Characterization of wide band gap semiconductors and multiferroic materials

Bo Cai
Graduate Center, City University of New York

Recommended Citation
http://academicworks.cuny.edu/gc_etds/408
CHARACTERIZATION OF WIDE BAND GAP SEMICONDUCTORS AND
MULTIFERROIC MATERIALS

by

BO CAI

A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for
the degree of Doctor of Philosophy, The City University of New York

2014
This manuscript has been read and accepted for the Graduate Faculty in Physics in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

Prof. Mim Nakarmi

Date  Chair of the examining committee

Prof. Igor Kuskovsky

Date  Executive Officer

Prof. Viraht Sahni

Prof. Karl Sandeman

Prof. Sang-woo Seo

Prof. Naresh Shakya

Supervisory Committee

THE CITY UNIVERSITY OF NEW YORK
Abstract

CHARACTERIZATION OF WIDE BAND GAP SEMICONDUCTORS AND MULTIFERROIC MATERIALS

by

BO CAI

Adviser: Professor Mim Lal Nakarmi

Structural, optical and electrical properties of zinc oxide (ZnO), aluminum nitride (AlN), and lutetium ferrite (LuFe2O4) have been investigated. Temperature dependent Hall Effect measurements were performed between 80 and 800 K for phosphorus (P) and arsenic (As) doped ZnO thin films grown on c-plane sapphire substrate by RF magnetron sputtering. These samples exhibited n-type conductivity throughout the temperature range with carrier concentration of $3.85 \times 10^{16}$ cm$^{-3}$ and $3.65 \times 10^{17}$ cm$^{-3}$ at room temperature for P-doped and As-doped ZnO films, respectively. The Arrhenius plots of free electron concentration of those doped samples showed double thermal activation processes with a small activation energy of about 0.04 eV due to shallow donors and a large activation energy of about 0.8 eV due to deep donors. The deep donor level could be related to oxygen vacancy. For undoped ZnO layer, growth condition was optimized to use as low background electron buffer layer. Hall Effect measurements showed that the resistivity and background electron concentration of the films decreases as the substrate temperature increases. The film deposited at 900 °C has more than two orders less background electron concentration than that deposited at 300 °C. Based on photoluminescence and Transmission Electron Microscopy (TEM) analysis, the ZnO grown under this condition is formed to be a greatly reduced density of stacking faults.
Transmission electron microscopy (TEM) was employed to investigate dislocations in aluminum nitride (AlN) epilayers grown on sapphire substrate using three-step growth method by metal organic chemical vapor deposition (MOCVD). AlN epilayers grown by this method have smooth surfaces, narrow width of X-ray rocking curves, and strong band edge photoluminescence (PL) emissions with low impurity emissions. Transmission electron microscopy revealed that most of the threading dislocations are annihilated within 300 nm. Stacking faults are greatly reduced in the epilayers grown by this method resulting in very low screw type threading dislocation density. Dominant threading dislocations in the AlN epilayers are edge type originated from misfit dislocations (MD).

The electro-optical and temperature-dependent electrical-transport properties of LuFe$_2$O$_4$ (LFO) thin films have been investigated. The LFO thin films at 78 K showed the electro-optical effects of size up to 5% near the Fe$^{2+}$ d to d on-site electronic transition. In the three-dimensional charge-ordered state of LFO, we observed hysteresis in dc voltage–current measurements and nonlinear voltage–current relationship in transient response of voltage under current pulses. The electro-optical and electrical properties of LFO thin films are interpreted in terms of the field-induced changes of the charge-ordered state mediated by the spin–charge–lattice coupling effect. We also discuss possible mechanisms of the complex electrical properties and electro-optical effects in conjunction with the Maxwell–Wagner effects.

**Keywords:** Zinc Oxide, Aluminum Nitride, Lutetium Ferrite, Hall Effect Measurement, Activation Energy, Transmission Electron Microscopy, Threading Dislocations, Electro Optical, Photoluminescence Spectroscopy
Acknowledgements

First of all, I would like to thank my professor Mim Lal Nakarmi. I have been working in his lab for the past 5 years. The most important thing I learnt from him is not physics, but a word called responsibility. This is something that changed me from a child to a grownup, and will be the most valuable treasure for the rest of my life. It is my honor to be his student and I am really proud of it.

My special thanks to Prof. Virant Sahni, Prof. Karl Sandeman at Brooklyn College, Prof. Sang-woo Seo at City College, and Dr. Naresh Shakva at NYU-Polytech. I would also like to thank Prof. Tom Oder at Youngstown State University and Prof. Ram C. Rai at Buffalo State College for providing samples for my thesis works. Also, thanks to Mr. Daniel Moy, Mr. Louis Tundis, Mr. Zakhar Yudovin, and Mrs. Marie Dumas for their great support during the period. I am also indebted to my friends Yang Li, Wei Long, Zhuo Chen, and Yuechao Chen for their help, encouragement and trust all the time.

Last but not least, my parents and my lovely wife, words are not enough to express my gratitude to them. Without their selfless love and endless support, I cannot be me today. Thank you for being always with me.

Bo Cai

New York, August 2014
# Table of Contents

Abstract ...................................................................................................................................... iv  
Acknowledgements .................................................................................................................... vi  
Table of Contents ....................................................................................................................... vii  
List of Figures ............................................................................................................................ ix  
List of Tables ............................................................................................................................. xii  

CHAPTER 1 INTRODUCTION ............................................................................................... 1  

CHAPTER 2 BACKGROUND AND LITERATURE REVIEW ............................................. 5  
  2.1 Zinc Oxide (ZnO) ....................................................................................................... 5  
    2.1.1 Crystal Structure ............................................................................................. 7  
    2.1.2 Electronic Band Structure of ZnO ............................................................... 8  
    2.1.3 Photoluminescence properties of ZnO ......................................................... 9  
    2.1.4 P-type doping of ZnO .................................................................................. 11  
  2.2 Aluminum Nitride (AlN) ............................................................................................ 14  
    2.2.1 Crystal Structure of AlN ............................................................................. 14  
    2.2.2 Band Structure of AlN ................................................................................. 15  
    2.2.3 Defects in AlN ............................................................................................. 15  
  2.3 Lutetium Ferrite (LuFe_2O_4) ..................................................................................... 19  
    2.3.1 Crystal Structure .......................................................................................... 19  
    2.3.2 Multiferroic properties of LFO .................................................................... 20  
    2.3.3 Charge-ordered states and phase transitions of LFO ................................. 20  

CHAPTER 3 CHARACTERIZATION TECHNIQUES ........................................................... 23  
  3.1 Atomic Force Microscopy (AFM) .............................................................................. 22  
  3.2 X-Ray Diffraction (XRD) .......................................................................................... 26  
  3.3 Hall Effect Measurement ......................................................................................... 28
3.3.1 Hall Effect Theory ................................................................. 28
3.3.2 Van der Pauw Resistivity Measurements ............................... 29
3.3.3 System set up ................................................................. 30
3.4 Transmission Electron Microscopy (TEM) ................................. 32
3.5 Photoluminescence (PL) Spectroscopy ...................................... 37

CHAPTER 4 EXPERIMENTAL RESULTS AND DISCUSSION ....................... 39

4.1a Elevated temperature dependent transport properties of phosphorus and arsenic doped zinc oxide thin films ................................................................. 39

b ZnO film with reduced background electron concentration for buffer layer ........ 54

4.2 TEM investigation of threading dislocation in Aluminum Nitride thin films .......... 60

4.3 Electro-optical effects and temperature-dependent electrical properties of LuFe2O4 thin films ................................................................. 69

CHAPTER 5 CONCLUSIONS AND OUTLOOK .............................................. 83

List of Publications ........................................................................ 86

Appendix ......................................................................................... 87

Bibliography .................................................................................... 90
List of Figures

