films on sapphire substrates are plotted in Fig. 6. Isothermal magnetization measurements were carried out at 10, 50, 100, 200 and 300 K. Both S1 and S2 films exhibited RTFM with significant hysteresis and high saturation magnetic moments. In the case of S1 film the saturated magnetization is 28 emu/cc and for S2, it is 61 emu/cc and the corresponding coercivities are 200 and 240 Oe, respectively. Plotted in the bottom inset are the low field M-H hysteresis loops between ± 400 Oe for all the samples clearly deciphering the large hysteresis shown by these films. The diamagnetic contribution due to the sapphire substrates has been subtracted in these samples. The observed room temperature ferromagnetism originates essentially from Zn vacancies in close proximity with substitutional oxygen in the absence of any external magnetic impurities or magnetic ion dopants.\textsuperscript{32} M-H plots in the top inset show measurements at several temperatures for the
sample S3. It is evident that this sample shows diamagnetic behavior at all measured temperatures. This is attributed to the higher oxygen partial pressure inside the chamber during sample growth, resulting in more stoichiometric films, in turn, reducing the oxygen and zinc vacancy concentrations.

The low resistivity, high transmittance and the occurrence of RTFM with high magnetic moments ought to have their origin in the intrinsic oxygen vacancies and zinc defects. Due to the non-equilibrium nature of PLD process and the creation of highly energetic species with energies in the range of 100-1000 $kT$, a large concentration of vacancies and interstitials are formed in oxygen and zinc sub-lattices. Oxygen interstitials have high formation energies and are not expected to exist in significant concentrations. Zinc vacancies have low formation energies and are deep acceptors, contributing as compensating defects in n-type samples. Among the two donor-like defects, oxygen vacancies are deep donors and zinc interstitials are shallow donors, but are energetically less favorable. However, hybridization between the deep-donor state and shallow-donor state creates an attractive interaction. The low migration energy of the zinc interstitials (~0.5 eV) facilitates a rapid diffusion in the lattice and these can quickly pair up with oxygen vacancies, leading to the formation of oxygen vacancy-zinc interstitial defect complex ($V_O-I_{Zn}$).\textsuperscript{32,33} We believe that this defect complex acts as a source for the n-type conductivity in ZnO.
5.5. **Summary and Conclusions**

We have grown highly transparent epitaxial ZnO thin films doped with 0.2 at% Ga and 2 at% Al on c-plane sapphire substrates using pulsed laser deposition. Films grown at 600°C show a metal-like conductivity at room temperature followed by an SMT at lower temperatures. We have achieved lowest resistivity values on the order of 100 μΩ·cm and resistivity minima at relatively high temperatures 115-145 K with high transmittance values ~85% making the films well suited for TCO based devices. The most interesting features are the concomitant occurrence of high temperature resistivity minima and room temperature ferromagnetism. We have investigated the temperature dependent conductivity behavior of these films in detail, taking into effect of weak localization and Coulomb interaction effects. Based on the fits to the resistivity data and analysis, the electron-electron scattering is found to be the dominant dephasing mechanism resulting in the resistivity minima. It is envisaged that the native point defects play a decisive role not only in the structural, optical and electrical properties but also in the onset of RTFM in AGZO films, yielding high saturation magnetic moments of 28 and 61 emu/cc with considerable coercivities. We propose that formation of oxygen vacancy-Zinc interstitial defect complex (VO-IZn) is responsible for the significant and concurrent enhancements in n-type conductivity, optical transparency and the onset of ferromagnetism. Further, we have established correlations between structural, electrical, optical, and magnetic properties in terms of defects and defect complexes. We conclude that the occurrence concurrent RTFM coupled with the enhancements in both optical transparency and electrical conductivity in Ga and Al doped ZnO epitaxial films ought to
have their origin in native point defects in the form of oxygen vacancies and Zn interstitials and their complexes.

5.6. Acknowledgements

Part of this research was supported by the National Science Foundation, Grant # DMR-1304607 and Army Research Office Grant # W 911 NF-04-D-0003-0015. The authors acknowledge the use of the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation.
### 5.7. Tables

Table 5.1 Average transmittance, resistivity values, carrier concentration, mobility, and optical band gaps of S1, S2, and S3 samples.