Fig. 2.1 Wurtzite crystal structure of ZnO ................................................................. 6
Fig. 2.2 Schematic diagram of ZnO band structure .................................................. 8
Fig. 2.3 Low temperature PL spectrum measured at 4.2 K ....................................... 10
Fig. 2.4 Wurtzite crystal structure of AlN ................................................................. 14
Fig. 2.5 Schematic representation of a (a) screw-type and (b) edge- type dislocation with the respective Burger vector $\mathbf{b}$ ............................................................ 16
Fig. 2.6 Burgers vectors of the three types of dislocation observed in (0001) III-nitride layers ........................................................................................................ 17
Fig. 2.7 Crystallographic model illustrating the accommodation of the lattice misfit by dislocations .............................................................. 18
Fig. 2.8 Crystal structure of LuFe$_2$O$_4$. .................................................................. 19
Fig. 2.9 Evidence of magnetic transitions of LuFe$_2$O$_4$ ........................................... 20
Fig. 3.1 Schematic diagram of Atomic Force Microscope ........................................ 23
Fig. 3.2 Nanoscope III Multimode AFM ................................................................. 24
Fig. 3.3 AFM image of 5 $\mu$m $\times$ 5 $\mu$m AlN epilayer grown on sapphire ............ 25
Fig. 3.4 Reflection of x-rays from two planes of atoms in a solid .............................. 26
Fig. 3.5 Hall setup and carrier motion for electrons and holes ................................. 28
Fig. 3.6 Van der Pauw resistance measurement configurations ............................... 30
Fig. 3.7 Hall Effect Measurements image and system configuration ....................... 31
Fig. 3.8 Layout of optical components in JEOL-2010 and microscope picture ........ 34
Fig. 3.9 Illustration of lattice planes in (a) real space with (b) the corresponding reciprocal points and (c) the components of a g vector ..................................... 35
Fig. 3.10 Diffraction pattern of AlN grown on sapphire substrate along the [0001] zone axis .................................................................................................. 36
Fig. 3.11 Typical PL Set-up ...................................................................................... 37
Fig. 4.1 X-ray diffraction patterns of (a) undoped, (b) P-doped, and (c) As-doped ZnO grown on sapphire substrates

Fig. 4.2 The Arrhenius plots of electron concentration of (a) P-doped and undoped, and (b) As-doped ZnO thin films with temperature varied between 80 and 800 K.

Fig. 4.3 Plots of mobility ($\mu$) vs temperature ($T$) from the variable temperature Hall effect measurement performed on undoped P-, and As-doped ZnO thin films

Fig. 4.4 Low temperature PL spectra measured at 11 K of (a) P-doped ZnO thin film compared with an undoped ZnO sample, and (b) As-doped ZnO thin film. Inset is the PL spectra in the energy range of 2.0-2.8 eV comparing the impurity transitions of undoped, P-doped, and As-doped ZnO samples.

Fig. 4.5 The power dependent PL spectra of P-doped ZnO measured at 11K showing emission peaks related to the donor-bound exciton (D'X), free electron to FA, and DAP transitions in (a) P-doped ZnO and (b) As-doped ZnO samples

Fig. 4.6 Low-temperature PL spectra of undoped ZnO films deposited at different substrate temperatures

Fig. 4.7 Cross-sectional TEM images of undoped ZnO films deposited at (a) 300 °C and (b) 700 °C

Fig. 4.8 The Arrhenius plot of free electron concentration of undoped ZnO

Fig. 4.9 XRD scan of annealed and unannealed ZnO films deposited at 900 °C

Fig. 4.10 A typical in situ optical reflection curve during the growth of AlN epilayer by three-step method. Inset: Schematic layer structure of three-step growth method. An intermediate layer is inserted between the buffer and high temperature layer

Fig. 4.11 (a) PL spectrum of AlN epilayers grown on sapphire substrates measured at room temperature. (b) AFM image taken in 1 mm × 1 mm scan size. RMS surface roughness is about 0.5 nm

Fig. 4.12 (a) Bright field plan view TEM images of AlN epilayer taken with $g = 11\bar{2}0$ and tilted at 18° from [0001] zone axis and (b) diffraction pattern

Fig. 4.13 (a) Bright field cross-section view TEM image of AlN epilayer taken near zone axis [21\bar{1}0]. (b) Dark field cross-section TEM image under two beam condition with $g = 0001$ and (c) dark field cross-section TEM image under two beam condition with $g = 1\bar{1}00$ and (d) diffraction pattern
Fig. 4.14 High resolution cross-section TEM image taken near zone axis [2\overline{1}10] near the interface of AlN and sapphire substrate ............................................................ 66

Fig. 4.15 (a) An SEM image of the surface of a 300 nm LFO thin film, grown on (001) sapphire substrate, (b) an AFM image of the LFO thin film taken in a 2 \mu m \times 2 \mu m scan size by tapping mode and (c) the X-ray diffraction pattern of the LFO thin film grown on sapphire. ........................................................................ 71

Fig. 4.16 Representative absorption spectra of the LFO thin film on sapphire at 78 and 300 K, extracted from the transmittance data. The arrows indicate the electronic transitions. The inset shows the Fe^{2+} (d^6) crystal-field splitting scheme ................................................................. 72

Fig. 4.17 Electro-optical effects in applied dc voltages up to 200 V, and the absorption coefficient of the LFO films in the photon energy range of 1-2.75 eV at (a) 78 K and (b) 170 K. .................................................................................. 74

Fig. 4.18 Representative V-I characteristics of a 300 nm LFO thin film at different temperatures. (a) Schematic of a linear four-probe VI measurement on a thin film sample, (b) a linear V-I relationship between current and voltage at 340 K, (c) the hysteresis effect in the V-I at curve for increasing and decreasing currents at 300 K, and (d) a strong hysteresis in the V-I curve at 80 K. The up-arrow (red) and down-arrow (blue) represent the increasing and decreasing current sweeps ........................................................................ 78

Fig. 4.19 Transient behaviors in voltage signals of the LFO thin film at temperatures 340 and 280 K (b, c) under the applied current pulse (a). At low temperatures, the LFO thin film starts to exhibit nonlinear transient behaviors ........................................................................ 80
**List of Tables**

Table 2.1  Physical parameters of ZnO ................................................................. 7

Table 4.1  Hall Effect data of undoped samples deposited at different substrate temperature .................................................................................................................. 54
Discovering and creating new materials and understanding their properties are always critical for human development. Material development is associated with human civilization ages. In the beginning of human history on earth, the Stone Age, people used natural materials like stone, clay, skins and wood to create tools. Once people learned making alloy of metal, the Bronze Age started. Development of semiconductor has played very important role in our modern age. Nowadays, our life is unthinkable without the products of semiconductors. Invention of semiconductor based transistor is considered as one of the most important invention of the 20th century for the fabricating all modern electronics. The first Silicon (Si) transistor was development at Bell Lab in 1947 [1]. Since then Si started to dominate the commercial market of semiconductors and still leading the semiconductor market. But due to the indirect band gap of silicon, it is not suitable for fabricating optoelectronic devices such as light emitting diodes (LED) and laser diodes. III-V compound semiconductors such as gallium arsenide (GaAs), indium phosphide (InP) are direct band gap semiconductors that can be used to fabricate LEDs in infrared-red range. Although GaAs based LEDs are in visible range, it cannot be used for producing light in blue or UV range. GaAs can be alloyed with AlAs making AlGaAs to increase
the bandbox. But it becomes indirect band gap when the Al content is more than 40%. Another group of wide band gap compound semiconductors such as III-nitride and, Zinc Oxide (ZnO) has potential application in the development of short wavelength LEDs. They are the main focus in the field of semiconductor research.

The first demonstration of GaN deposition was achieved by Naruska and Tietjen at RCA laboratories using hydride vapor-phase epitaxy on a sapphire substrate in 1969 [2]. First-generation blue LEDs were grown on foreign substrates e.g., sapphire, silicon carbide. These LEDs have very low efficiency. It is mainly due to the lack of high quality p-type material. In 1986, high crystalline quality GaN epilayers were obtained by depositing a buffer layer at low temperature, which led to the commercialization of high-performance blue LEDs and long-lifetime violet-laser diodes [3, 4]. Blue-ray players are already in the market that uses GaN based laser for reading the Blue-Ray discs. Development of blue emitter also completed the full range of primary colors and made it possible to realize daylight visible full-color LED displays.

ZnO is another candidate which can potentially compete with GaN. Compared to GaN, which is already widely commercialized for LED devices, ZnO has many interesting properties. Although its energy band gap (3.37 eV) is close to GaN (3.42 eV) at room temperature, ZnO has exciton binding energy about 60 meV which is much larger than that of GaN (21 meV). Thermal energy at room temperature is about 25 meV. Such a large exciton binding energy means the excitons will be survived even at the temperatures above the room temperature. It ensures the excitonic transition in ZnO based LEDs. Therefore, theoretically, we can use this property for high efficient room temperature UV light generation due to emission related to excitonic transition. Moreover, ZnO has many other interesting properties such as high melting point of about 1975 ºC which makes its high thermal and chemical stability, potential commercial value
due to abundant resources in the nature, environment-friendly, and simple fabrication process [5]. Thus ZnO became a new hot topic in the field of short-wavelength laser and optoelectronic devices in succession to GaN.