<table>
<thead>
<tr>
<th></th>
<th>Avg %T</th>
<th>$\rho_{300K}$ (mΩ-cm)</th>
<th>$\rho_{15K}$ (mΩ-cm)</th>
<th>$n_e$ (cm$^{-3}$) $\times 10^{20}$</th>
<th>$\mu$ (cm$^2$/V.s)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>83</td>
<td>0.11</td>
<td>0.095</td>
<td>6.73</td>
<td>41.62</td>
<td>3.59</td>
</tr>
<tr>
<td>S2</td>
<td>88</td>
<td>4.0</td>
<td>3.79</td>
<td>0.61</td>
<td>34.79</td>
<td>3.34</td>
</tr>
<tr>
<td>S3</td>
<td>91</td>
<td>3.5</td>
<td>3.3</td>
<td>0.84</td>
<td>9.9</td>
<td>3.32</td>
</tr>
</tbody>
</table>
Table 5.2 All the important parameters extracted from the fits to the temperature dependent resistivity data to Equation (5.1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameters</th>
<th>Fit Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\rho(T) = \frac{1}{(\sigma_0 + \alpha_1 T^{p/2} + \alpha_2 \sqrt{T})} + \beta T^2$</td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>$\sigma_0$ (S cm$^{-1}$)</td>
<td>10518.01</td>
</tr>
<tr>
<td></td>
<td>$\alpha_1$ (S cm$^{-1}$ K$^{2p}$)</td>
<td>0.361</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>\alpha_2</td>
</tr>
<tr>
<td></td>
<td>$\beta$ (Ω cm K$^{-2}$)</td>
<td>$3.4 \times 10^{10}$</td>
</tr>
<tr>
<td></td>
<td>$p$</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Adj. R-Square</td>
<td>0.9981</td>
</tr>
<tr>
<td>S2</td>
<td>$\sigma_0$ (S cm$^{-1}$)</td>
<td>262.07</td>
</tr>
<tr>
<td></td>
<td>$\alpha_1$ (S cm$^{-1}$ K$^{2p}$)</td>
<td>0.232</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>\alpha_2</td>
</tr>
<tr>
<td></td>
<td>$\beta$ (Ω cm K$^{-2}$)</td>
<td>$8.5 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>$p$</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Adj. R-Square</td>
<td>0.9996</td>
</tr>
<tr>
<td>S3</td>
<td>$\sigma_0$ (S cm$^{-1}$)</td>
<td>305.25</td>
</tr>
<tr>
<td></td>
<td>$\alpha_1$ (S cm$^{-1}$ K$^{2p}$)</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>\alpha_2</td>
</tr>
<tr>
<td></td>
<td>$\beta$ (Ω cm K$^{-2}$)</td>
<td>$6.11 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>$p$</td>
<td>1.96</td>
</tr>
<tr>
<td></td>
<td>Adj. R-Square</td>
<td>0.9994</td>
</tr>
</tbody>
</table>
5.8. Figures

Figure 5.1 (a) 0-20 XRD spectra for all three samples S1, S2 and S3 (b) φ-scan plot for S2.
Figure 5.2 TEM micrographs for sample S2 (a) Cross section HRTEM image shows highly epitaxial film with atomically sharp interface. FFT filtered HRTEM image (bottom) shows epitaxial matching of 6/7 and 5/6 domains to accommodate the 16\% misfit between the film and the substrate. (b) SAED pattern of film-substrate interface. (c) Bright-field low magnification image showing film thickness of ~450 nm.
Figure 5.3 (a) UV-Vis optical transmittance spectra for all the three films (b) Corresponding Tauc plots to estimate the optical band gaps.
Figure 5.4 Variation of resistivity of AGZO films as a function of temperature for all the three films, S1 (right y-axis), S2 and S3 (left y-axis).
Figure 5.5 Resistivity vs. temperature plots of AGZO samples grown on c-plane sapphire. The solid red lines are the corresponding fits to experimental data to Eq. (5.1). It is evident that the fits to the data are excellent in all the three films, S1, S2 and S3.
Figure 5.6 Isothermal magnetic-field dependent magnetization curves for the AGZO (S1 and S2) films on sapphire substrates at 300 K. Plotted in the bottom inset are the low field M-H hysteresis loops between ±400 Oe for S1 and S2 samples (at 10, 50, 100, 200 and 300 K) deciphering clearly the significant hysteresis shown by these films. S1 and S2 films exhibited RTFM with maximum saturation magnetization up to 28 emu/cc for the case of S1, and about 61 emu/cc for S2. Top inset shows the M-H plot measured at several temperatures (10, 50, 100, 200 and 300 K) for S3. It is evident that this sample shows diamagnetic behavior at all the temperatures of measurement.
5.9. References