However, one important problem should be overcome before ZnO could potentially be used to fabricate real devices such as LEDs, that is, the growth of reliable p-type ZnO. In order to fabricate an LED or laser diode, it requires a junction of p-type and n-type materials. Despite the reports of p-type conductivity in ZnO films using various growth methods and various dopants, achieving reliable and reproducible high quality p-type conductivity in ZnO is still a challenge. Hence, it is one of the main research topics in my thesis. We studied electrical and optical properties of Phosphorous (P) and Arsenic (As) doped ZnO thin films deposited on sapphire substrates. The samples were grown in Prof. Tom Oder’s lab at Youngstown State University.

On the other hand, AlN, which has band gap of 6.1 eV at room temperature, also emerged as a promising candidate for fabricating deep ultra-violet (DUV) LEDs and photo detectors operating down to 200 nm. At present, the main obstacle for the fabrication of such devices is related to the difficulties in the growth of reduced dislocation AlN epilayers due to the lack of native substrates. Therefore, investigation of the threading dislocations could help improve the crystalline quality of AlN epilayers. One part of my thesis works is related to the investigation of threading dislocations of AlN epilayers. The AlN epilayer samples were grown at Kansas State University.

Functional electronic and magnetic materials form an important part of modern technology. For example, ferroelectric materials with a spontaneous electric polarization that can be switched by an applied electric field are widely used as tunable capacitors and form the basis
of ferroelectric random access memory (Fe-RAM) in computers. On the other hand, the most widely used materials for recording and storing data such as in the hard drive are ferromagnetic materials with a spontaneous magnetic polarization that can be reversed by a magnetic field. Materials in which ferroelectric and ferromagnetic properties coexist are known as multiferroic materials.

Lutetium Ferrite (LuFe$_2$O$_4$) has drawn a great attention for its multiferroic properties originated from its electric ferroelectricity. Unlike conventional ferroelectric material, where the ferroelectric is driven by ion shift, the ferroelectricity in LFO is driven by the charge ordered state (CO) in the so-called Fe-O double triangle layers with mixed valence of Fe$^{2+}$ and Fe$^{3+}$ [6]. Giant room temperature magneto dielectric and dielectric tenability under electric field suggests that LFO is a promising multifunctional material. However, the complexity of the CO state is still not well understood. Even its multiferroic property is considered questionable by many researchers. Furthermore, there is little work on thin film materials of LFO which is essential for device application. In this thesis work, we also investigated electrical and optical properties of LFO thin films. The LFO thin films samples were grown in Prof. Ram Rai’s lab at SUNY Buffalo State College.

In the first chapter of my thesis, I have discussed about the motivation of my research. In the next chapter, I have presented a brief background and literature reviews of related works. Chapter 3 describes the characterization techniques applied in my research. Chapter 4 discusses the experimental details with results and discussion. Finally, the thesis ends with some concluding remarks and future outlooks in Chapter 5.
CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Zinc Oxide (ZnO)

ZnO has a direct wide band gap ~3.37 eV at room temperature. Due to the wide band gap of this material, it has potential application in the development of UV LEDs. Actually, ZnO research dates back to as early as 1929 [7]. During the last 5 to 10 years, there has been a surge of research interest in ZnO due to its potential applications in blue and ultraviolet (UV) range optical devices. The most attracting factor about ZnO is mainly due to the large exciton binding energy. The number of ZnO related articles increased every year. In 2007, ZnO became the second most popular semiconductor material. Now the total number of ZnO publications has exceeded 26000 as indicated by Web of Science database. Since there are such a huge number of publications on ZnO, it is impossible to cite or read all of them. In the next section, we have presented a small review with some aspects of ZnO including its crystal structure, electronic band structure, optical properties and the issues of p-type doping.

2.1.1 Crystal Structure
ZnO normally crystalizes in wurtzite structure as shown in Fig. 2.1 [9]. This is a hexagonal lattice belonging to the space group P63mc with lattice parameters $a = 0.3296 \text{ nm}$ and $c = 0.52065 \text{ nm}$. Their $c/a$ ratio is $\sim 1.602$ which is close to the ideal value for hexagonal cell $c/a = 1.633$. This structure consists of a stacking sequence of alternating bi-atomic close-packed planes of $\text{Zn}^{2+}$ and $\text{O}^{2-}$ pairs along the $c$-axis. It also can be viewed by two interconnecting sublattices of $\text{Zn}^{2+}$ and $\text{O}^{2-}$ such that each Zn ion is surrounded by a tetrahedral O ions, and vice-versa. This kind of tetrahedral coordination in ZnO forms a noncentral symmetric structure with polar symmetry along the hexagonal axis.

In addition to the wurtzite phase, ZnO is also known to crystallize in cubic zincblende and rocksalt (NaCl) structures [9]. Table 2.1 shows some of the physical parameters of wurtzite ZnO.
Table 2.1: Physical parameters of ZnO

<table>
<thead>
<tr>
<th>Physical parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters at 300 K</td>
<td></td>
</tr>
<tr>
<td>(a_0)</td>
<td>0.32495 (\text{nm})</td>
</tr>
<tr>
<td>(c_0)</td>
<td>0.52069 (\text{nm})</td>
</tr>
<tr>
<td>(a_0/c_0)</td>
<td>1.602</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 (\text{g/cm}^3)</td>
</tr>
<tr>
<td>Stable phase at 300K</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>Melting point</td>
<td>1975 °C</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>8.656</td>
</tr>
<tr>
<td>Energy gap</td>
<td>3.37 eV, direct</td>
</tr>
<tr>
<td>Intrinsic carrier concentration</td>
<td>(&lt;10^6 \text{cm}^{-3})</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>Electron effective mass</td>
<td>0.24 (m_e)</td>
</tr>
<tr>
<td>Electron Hall mobility at 300 K</td>
<td>200 (\text{cm}^2/\text{Vs})</td>
</tr>
<tr>
<td>Hole effective mass</td>
<td>0.59 (m_e)</td>
</tr>
<tr>
<td>Hole Hall mobility at 300 K</td>
<td>5-50 (\text{cm}^2/\text{Vs})</td>
</tr>
</tbody>
</table>

Table 2.1 shows a compilation of basic physical parameters for ZnO [10, 11].

2.1.2 Electronic Band Structure of ZnO

Band structure of a given semiconductor is the most important physical parameter that dictates its applications. Several theoretical approaches have been employed to calculate the band structure of ZnO for its wurtzite, zinc-blende, and rocksalt polytypes. Green’s functional method [12], Local Density Approximation (LDA) [13, 14], GW approximation (GWA) [15, 16] and First-principles (FP) [17-19] have been employed to calculate the band structure of wurtzite...
ZnO. Additionally, a number of experimental data have also been published regarding the band structure and electronic states in wurtzite ZnO [20-25].

Figure 2.2 shows the schematic diagram of ZnO band structure with well accepted parameters [26]. The conduction band has a $\Gamma_7$ symmetry. The valance band is split by crystal field and spin orbit interaction into three states named A, B and C with $\Gamma_9$, $\Gamma_7$, $\Gamma_7$ symmetry, respectively. The corresponding excitonic band gaps at room temperature for the A, B and C states are 3.309 eV, 3.315 eV and 3.355 eV, respectively [27, 28]. Experimentally, at low
cryogenic temperatures, bound exciton emissions are the dominant radiative channel, whereas at higher temperatures free exciton emission usually takes over [26]. In bulk ZnO crystals, the free exciton is observed to be at about 3.37 eV at room temperature with the exciton binding energy \( \sim 60 \text{ meV} \) [29]. Up to eleven excitonic recombinations have been reported so far [29-33]. A fine structure of A exciton transition has also been reported by Bernard et al. [34].