6. Structure-Property Correlations and Room Temperature Ferromagnetism and
   in Nanostructured Zinc Oxide Thin Films

Namik K. Temizer¹, and Jagdish Narayan¹

¹NSF Center for Advanced Materials and Smart Structures, Department of Materials Science
   and Engineering, North Carolina State University Raleigh, NC 27695

6.1. Abstract

We report on the micro-structural, transport, optical and magnetic properties in ZnO
   nanostructured films grown by pulsed laser deposition under different ambient conditions.
We have investigated the nanostructures in detail through x-ray diffraction, SEM and TEM
   techniques. Smallest average grain size of 7nm was achieved for the sample grown in Argon.
The most interesting features in this film were the relatively low room temperature resistivity
   and the occurrence of room temperature ferromagnetism with significant saturation magnetic
   moment of 1000 A/m with coercivity in the range of 100-150 Oe. These properties have their
   origin in native point defects in the form of oxygen and zinc vacancies and interstitials and
   their complexes. Photoluminescence measurements were conducted to get an insight about
   the types of defects that occur under different growth conditions. Correlations between
   transport, optical and magnetic properties has been established in terms of these defects and
their complexes. These nanostructured oxides with magnetic and optical properties are promising candidates in multifunctional spintronic and photonic devices.

*Keywords:* A. Zinc oxide; B. Nanostructures; C. Ferromagnetism; D. Electrical transport; E. Multifunctional oxides

1 Corresponding author’s email: nktemize@ncsu.edu
6.2. Introduction

Zinc oxide nanostructures have recently received considerable attention due to their physical properties and potential technological applications in a wide variety of fields, including biomedical, energy, sensors and optoelectronics.\textsuperscript{1-3} After the theoretical prediction of room temperature ferromagnetism (RTFM) in Mn doped ZnO\textsuperscript{4}, studies on undoped and transition metal doped ZnO systems have intensified.\textsuperscript{5-10} The RTFM in ZnO makes it a potential candidate for spintronic applications.\textsuperscript{11} One of the key approaches for future spintronic devices is the development of nanoparticle based dilute magnetic semiconductors with Curie temperature ($T_C$) above room temperature.\textsuperscript{12}

Room temperature ferromagnetism has been reported in powders, nanostructures and thin films of ZnO.\textsuperscript{13-16} Ferromagnetism in undoped ZnO is widely linked to poor crystalline quality, grain boundaries, strain, intrinsic defects and defect complexes, namely oxygen vacancies, zinc vacancies and zinc interstitials. In a study based on ab initio calculations\textsuperscript{17}, it was suggested that the magnetic moment arises from unpaired 2p electrons at the O sites surrounding the zinc vacancy, with each O atom carrying a magnetic moment ranging from 0.49 to 0.74 $\mu_B$. Recently, ferromagnetic coupled electron states in ZnO grain boundaries was observed using low energy muon spin relaxation in combination with SQUID and TEM.\textsuperscript{18} Low energy muons implanted into the host material were used as probes of magnetic field originating from magnetic moments in their close proximity. Based on the study, it was suggested that the ferromagnetism in ZnO stems from magnetic moments located in the grain
boundaries, and the grain area to volume fraction plays an important role for ferromagnetism in ZnO nanostructures.

Our research group has previously investigated the properties of doped and undoped ZnO films. In the case of undoped ZnO, we have found that ZnO thin films can be tailored to be ferromagnetic by invoking nonstoichiometric processing conditions, such as growth in low oxygen partial pressures, vacuum annealing, and further that the magnetization can be switched “on” and “off” by employing a high temperature vacuum and oxygen annealing, respectively. These studies strongly suggest that the intrinsic point defects play an important role in introducing and controlling ferromagnetism in ZnO.

The focus of our current study is to deposit ZnO nanostructures on sapphire substrates and investigate the role of point defects in establishing electrical, optical and magnetic properties of undoped ZnO films. We have carried out optical, electrical, and magnetic measurements on the films grown under different deposition ambients at room temperature. With the help of photoluminescence and Hall Effect methods, the role of defects in modifying magnetic properties in ZnO nanostructures has been illustrated.
6.3. Experimental Details

ZnO thin films have been deposited on single crystal c-plane sapphire substrates using pulsed laser deposition (PLD). Solid sintered targets were prepared from high purity ZnO powder by the conventional solid-state reaction technique. Thin films were deposited using a KrF excimer laser source \( (\lambda = 248 \text{ nm}, \tau = 25 \text{ ns}) \), with a pulse energy density of 0.5-1 J/cm\(^2\), and a repetition rate of 25 Hz. Target to substrate distance was maintained at 4.5 cm during the film deposition. The c-plane (0001) sapphire substrates were cleaned in an ultrasonic bath in acetone, followed by cleaning in methanol before being transferred to the deposition chamber. Three samples were deposited at room temperature using 5000 pulses in 100 mTorr Ar (S1), in vacuum (S2), and in 100 mTorr \( \text{O}_2 \) (S3). The deposition chamber was evacuated to a base pressure of less than \( 10^{-6} \text{Torr} \) prior to deposition. The structure of these films was characterized by x-ray diffraction (XRD) using a Rigaku SmartLab x-ray diffractometer with \( \text{Cu} \ K_\alpha \) radiation \( (\lambda=0.154 \text{ nm}) \), a JEOL 2010F field emission transmission electron microscope (TEM), and a Verios XHR 460L scanning electron microscope (SEM). Temperature variation of electrical resistivity was measured in the range of 15-300 K by employing a Van-der-Pauw configuration using thin gold wires and freshly cleaved indium to make very fine contacts onto the sample surface. Hall Effect measurements were performed using an Ecopia HMS-3000 Hall Effect Measurement System. Optical measurements (absorption/transmission) were recorded using a Hitachi U-3010 UV-Visible Scanning Spectrophotometer. Field dependent magnetization (M-H) measurements were carried out using a physical property measurement system (PPMS) in conjunction with an Evercool-2
vibrating sample magnetometer (VSM) attachment (Quantum Design). All the magnetization measurements were carried out on rectangular sample strips of 5 mm x 3 mm. Hysteresis measurements were performed by sweeping the magnetic fields from -10 to +10 kOe at 10, 100, and 300K. The magnetic field was applied parallel to the surface of the films. Great care was exercised to keep the samples in a dust-free environment and non-magnetic plastic tweezers were used for handling during growth and measurement in order to avoid contamination.

6.4. Results and Discussion

θ-2θ XRD and high resolution scan results for all three samples in Fig. 1a and 1b, respectively. S1 does not show any predominant peaks, suggesting very small grain size with no epitaxial relation with respect to the substrate. The (0002) and (0004) peaks are observed in S2 and S3, which indicate that these films are textured with c-axis as their preferred orientation. The (000l) peaks are lower in intensity and broader in S2 than S3, which indicates smaller grain size.

Further structural details were obtained using high-resolution TEM and selective area electron diffraction (SAED). Figure 2a and 2b show cross-section HRTEM micrographs for S1 and S2, respectively. Individual nano-sized grains with varying orientations can be observed in S1. Film thickness of ~140 nm is obtained from low magnification image shown in the left inset. The low magnification image along with the SAED pattern in the right inset
reveal that ZnO grows 3D with nano-sized grains. This change in growth mode from layer-by-layer to 3D is possible due to growth in high Ar partial pressure inside the chamber, which results in reduction of particle energetics inside the plume. In S2, the grains are observed to be elongated and their orientation is normal to c-plane. Columnar grain structure can also be observed in the low magnification image shown in the left inset. Film thickness for this particular sample is found to be ~175 nm. Arcs in the SAED pattern confirms textured growth (right inset).