### 2.1.3 Photoluminescence properties of ZnO

Photoluminescence (PL) is the most widely used technique to study optical properties of ZnO. Typical PL spectrum of ZnO consists of a UV emission band and a broad emission band in visible range at room temperature. The UV emission band is related to a near band-edge transition of ZnO due to the recombination of the free excitons. The broad emission band between 420 and 700 nm observed nearly in all samples is due to deep level emissions (DLE). The DLE band has previously been attributed to several defects in the crystal structure such as oxygen vacancy (V\(_{\text{O}}\)) [35], Zinc vacancy (V\(_{\text{Zn}}\)) [36], oxygen interstitial (O\(_{\text{i}}\)) [37], zinc interstitial (Zn\(_{\text{i}}\)) [38], and extrinsic impurities such as substitutional Cu [39]. Recently, this DLE band had been identified mainly due to two different defects related to V\(_{\text{O}}\) and V\(_{\text{Zn}}\) with different optical characteristics contributing to this emission band [40].
Fig. 2.3. Low temperature PL spectrum measured at 4.2 K [26].

Person names et al., has reported a detailed PL study of ZnO measured at cryogenic temperature (4.2 K) [26]. Figure 2.3 shows a typical photoluminescence spectrum of n-type bulk ZnO measured at 4.2 K [26]. As shown in the figure, bound exciton (BE) emission is the dominant radiative channel at low temperatures. The lines dominating the spectrum are originated from excitons bound to neutral donors (D⁰X) and acceptors (A⁰X) followed by longitudinal optical (LO) phonon replicas with an energy separation of 72 meV. The free exciton emission with the A-valence band (FXA) was found to be at 3.375 eV as shown in the figure. Additionally, there is a donor-acceptor-pair (DAP) transition around 3.22 eV which is again followed by phonon replicas. There is a broad band centered about 2.45 eV extending from the blue into the green range.
2.1.4 P-type doping of ZnO

Although ZnO has many attractive properties for fabricating UV LED and lasers, obtaining stable and reproducible p-type doping in ZnO is still a challenge. The difficulties might be arisen from a variety of reasons including compensation of dopants, low-energy native defects generating background free electrons, and low solubility of the dopants in ZnO. These lead to significant difficulty in getting p-type doping in ZnO.

P-type doping in ZnO could be possible by substituting group-I elements (Li, Na, and K) for Zn sites or group-V elements (N, P and As) on O sites. Due to the small atomic radii of group-I elements, they tend to occupy the interstitial sites rather than substitutional Zn sites. These interstitial sites are generally donors instead of acceptors [Ref]. Moreover, significantly larger bond length for Na and K than ideal Zn-O bond length induces lattice strain forming native defects such as vacancies. Similarly group-V elements such as P and As also have significantly larger bond lengths. Therefore, it was thought that the best candidate for p-type doping in ZnO could be nitrogen. A number of groups have worked on realizing p-type ZnO using nitrogen as an acceptor dopant. Iwata et al. have reported p-type doping of ZnO using molecular-beam epitaxy (MBE) by simultaneously introducing O₂ and N₂ through a rf plasma source [41]. Even with the nitrogen concentration as high as $10^{19}$ cm⁻³, they could not achieve p-type conductivity. However, Look et al. reported p-type ZnO by MBE with N doping using N₂ rf plasma as N source [42]. Hall measurements showed p-type conductivity with resistivity of 40 Ωcm, hole mobility of 2 cm²/V and hole concentration of $9\times10^{16}$ cm⁻³ at room temperature. In the PL spectrum of the thin films had a strong emission peak near 3.32 eV probably due to neutral-acceptor-bound excitons. The estimated activation energy of the acceptor was between 170 and 200 meV based on the low-temperature PL measurements.
NH₃ has also been used in an effort to achieve p-type doping in ZnO. Minegishi et al. and have reported p-type doping in ZnO by using NH₃ in O₂ or H₂ gas [43]. The resistivity was relatively high about 100 Ω cm. Ye et al. also reported p-type ZnO by using NH₃ source with hole concentration of around 3.2×10¹⁷ cm⁻³ and a resistivity of 35 Ω cm [44].

Despite the above-mentioned reports on successful growth of p-type ZnO films by N doping, there were also a number of reports in which the authors were not able to reproduce these results. Recently revised theoretical calculation using first principles calculation and experimental investigation showed that N in ZnO is a deep acceptor [45, 46]. Therefore, the reported results on p-type ZnO are questionable.

Aoki et al. used Pulsed Laser Deposition (PLD) technique to produce phosphorus-doped p-type ZnO films using a zinc-phosphide (Zn₃P₂) compound as the phosphorus [47]. They claimed achievement of P-doped ZnO through the replacement of O atoms by P atoms. In this case, a p-n-junction-like behavior was observed between an n-type ZnO substrate and P-doped layer although Hall measurements did not confirm p-type conductivity. Similar results were obtained by Lee et al. who also transformed a Zn₃P₂ layer on ZnO/sapphire to p-type ZnO by laser annealing [48].

Kim et al. reported p-type ZnO by using P₂O₅ as phosphorus source. Hall Effect measurements showed p-type conductivity with hole concentration of 1.0 × 10¹⁷ – 1.7 × 10¹⁹ cm⁻³, hall mobility of 0.53 – 3.51 cm²/Vs, resistivity of 0.59 – 4.4 Ω cm. The film showed strong photoluminescence peak at 3.35 eV at 10 K, which could be related to neutral acceptor bound excitons [49].
Ryu et al. reported p-type conductivity by As-doping by using GaAs substrate as an arsenic source for p-type doping by PLD [50]. After annealing the thin films exhibited p-type conductivity confirmed by Hall Effect measurements.

As a conclusion to this section we can state that despite of a large number of recent reports on p-type ZnO, no reproducible high-quality p-type layers are available yet. Lack of reports on the demonstration of fabrication of operational ZnO based LED of supports this conclusion. Further efforts are needed to resolve this problem.
2.2 Aluminum Nitride (AlN)

2.2.1 Crystal Structure of AlN

Figure 2.4 shows wurtzite crystal structure of AlN. It has lattice parameters of are $a = 3.1106 \, \text{Å}$ and $c = 4.982 \, \text{Å}$ [51]. In the structure of a hexagonal wurtzite unit cell of AlN as sketched in Fig. 2.4, this structure consists of a stacking sequence of alternating bi-atomic close-packed (0001) planes of Al and N pairs (marked by A and B) along the c-axis. The sub-lattices of Al and N atoms are shown in different colors.

Fig. 2.4. Wurtzite crystal structure of AlN.
2.2.2 Band Structure of AlN

AlN has the widest direct band gap of about 6.1 eV (at the Γ point) at low temperature (10 K) in the WZ structure [52-54]. Li et al. provided a coherent picture for the band structure parameters of wurtzite AlN near the Γ point from PL spectroscopy measurements and first-principles calculations [52]. In AlN, the Γ point valance band splits into three levels due to the crystal field and spin-orbit interactions. The band split between A and B is attributed to spin-orbit whereas the split of C is attributed to crystal field. Much works need to be done to conclusively determine many key parameters of AlN.

2.2.3 Defects in AlN

The properties of semiconductor materials are often controlled by defects and the incorporation of impurities. The III-nitrides contain large densities of structural and native defects compared to II-VI compound semiconductors. Due to the wide band gap, these defects could easily give rise to electronic states throughout the band gap. These defects could be point defects, line defects, and planar defects. Point defects include vacancies, interstitials, and antisites. Planar defects include grain boundaries and stacking faults. These are structural defects that are formed during crystal growth. In this thesis, we are mainly interested in linear defects which are also named dislocations and discussed briefly below.
Fig. 2.5. Schematic representation of (a) screw-and (b) edge-type dislocation with the respective Burger vector $b$.

There are mainly three types of dislocations in AlN; edge type, screw type and mixed type. Figure 2.5 (a) shows the schematic diagram of a screw type dislocation. We can imagine cutting a crystal along a plane and slipping one half across the other by a lattice vector, the boundary of the cut is a screw dislocation. In screw type dislocations, the Burgers vector is parallel to the dislocation boundary.

In an edge type dislocation an extra half-plane of atoms is introduced midway through the crystal, distorting nearby planes of atoms as shown in Fig. 2.5 (b). For edge type dislocations, the Burgers vector is perpendicular to the dislocation boundary. In many cases, dislocations are found where the Burgers vector and dislocation boundary are neither perpendicular nor parallel and these dislocations are called mixed dislocations, consisting of both screw and edge character. Figure 2.6 shows the Burger’s vector of three types of dislocations in the aluminum nitride films: edge-type ($a$-type), screw-type ($c$-type), and mixed-type ($c+a$-type) corresponding to Burger’s vector $b = \frac{1}{3} < 1\bar{2}10 >$, $<0002>$, and $\frac{1}{3} < 1\bar{2}13 >$, respectively.
Fig. 2.6. Burgers vectors of the three types of dislocation observed in (0001) III-nitride layers.
Fig. 2.7. Crystallographic model illustrating the accommodation of the lattice misfit by dislocations [55].

Misfit dislocations (MDs) are generated due to the lattice and thermal expansion coefficient mismatches, and threading dislocations (TDs) due to the tilt and twist of crystal grains. Figure 2.7 shows a crystallographic model, presented by Masu et al. [55], at the AlN/sapphire interface. Due to lattice mismatch between lattice constants of N-N and O-O, periodical MDs, which are indicated by white arrows are usually introduced in regular intervals of 8 atomic planes in terms of the AlN lattice or 9 atomic planes in terms of the Al₂O₃ lattice.

During crystal growth, unevenness of the substrate surface or the collision of growth islands leads to the nucleation of dislocations. Some of the TDs propagates along the direction parallel of the growth and may reach up to the surface of the film. The presence of TDs adversely affects the device properties causing non-radiative recombination, carrier scattering effects, and diffusion of dopants and impurities.
2.3 Lutetium Ferrite (LuFe$_2$O$_4$)

2.3.1 Crystal Structure

LuFe$_2$O$_4$ (LFO) belongs to RFe$_2$O$_4$ family in which R is rare earth material from Dy to Lu and Y in periodic table. RFe$_2$O$_4$ family is compounds having a rhombohedral structure with space group R3m [56]. Its crystal structure consists of alternating stacks of mixed valence Fe and rare earth oxide triangular lattice is shown in Fig 2.8 in hexagonal form. RFe$_2$O$_4$ is considered a spin- and charge-frustrated system of triangular lattices, occupied by the mixed valence states of Fe with an equal number of Fe$^{2+}$ and Fe$^{3+}$ ions. Recently, LuFe$_2$O$_4$ (LFO) compound has attracted extensive research interest due to its unique multiferroic properties.

![Crystal structure of LuFe$_2$O$_4$](image_url)
2.3.2 Multiferroic properties of LFO

LFO was first proved to be a ferroelectric material by N. Ikeda in 2005 [6]. The macroscopic electric polarization was deduced from piezoelectric current measurement, in which the sign of current changes by applying electric field in different directions. Moreover, an observable current drop was found at 250 K, the Neel temperature of this material indicating a coupling between magnetism and electric polarization. This experiment is a milestone in the LFO research, which attracts more attention to this material since then.

2.3.3 Charge-ordered states and phase transitions of LFO

![Evidence of magnetic transitions of LFO](image)

Fig. 2.9. Evidence of magnetic transitions of LFO [57].
Because of unique geometrical and charge frustrations, LFO undergoes several charge order and magnetic transitions at different temperature. Three dimensional (3D) to two dimensional (2D) transitions at ~330 K, and 2D to disordered state transitions at ~500 K have been reported [58]. Charge ordered states were considered as an essential factor behind various behaviors of LFO, including magneto dielectric, electric field induced magnetization, dielectric tenability and insulator-to-metal transitions [59-64]. However, the explanation of charge-ordered state is not fully built up yet. A postulate model of Fe$^{2+}$ and Fe$^{3+}$ superstructure in adjacent triangle layers has been proposed by N. Kimizuka et al. [65], and later improved by Ikeda [6].

Recently, H. J. Xiang et al. reported a new model based on first-principle calculation, in which two CO states in ferroelectric order were given out to be the possible states in LFO at room temperature [66]. However, this model cannot demonstrate how magnetic field works with the CO states switching. Direct observation of CO states from TEM has also been reported in 2007 [67]. Recently, Christianson et al. reported two more magnetic transitions at ~170 and ~240 K based on neutron scattering results as shown in Fig. 2.9 [57].

Although LFO has been known as a high temperature (T ~240 K) multiferroic for some time, its ferroelectricity and high dielectric properties have been controversial in recent years. In particular, ferroelectricity and high dielectric properties of LFO have been linked to the Maxwell-Wagner effects at the contact interfaces [11-15]. In order to further explore and understand ferroelectricity and multiferroic properties of LFO, a detailed systematic study is essential.
CHAPTER 3

CHARACTERIZATION TECHNIQUES

3.1 Atomic Force Microscopy (AFM)

Atomic force microscope (AFM) was mainly used for surface characterization of the materials in this thesis work. All the images were taken in tapping mode. We have of Nanoscope-III multimode AFM in our lab. It is a high resolution AFM that can be operated in contact and tapping mode.

AFM generally consists of a micro scale cantilever with a sharp tip at its end. The tip is brought near the surface and scanned sample to produce the morphology of the surface. When the tip is brought into proximity of a sample surface, Van der Waals forces between the tip and the sample lead to a deflection of the cantilever. The deflection is amplified by using a laser light incident on the cantilever. Signals in quad photo detectors can be calibrated to measure the amount of deflection of the cantilever. When the tip scans along lines by line to covering the surface, the plot of the data matrix of the detector signal generates ‘image’ of the sample
A typical schematic diagram of AFM is shown in Fig. 3.1. A probe consists of a thin and reflecting cantilever with a sharp tip on the free-swinging end. Laser light is reflected from the cantilever and collected by a position-sensitive detector consisting of two closely spaced photodiodes whose signal is collected by a differential amplifier. The sample or the probe is moved up and down by piezoelectric materials.

AFM is usually operated in two modes according to the nature of the tip motion: contact mode and tapping mode. In contact mode, the tip is scanned closed to the sample by fixing a specific force between the sample and the tip. Closed loop computer control system try to maintain the force constant by moving the sample stage (or probe in some cases). These data constitutes the raw data to produce the AFM image. In tapping mode, the cantilever is driven to...
oscillate at near its resonance frequency by a small piezoelectric element mounted in the AFM tip holder. This mode reduces the damage of sample and the probe (if used properly!).

Fig 3.2. Nanoscope-III Multimode AFM

Figure 3.2 shows the picture of Nanoscope-III multimode AFM in our lab. The Nanoscope-III is a high resolution AFM that can be operated in both contact and tapping mode.
Figure 3.3 shows an example of AFM image of AlN epilayer scanned in size of 5 μm × 5 μm taken by our Nanoscope-III multimode AFM. The sample was grown on (0001) sapphire substrate. We can see terrace like morphology due to layered growth of AlN in the AFM image.
3.2 X-Ray Diffraction (XRD)

X-ray diffraction was used to characterize the crystalline structure and quality of the samples used in this thesis work. X-ray patterns are obtained with θ–2θ scans for all samples.

Figure 3.4 illustrates the reflection of x-rays from two planes of atoms in a crystal. Based on Bragg's Law, when a monochromatic X-ray beam with wavelength $\lambda$ is incident onto a crystal lattice at an angle $\theta$, maximum of diffraction occurs when the distance traveled by the reflected rays from successive planes is integer multiple of wavelength, which leads to famous:

$$n\lambda = 2d\sin\theta$$  \hspace{1cm} (3.1)
where \( n \) is an integer, \( \lambda \) is wavelength in angstroms, \( d \) is interatomic spacing in angstroms, and \( \theta \) is the diffraction angle in degrees. By varying the angle \( \theta \), the Bragg's Law conditions are satisfied by different d-spacing in polycrystalline materials. Plotting intensity versus the angular positions produces a pattern which is characteristic of the sample.

XRD has been in use in two main areas: i.e. the fingerprint characterization of crystalline materials and the determination of their structure. Today about 50,000 inorganic and 25,000 organic single components, crystalline phases, and diffraction patterns have been collected as standards.
3.3 Hall Effect Measurement

3.3.1 Hall Effect Theory

The Hall Effect is due to the behavior of free carriers in a specimen when an electric field and magnetic field together. The experimental setup is shown in Fig. 3.5. In a simple geometry as shown in the figure, we apply a voltage $V_x$ between at the two ends a semiconductor bar with a rectangular cross section and length $L$, resulting in a field along the $x$-direction. The magnetic field is applied in the $z$ direction.

![Fig. 3.5. Hall setup and carrier motion for (a) electrons and (b) holes](image)

As shown in Fig 3.5, the holes and electrons deflect towards positive $y$-direction due to the Lorenz force given by

$$\vec{F} = q(\vec{v} + \vec{\nu} \times \vec{B})$$  \hspace{1cm} (3.2)

Due to this effect, it generates an electric field along $y$-direction. Hall coefficient is defined as:
Based on the transport theory of carrier, Hall coefficient for metal is given by

\[ R_H = \frac{E_y}{I_x B_z} \]  \hspace{1cm} (3.3)

Thus the Hall coefficient is negative for the specimen which has only electrons as free carrier.