In order to get an idea about the growth and morphology of ZnO nanostructures, samples are observed under the SEM. Shown in figures 3a, 3b, and 3c are the micrographs for S1, S2 and S3, respectively. It can be observed that S1 has the smallest grain size of ~7nm, which is in agreement with the TEM results.

The transmission spectra of the ZnO films is shown in Fig.4. Samples S1 and S2 show an average transmittance around 30% in the visible range, whereas the average transmittance for S3 is around 75%. The low transparency in S1 and S2 is due to the increased defect content in the films, which results from growth in oxygen deficient atmosphere.

In an attempt to understand the role of morphology and defects on electronic transport as well as on other physical properties of the films, we have measured the electrical resistivity
of the samples in the temperature range from 15-300 K. In addition, Hall effect measurements were performed on the samples at room temperature and results are given in Table 1. Figure 5 shows the temperature dependence of electrical resistivity ($\rho$) for samples S1, S2 and S3. All three samples display a negative temperature coefficient of resistivity (TCR), which is indicative of semiconducting behavior. Lowest resistivity is observed in S1, which is around 4.3 m$\Omega$-cm at room temperature. Mobility values are quite low in all three samples (Table 1). In films with such small grain structures, grain boundary scattering is expected to be the dominant scattering mechanism limiting the conductivity.$^{22-24}$

Field-dependent magnetization curves for all the three samples of ZnO films on sapphire substrates are plotted in Fig. 6. Isothermal magnetization measurements were carried out at 10, 100 and 300 K. The diamagnetic contribution due to the sapphire substrates has been subtracted in these samples. S1 exhibited RTFM with significant saturation magnetic moment with considerable hysteresis. The saturation magnetization is about 1000 A/m, and the corresponding coercivity is around 100 Oe. Plotted in the top inset are the low field M-H hysteresis loops between $\pm$ 300 Oe for S1, clearly displaying the hysteresis shown by this sample. The observed room temperature ferromagnetism in undoped ZnO originates essentially from Zn vacancies in close proximity with substitutional oxygen in the absence of any external magnetic impurities or magnetic ion dopants.$^{20}$ M-H plots in the bottom inset show measurements at several temperatures for the samples S2 and S3. It is evident that these samples show very weak ferromagnetism at all measured temperatures. For S3, weak
ferromagnetic signal is attributed to the high oxygen partial pressure inside the chamber during sample growth resulting in more stoichiometric film with reduced oxygen and zinc defect concentrations. In the case of S2, growth without any ambient gas results in a more forward directed plume and the ablated species do not lose much of their energy during travel. Hence, the film grows in a layer-by-layer (2D) scheme, having less surface area for defect formation compared with the 3D nanostructures.

Room temperature PL measurements were performed on the ZnO films grown in different gas ambients in an attempt to understand and correlate observed sample properties with native defects. The PL spectra for zinc oxide consists of a free exciton emission peak near 375 nm usually merged with a neutral donor bound exciton emission at 381 nm and a characteristic broad green band (GB) emission around 530 nm. The origin of GB emissions has been widely debated in literature. The GB thus far has been attributed to Cu impurities, zinc vacancies, oxygen vacancies and zinc interstitials. GB usually appears around 2.35 eV, which is lower than the band gap energy (3.3 eV) of ZnO, and its intensity should be related to the concentration of intrinsic defects. Figure 7 shows the PL spectra of the three films. It is observed that the UV emission that identifies near band edge (NBE) emission is most prominent in the sample grown in O₂ ambient (S3). This demonstrates better crystalline quality of the sample with dominant c-axis orientation, as also identified by XRD studies. Reduced NBE and defect band emissions are indicative of structural defects and traps that prevent luminescent behavior. The defect bands for S1 and S3 are shown in Figure 8a and 8b
deconvoluted into four different emissions; green, yellow, orange and red. A closer look at both spectra reveals that the main difference between the two samples is the greatly reduced yellow emission around 2.1 eV. We are inclined to suggest that this luminescence is due to the oxygen interstitials\(^{25-27}\), which are easily formed in oxygen-rich growth environments.\(^{28}\) There is a growing consensus that the green band emission around 2.3 eV is a result of zinc vacancies.\(^{29}\) In a recent study involving spatially resolved cathodoluminescence spectroscopy and imaging, the green luminescence was shown to be related to states at the non-polar surfaces where zinc vacancies are particularly stable.\(^{30}\) The two closer peaks corresponding to orange-red emissions are attributed to the band transitions from zinc interstitials to oxygen vacancies, and from conduction band to oxygen vacancies.\(^{31}\)