For semiconductor, Hall coefficient is given by

\[ R_H = -\frac{1}{ne} \]  \hspace{1cm} (3.4)

where \( p \) is the hole concentration, \( n \) is electron concentration, \( \mu_e \) is electron mobility and \( \mu_h \) is the hole mobility.

Once the Hall coefficient is obtained one can easily determine the carrier density and Mobility. In practical method, resistivity is first measured by Van der Pauw method and with Hall coefficient obtained from Hall Effect measurement, carrier concentration and mobility are separated.

### 3.3.2 Van der Pauw Resistivity Measurements

Figure 3.6 illustrates van der Pauw resistivity measurement configurations and equations. In this technique, four contacts are made at the edge of the specimen. Two contacts are used for applying current and other two are used for measuring voltage. An averaging technique by changing the contacts and reversing the source polarity is used to obtain accurate results. Eight measurements are performed as shown in Fig 3.6. Specimen sheet resistance, \( R_s \), is determined by using Van der Pauw equation given in Eq. 3.6. Calculation of sheet resistance involves determining two parameters \( R_A \) and \( R_B \) in the equation and is done by iteration.
\[ R_A = \frac{(R_{21,34} + R_{12,43} + R_{43,12} + R_{34,21})}{4} \]
\[ R_B = \frac{(R_{32,41} + R_{23,14} + R_{14,23} + R_{41,32})}{4} \]
\[ e^{-\frac{\pi R_A}{R_s}} + e^{-\frac{\pi R_B}{R_s}} = 1 \]
\[ \rho = R_s \cdot t \]  

Fig. 3.6. Van der Pauw resistance measurement configurations

In practice, Hall Effect measurement is performed after resistivity measurement since the same Van der Pauw configuration can also be used for both.

### 3.3.3 System set up

Our Hall Effect measurement system consists of Keithley’s matrix switching card, the Model 7065, housed in a Switch Mainframe, Model 7001, as shown in Fig 3.7(b). The system also includes a Model 6220 DC current source, Model 6485 Picoammeter, and the Model 2182A Nanovoltmeter for voltage meter. The Model 6485 Picoammeter is used to measure leakage currents so they can either be subtracted out or monitored to make sure they are not impacting the high resistance measurement.
The Model 6220 and the Model 2182A are designed to work together seamlessly to cancel out the drifting thermoelectric offsets. A bipolar magnetic field of ~1T is employed for Hall Effect measurement. The Hall Effect system control software was developed by LabVIEW 2010. The program detail can be found in appendix. For temperature dependent measurements, we have a Janis Cryostat which can be operated from 20 to 800 K.
3.4 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) uses electron beam to generate image. Theoretically, the maximum resolution $\delta$ of an optical device is proportional to the wavelength $\lambda$ of the photons that are being used in the system:

$$\delta \approx \frac{\lambda}{2(NA)}$$  

(3.7)

where NA is the numerical aperture of the system.

For optical devices, the resolution was limited to ~200 nm. Using the wave nature of electron as proposed by de Broglie, the wavelength of an electron with momentum $p$ is:

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_eE_b}}$$  

(3.8)

where $h$ is Planck constant, $m_e$ is electron rest mass, and $E_b$ is the electron kinetic energy. If an electron is accelerated from rest to 100 keV, the De Broglie wavelength is only 1 pm according to the equation. Wave nature of electrons made people quickly realized that electrons can be used as a new source for imaging atomic scale objects. The first TEM was developed in 1931. The point-to-point resolution of modern TEM can reach to 0.23 nm. TEM is very similar to light microscope. Instead of light it uses electron beam and electromagnets are used as lenses. The sample thickness has to be sufficient thin enough so that electrons can transmit through it. Many improvements have been done in designing TEM for the new models of TEMs.

Figure 3.8 illustrates the optical components of the JEOL-2010 TEM in Brooklyn College, inset is the picture of the microscope. It consists of:
- An electron gun, which is lanthanum hexaboride (LaB₆) source. It provides the source of illumination by connecting to a high voltage (~100-400 kV). Electron beam was generated into the vacuum chamber.

- Electron lenses. These are the magnetic equivalent of the glass lenses in an optical microscope, they are used for focusing the electron beam and magnifying the image.

- Vacuum Chamber. The electron beam must be generated and used in a high vacuum of 10⁻⁵ pa or less. This ensures the electrons are not deflected by gas molecules and the filament and specimen are not contaminated.

- Specimen holder. A goniometer stage is used to traverse and tilt the sample so that every part and different angle of the sample can be examined.

- Camera and display. TEM consists of a phosphor screen for direct observation. It has for a CCD camera for image recording and analysis.
Fig. 3.8. Layout of optical components in JEOL-2010. Inset is the microscope picture.
For crystalline materials, diffraction pattern generated by the electron beam can also be used for analysis of the crystal structure and defects.

Fig. 3.9. Illustration of (a) lattice planes in real space with (b) the corresponding reciprocal points and (c) the components of a \( g \) vector.

Figure 3.9 shows the relation between the crystal planes (hkl) in real space of a cubic structure and the corresponding reciprocal lattice points, defined by \( g(\text{hkl}) = 1/d(\text{hkl}) \).
Fig. 3.10. Diffraction pattern of AlN grown on sapphire substrate along the [0001] zone axis.

Figure 3.10 shows an example of the diffraction pattern from a plan view AlN sample grown on sapphire substrate along the [0001] zone axis.
3.5 Photoluminescence (PL) Spectroscopy

In my thesis, the optical properties of unodped, phosphorus doped and arsenic doped ZnO thin films were characterized by photoluminescence (PL) Spectroscopy. The PL measurements were performed at Youngstown State University using a 325-nm He-Cd laser source.

![Fig. 3.11. Typical PL Set-up. Reprinted from ref [68]](image)

The basic scheme of PL set-up is illustrated in Fig. 3.11. In PL measurement the sample is illuminated by a light source, typically laser light, which has energy greater than the band gap of the materials. The incident light generates photo-induced carries in the conduction and valance band. During the process of returning the carriers to the ground states, they emit radiations depending upon the allowed energy levels available. By scanning the luminescence from the sample at different frequency (or wavelength) using a monochromator, PL spectrum can be collected. A variety of material information can be obtained by PL measurements. For example,
the band gap structure, impurity levels, recombination mechanisms, etc. We can also change other external parameters, such as temperature, excitation power and magnetic field or electrical field to the sample to help further understand the material optical properties. More information about PL can be found in this review article [68].
CHAPTER 4

EXPERIMENTAL RESULTS AND DISCUSSION

4.1a. Elevated temperature dependent transport properties of phosphorus and arsenic doped zinc oxide thin films

The unique optical, electrical, magnetic, and thermal properties of ZnO make it attractive for various applications with potentially huge technological and economic impact. Such properties include its large direct band gap of around 3.37 eV, a large exciton binding energy of about 60 meV, high resistance to radiation damage, and amenability to wet chemical etching. Since as-grown ZnO is n-type with usually very high concentration of electrons, obtaining stale and reproducible p-type doping in ZnO is still a challenge. Group V elements such as nitrogen (N), phosphorus (P), arsenic (As), and antimony (Sb) have been experimentally investigated for obtaining p-type ZnO by substituting oxygen. Nitrogen, in particular, has been extensively explored as its atomic radius is similar to that of oxygen [69-71]. However, recently revisited theoretical work and experimental investigation showed that nitrogen in ZnO is a deep acceptor with large ionization energy of 1.3 eV [45, 46].
Achievement of p-type conductivity in ZnO using P, As, and Sb as dopants with estimated activation energies about 0.12–0.18 eV has been reported [49, 72-76]. The mechanism of p-type conductivity in X-doped (X=P, As, Sb) ZnO has been attributed to the formation of a \((X_{\text{Zn}}-2V_{\text{Zn}})^{1-}\) complex [48, 77, 78]. Despite these reports, reliable p-type conductivity in ZnO is still problematic due to the high background concentration of free electrons and compensating centers originating from defects, some of which are deep level defects.

For this reason, further study of the electrical and optical properties of doped ZnO is important especially with tools that enable probing the deep energy levels that accompany attempts to realize p-type conductivity. Hall Effect measurement performed in the temperature range of 80 to 800 K offers a unique way to study thermal activation of deep levels and determine energy levels associated with them. In ZnO research, reported variable temperature transport measurements mostly cover low temperature up to room temperature (300 K) limiting ability to probe deep levels [73, 79, 80]. Measurements performed in the temperature range above 300 K would offer a way to study activation of these deep level defects. However, very little work has been reported on doped ZnO transport measurements above 300 K and yet the study of deep levels in doped ZnO clearly requires probing at higher temperatures [81].

We present here the investigation on the transport properties of ZnO thin films heavily doped with P and As. The samples were grown at Youngstown state University. About 700 nm thick ZnO films were grown on c-plane sapphire substrate via the RF magnetron sputtering technique. The sapphire substrates were first degrease-cleaned in boiling acetone and in alcohol, then rinsed in DI-water and dried. The samples were then loaded into a vacuum chamber pumped to a base pressure of \(2\times10^7\) Torr. A gas mixture comprising Ar/O\(_2\)=1/1, an RF power of 100 W and a substrate temperature of 300 °C were used for the deposition of the films sputtered from a
Fig. 4.1. X-ray diffraction patterns of (a) undoped, (b) P-doped, and (c) As-doped ZnO grown on sapphire substrates.
high purity ZnO sintered target. The deposition pressure used was 10 mTorr. Doping with P or As was effected by sputtering from high purity Zn$_3$P$_2$ or Zn$_3$As$_2$ sputter targets. The growth of the doped ZnO films started with deposition of a ZnO buffer layer, followed by periodic deposition of ZnO (20 nm)/Zn$_3$X$_2$(20 nm) (X = P or As). Post growth annealing was performed on all samples at 900 °C for 5 min under oxygen ambient using a rapid thermal processor (RTP). The concentrations of P and As in the doped samples, measured by Energy Dispersive Spectroscopy (EDS) were about 5 and 3 atm. %, respectively.

Figure 4.1 shows X-ray Diffraction (XRD) patterns of the doped ZnO samples compared with that of an undoped sample. Note that despite heavy doping, the P- and As-doped samples similarly exhibit intense and narrow peaks at 34.4° corresponding to the diffraction from the (002) plane of ZnO indicating a strong c-axis orientation perpendicular to the surface of the sapphire substrate. Peaks associated with Zn$_3$P$_2$ or Zn$_3$As$_2$ (such as from the (401) plane of Zn$_3$P$_2$ at 45.0° or from the (440, 408) plane of Zn$_3$As$_2$ at 43.3°) do not appear in the XRD patterns as shown in Fig.4.1 [82, 83]. The XRD peak positions from the doped samples did not show a significant shift compared to that from the undoped ZnO. From these observations, we infer that the heavy doping did not result in alloying of the films. However, the XRD intensities from the doped films were reduced and the peak line widths were broadened compared to that from the undoped sample.

The XRD diffraction patterns show small additional peaks at about 31.7°, 36°, and 47.6° corresponding to diffractions from the (100), (101) and (102) ZnO planes, respectively. Though these peaks have very low intensities barely above the background noise, their appearance indicates some undesirable degradation of the quality of the doped ZnO crystal film in
Fig. 4 2. The Arrhenius plots of electron concentration of (a) P-doped and undoped, and (b) As-doped ZnO thin films with temperature varied between 80 and 800 K. Double thermal activations are clearly observed in both doped samples.
comparison with the undoped film. Note that these peaks have been previously observed in both undoped and doped ZnO films [79, 80, 84].

Figure 4.2 shows the temperature dependence of the carrier concentration from the Hall effect measurements of the (a) P-doped and undoped, and (b) As-doped ZnO samples. The data points are the average of at least two measurements at each temperature. The undoped ZnO is n-type with high electron concentration. From the room temperature Hall effect measurements, the undoped sample has a resistivity of $0.037 \, \Omega \cdot \text{cm}$, a mobility of $28 \, \text{cm}^2/\text{V s}$ and a concentration of about $6.3 \times 10^{18} \, \text{cm}^{-3}$.

As shown in Fig. 4.2, the carrier concentration of undoped sample is almost constant at elevated temperatures. The background free electrons in undoped ZnO are believed to be from shallow donors associated with intrinsic defects. Possible donors are group III elements such as Al, Ga, and In which are believed to be shallow donors with activation energy ranging from 51 to 73 meV [26]. However, zinc interstitial (ZnI) or its related complexes and hydrogen have been identified to have lower formation energies and lower donor ionization energies of 25-40 meV [26, 80, 84].

Although P- and As-doped ZnO thin films were prepared with the objective of producing p-type conductivity, these samples exhibited n-type conductivity throughout the temperature range with carrier concentrations of $3.85 \times 10^{16} \, \text{cm}^{-3}$ and $3.65 \times 10^{17} \, \text{cm}^{-3}$ for the P-doped and As-doped ZnO films, respectively, as obtained from room temperature Hall effect measurements. The lower carrier concentrations in the doped ZnO in comparison with that of the undoped ZnO film could be due to the charge compensation with deep acceptors. The Arrhenius plots of free electron concentration from the doped ZnO films clearly showed double thermal activations of
the carriers as shown in Figs. 4.2(a) and 4.2(b). The data were fitted using the following equation to estimate the activation energy ($E_0$) in the two different temperature regions:

$$n(T) = n_0 \exp\left(\frac{E_0}{k_BT}\right)$$  \hspace{1cm} (4.1)

where $n(T)$ and $n_0$ are the electron concentration at temperatures $T$ and 0 K, respectively, and $k_B$ is the Boltzman constant. For region-I covering the temperature range from 80 to ~500 K, the thermal activation has a small activation energy ($E_{01}$) of about $0.04 \pm 0.01$ eV in the P- and As-doped ZnO films. For region-II covering the temperature range from ~500 to 800 K, the thermal activation has a larger activation energy ($E_{02}$) of about $0.85 \pm 0.03$ and $0.82 \pm 0.05$ eV for the P- and As-doped ZnO thin films, respectively.
Figure 4.3 shows the variation of mobility ($\mu$) with temperature ($T$) in the temperature range 80 to 800 K from the Hall effect measurements performed on undoped P-, and As-doped ZnO thin films. It is interesting to note that in both doped samples, mobility increases with increasing temperature. The mobility of the P-doped ZnO sample has slightly higher values for all temperatures compared to As-doped but mostly less than 1 cm$^2$/Vs. The increase in mobility with temperature and the low values of mobility indicate that the carrier scattering in the temperature range is dominated by ionized impurities as expected form the heavily doped samples [85]. For undoped sample, the mobility is within 28-34 cm$^2$/Vs.
Fig. 4.4. Low temperature PL spectra measured at 11 K of (a) P-doped ZnO thin film compared with an undoped ZnO sample, and (b) As-doped ZnO thin film. Inset is the PL spectra in the energy range of 2.0-2.8 eV comparing the impurity transitions of undoped, P-doped, and As-doped ZnO samples.
In order to determine the energy levels associated with the thermal activation processes observed in the Hall Effect measurements, we performed low temperature PL measurements. This part was done at Youngstown State University. Figure 4.4(a) shows normalized PL spectra of the P-doped ZnO sample along with that of the undoped ZnO measured at 11 K. The intensity from the undoped sample is about 25 times more than that from the P-doped sample, which correlates with the higher crystalline quality of the undoped ZnO sample as also revealed by the XRD data shown in Fig. 4.1. The undoped sample has a dominant emission peak at 3.362 eV, which is typically assigned to emission from donor bound excitons (D\textsuperscript{0}X) transitions and is consistent with the n-type conductivity of the sample [26, 86]. The identity of donor responsible for this transition is still debatable. In the literature, the emission line that appears at 3.3628 eV at cryogenic temperatures is labeled as I\textsubscript{4} and the donor responsible for this line is identified to be H, with a binding energy of about 0.046 eV. It was first predicted by first-principles calculations and later experimentally verified that interstitial hydrogen acts as a shallow donor in ZnO [87, 88]. On the other hand, the line that appears at 3.3608 eV, labeled I\textsubscript{6}, is attributed to Al donor, with a higher binding energy [26, 86, 89]. As shown in Fig.4.4, the PL spectrum of P- and As-doped ZnO also have an emission peak at 3.362 eV arising from the D\textsuperscript{0}X transition. Thus, one possibility of the small activation energy obtained in the doped samples in the temperature region-I with thermal activation energy of 0.04 eV could be related to the activation of the shallow donor like hydrogen [26]. First-principles pseudopotential calculation performed by Lee et al. for P-doped ZnO indicated that P\textsubscript{Zn} could act as shallow donor [48]. So, another possible donor responsible for the thermal activation in temperature region-I with activation energy of 0.04 eV could be X\textsubscript{Zn} (X=P or As).
Additionally, the PL spectrum in Fig.4.4 (a) shows that the P-doped sample has emission peaks at 3.311, 3.242, and 3.169 eV. The emission peak at 3.311 eV in P-doped ZnO could be due to transition of a free conduction band electron to a hole bound to a neutral acceptor state (FA), while the emission peak at 3.242 eV is due to a donor to acceptor pair (DAP) transition [86, 90]. The weak emission peak at 3.169 eV is possibly an LO-phonon replica of the DAP transition since the LO-phonon in ZnO is about 73 meV [91]. Similarly, the PL emission peaks observed in the As-doped sample at 3.327, 3.260, and 3.187 eV, which are slightly blue shifted compared to P-doped ZnO as shown in Fig. 4.8(b), are assigned to FA transitions, DAP transitions, and LO-phonon replica of the DAP, respectively. In the inset of Fig. 4.8(b), we show the PL spectra of the undoped, P-doped, and As-doped samples measured at 11 K and covering the spectral range from 2.0 to 2.8 eV with the normalized PL intensity plotted in log scale. As can be seen from this inset, the defect luminescence from the undoped ZnO sample has a peak at around 2.42 eV, while that from the doped samples are blue-shifted and appearing at around 2.51 and 2.56 eV for the P-doped and As-doped films, respectively. The blue shift in the spectral position of this defect luminescence was also noted by Kwon et al., in the P-doped ZnO films [92]. The larger impurity emission intensities from the doped samples could be due to increased number of impurities related to this band compared to undoped ZnO sample. The broad impurity band in ZnO (~2.3–2.6 eV) has been attributed to several native defects including zinc vacancy (V_{Zn}) and oxygen vacancy (V_{O}) [92-96].
Fig. 4.5. The power dependent PL spectra of P-doped ZnO measured at 11K showing emission peaks related to the donor-bound exciton (D\textsuperscript{0}X), free electron to FA, and DAP transitions in (a) P-doped ZnO and (b) As-doped ZnO samples.
In order to further confirm the assignment of the PL emission peaks, PL emissions from the doped samples were collected at varying laser excitation power at 11 K. Figure 4.5(a) is the PL result for the P-doped ZnO sample obtained using different laser excitation powers. The peak position at 3.311 eV is independent of the laser power density, indicating a band related transition whereas the peak at 3.242 eV shifts to the higher energy side with increasing laser power. The blue shift of the 3.242 eV peak with increasing excitation power clearly confirms the transition to be a DAP, as has been identified by other researchers [86]. Figure 4.5 (b) shows the power dependent PL result for As-doped ZnO sample. Similar results were obtained for the As-doped ZnO samples confirming the peaks at 3.327 and 3.260 eV as band related transition and DAP, respectively.