### 6.5. Summary and Conclusions

We have grown nanostructured ZnO thin films on c-plane sapphire substrates using pulsed laser deposition at room temperature. Growth under high oxygen and argon partial pressures results in 3D mode of growth, whereas the film grows layer-by-layer under vacuum. Complete structural characterization of these samples was performed with x-ray diffraction, TEM and SEM techniques. Temperature variation of resistivity measurements showed semiconducting behavior for all samples. Lowest resistivity of 4.3 m\(\Omega\)-cm was observed in the film grown under Ar, which also had the smallest average grain size of \(~7\) nm. The most interesting feature is the significant room temperature ferromagnetic behavior observed in this sample. We have investigated the transport and magnetic properties of these films in
detail, taking into effect the contribution from defects. The native point defects play a
decisive role not only in the structural, optical and electrical properties but also in the onset
of RTFM in ZnO films, yielding significant saturation magnetic moments of ~1000 A/m with
considerable coercivities. These materials find potential applications in spintronic and photonic
devices.

6.6. Acknowledgements

Part of this research was supported by the National Science Foundation, Grant # DMR-
1304607 and Army Research Office Grant # W 911 NF-04-D-0003-0015. The authors
acknowledge the use of the Analytical Instrumentation Facility (AIF) at North Carolina State
University, which is supported by the State of North Carolina and the National Science
Foundation.
Table 6.1 Average transmittance, film thicknesses, carrier concentration, and mobilities of S1, S2, and S3 samples.

<table>
<thead>
<tr>
<th></th>
<th>Avg %T</th>
<th>Film Thickness (nm)</th>
<th>( n_e ) (cm(^{-3})) \times 10^{19}</th>
<th>( \mu ) (cm(^2)/V.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>28</td>
<td>140</td>
<td>4.27</td>
<td>1.6</td>
</tr>
<tr>
<td>S2</td>
<td>29</td>
<td>175</td>
<td>1.37</td>
<td>2.34</td>
</tr>
<tr>
<td>S3</td>
<td>78</td>
<td>210</td>
<td>0.008</td>
<td>0.58</td>
</tr>
</tbody>
</table>
6.8. Figures

Figure 6.1 (a) XRD patterns of ZnO films grown at different ambient conditions on c-sapphire substrate (b) High resolution XRD shows different grain orientations present in the films.
Figure 6.2 Cross section HRTEM micrographs for samples S1 and S2. a) Individual grains with varying orientations can be observed. Left inset shows bright-field low magnification image. SAED pattern confirms nano crystalline structure (right inset) of S1. b) S2 has larger columnar grains. Same grain structure can be observed in the low magnification image (left inset). Arcs in the SAED pattern are due to textured grain growth (right inset).
Figure 6.3 SEM micrographs for all the samples a) S1, b) S2 and c) S3. Higher magnification images are shown in the insets.
Figure 6.4 UV-Vis optical transmittance spectra for all the three films.
Figure 6.5 Variation of resistivity of nanostructured ZnO films as a function of temperature for all the three films.
Figure 6.6 Isothermal magnetic-field dependent magnetization curves for the ZnO films on sapphire substrates. Plotted in the top inset are the low field M-H hysteresis loops between ± 250 Oe for S1 deciphering clearly the significant hysteresis shown by this film. Bottom inset shows the M-H plot measured at several temperatures (10K, 100K, and 300K) for S2 and S3.
Figure 6.7 Photoluminescence spectra for all three films obtained with HeCd laser source. Peaks at 325 nm and 650 nm correspond to line excitation and second order harmonics.
Figure 6.8 Photoluminescence measurements of samples a) grown in oxygen (S3) b) grown in argon (S1). Best fits are obtained with a minimum number of four Gaussian peaks.
6.9. References


7. Conclusion

We have grown highly transparent Ga (0.2%) and Al (2%) ZnO thin films were grown on c-plane sapphire substrates using pulsed laser deposition. Samples grown at $P_{O_2}=50$ mTorr show semiconducting behavior, whereas samples grown at $P_{O_2}=1$ mTorr show mostly metallic behavior. The films deposited under 50 mTorr showed increasing resistivity with decreasing temperature; resistivity was saturated with values in the range 3.0-375 m$\Omega$-cm at low temperatures, 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 that resulted in the interesting resistivity minimum. The structure-property correlations reveal that the oxygen vacancies or point defects play an important role in the structural, optical and electrical properties and that the electrical and optical characteristics stemmed out are essentially defect driven. We were able to achieve the lowest resistivity of ~110 $\mu\Omega$-cm and a resistivity minimum at relatively high temperatures 110-130 K with high transmittance values ~90% making the samples well suited for TCO based devices. Optical and electrical properties were found to be a strong function of growth conditions implying that the drastic changes are brought about essentially by native point defects. These results suggest that the Al and Ga codoped ZnO thin films have a potential to substitute for ITO in transparent electrode applications.
The interesting phenomena of semiconductor to metal transition in Ga and Al codoped films grown at 600°C and the ferromagnetic behavior of these samples were investigated. We have achieved lowest resistivity values on the order of 100 $\mu\Omega$-cm and resistivity minima at relatively high temperatures 115-145 K with high transmittance values ~85% making the films well suited for TCO based devices. The most interesting features are the concomitant occurrence of high temperature resistivity minima and room temperature ferromagnetism. We have investigated the temperature dependent conductivity behavior of these films in detail, taking into effect of weak localization and Coulomb interaction effects. Based on the fits to the resistivity data and analysis, the electron-electron scattering is found to be the dominant dephasing mechanism resulting in the resistivity minima. It is envisaged that the native point defects play a decisive role not only in the structural, optical and electrical properties but also in the onset of RTFM in AGZO films, yielding high saturation magnetic moments of 28 and 61 emu/cc with considerable coercivities. We propose that formation of oxygen vacancy-Zinc interstitial defect complex ($V_O$-$I_{Zn}$) is responsible for the significant and concurrent enhancements in n-type conductivity, optical transparency and the onset of ferromagnetism. Further, we have established correlations between structural, electrical, optical, and magnetic properties in terms of defects and defect complexes. We conclude that the occurrence concurrent RTFM coupled with the enhancements in both optical transparency and electrical conductivity in Ga and Al doped ZnO epitaxial films ought to have their origin in native point defects in the form of oxygen vacancies and Zn interstitials and their complexes.
We have investigated the growth and properties of nanostructured ZnO thin films deposited on c-plane sapphire substrates using pulsed laser deposition at room temperature. Growth under high oxygen and argon partial pressures results in 3D mode of growth, whereas the film grows layer-by-layer under vacuum. Complete structural characterization of these samples was performed with x-ray diffraction, TEM and SEM techniques. Temperature variation of resistivity measurements showed semiconducting behavior for all samples. Lowest resistivity of 4.3 mΩ-cm was observed in the film grown in Ar, which also had the smallest average grain size of ~7 nm. The most interesting feature is the significant room temperature ferromagnetic behavior observed in the sample grown in Ar. We have investigated the transport and magnetic properties of these films in detail, taking into effect the contribution from defects. The native point defects play a decisive role not only in the structural, optical and electrical properties but also in the onset of RTFM in ZnO films, yielding significant saturation magnetic moments of ~1000 A/m with considerable coercivities. The demonstration that nanocrystalline ZnO films can be grown with low resistivities and significant ferromagnetic properties at room temperature is an exciting development for applications requiring substrates that cannot withstand high processing temperatures, such as flexible polymer substrates.