The emission band with a peak appearing around 3.31–3.32 eV has been observed in films intentionally doped with group V elements as well as in undoped ZnO bulk samples and in ZnO nanostructures [42, 97-100]. It has been interpreted to arise from several different origins including surface effects, optical phonon replica of the free exciton (FX), or to the presence of acceptor impurities such as a donor acceptor pair, a free to bound transition or an exciton bound to a defect, etc [101-105]. The transition was interpreted as acceptor-bound excitons (A°X) in P-doped and nitrogen doped ZnO [98, 106]. From a detailed study conducted on undoped ZnO films, Schirra et al. determined that this emission line is due to transition of a free conduction band electron to a hole bound to a FA and emitted exclusively from basal plane stacking faults in which the acceptors reside [101]. In the case of intentionally doped ZnO films, it is suggested that the presence of group V elements leads to an increased number of stacking faults at which high-density acceptor states are located [105, 107]. In yet another study of different ZnO samples, Tainoff et al. concluded that this luminescence peak is a result of competition between the
optical phonon replica of the free exciton (FX-1LO) and the FA transition. They further concluded that this peak is not significantly influenced by a huge surface to volume ratio of the ZnO material [105]. On the basis of first principles calculation, the acceptor has been attributed to the \((\text{X}_{\text{Zn}}-2\text{V}_{\text{Zn}})^{1-}\) complex for samples grown under oxygen-rich condition [78, 93, 108-111]. In this case, the FA transition is believed to be due to the transition of free electron to the \((\text{X}_{\text{Zn}}-2\text{V}_{\text{Zn}})^{1-}\) complex. Thus, the origin of an emission peak at around 3.31–3.32 eV is still in debate.

Donors associated to DAP transitions in the PL spectra of n-type materials are usually in shallow energy states therefore they can easily be activated with relatively small thermal energy. For this reason, the DAP transition peaks observed in the low temperature PL spectra of the P- and As-doped samples could be related to the transition of electrons in the shallow donor levels observed from the first thermal activation \((E_{01})\) to the shallow acceptor level possibly related to stacking fault or \((\text{X}_{\text{Zn}}-2\text{V}_{\text{Zn}})^{1-}\). The second thermal activation with larger activation energy (~0.8 eV) obtained from the temperature dependent Hall effect measurements is associated with a deep donor level. We have tentatively assigned the deep donor related to the large activation energy to \(V_\text{O}\). Although \(V_\text{O}\) was previously thought to be a shallow donor responsible for n-type conductivity in ZnO, recent theoretical calculations performed on defects of ZnO showed that \(V_\text{O}\) is a deep donor [48, 112, 113]. Based on these calculations, the \(\varepsilon(2+/0)\) transition level of \(V_\text{O}\) has been found to be in the range of ~0.6–1 eV below the conduction band and this range covers the activation energy of 0.8 eV that we obtained from the temperature dependent Hall effect measurements.

Calculation of X-doped ZnO also showed that \((\text{X}_{\text{Zn}}-2\text{V}_{\text{Zn}})\) complex has low formation energy [48, 78]. In a situation, where the Fermi level is near the conduction band, formation of \((\text{X}_{\text{Zn}}-2\text{V}_{\text{Zn}})\) complex with 3-charge state is possible. The \((\text{X}_{\text{Zn}}-2\text{V}_{\text{Zn}})^{3-}\) complex is a deep acceptor
that captures 3 electrons. The existence of deep impurity acceptors reduces the concentration of free electrons since they act as compensating centers. The lower carrier concentrations in the doped ZnO samples could be due to the charge compensation with \((X_{\text{Zn}}-2V_{\text{Zn}})\) complex. Although P and As substituting O, which have ionization energy above 1 eV, are other possibilities of compensation centers because of the large formation energies they are less likely to form [78, 114]. The first-principles calculation also predicted that \((X_{\text{Zn}}-2V_{\text{Zn}})^{1-}\) complex could be shallow acceptor for producing p-type conductivity in ZnO. Existence of \((X_{\text{Zn}}-2V_{\text{Zn}})^{1-}\) complex is possible when the Fermi level is near the valence band. However, it is a challenge to lower the Fermi level due to the large background electron concentration originated from intrinsic defects. Developing a method to produce ZnO with low background electron concentration is needed in an effort to achieve p-type conductive ZnO.

In summary, we have performed temperature dependent Hall Effect measurements between 80 and 800 K for phosphorus (P) and arsenic (As) doped ZnO thin films grown on c-plane sapphire substrate by RF magnetron sputtering. These samples exhibited n-type conductivity throughout the temperature range with carrier concentration of \(3.85 \times 10^{16} \text{ cm}^{-3}\) and \(3.65 \times 10^{17} \text{ cm}^{-3}\) for P-doped and As-doped ZnO films, respectively at room temperature. The Arrhenius plots of free electron concentration of those doped samples showed double thermal activation processes with a small activation energy of about 0.04 eV due to shallow donors and a large activation energy of about 0.8 eV due to deep donors. The deep donor level could be related to oxygen vacancy.
4.1b ZnO film with reduced background electron concentration for buffer layer

The quality of ZnO film depends on many factors including the substrate on which it is deposited. Homoepitaxy would be the ideal method as it would yield no mismatch. However, the high cost of bulk ZnO materials as well as the defects in untreated bulk substrates make this option a difficult choice [115]. The immediate problem with heteroepitaxy is the lattice and thermal mismatch, which introduce defects in the films. Sapphire is commonly used as the substrate for ZnO film due to its relatively low cost as well as its transparency in the UV range. Sapphire is also presently used in commercial growth of GaN based optoelectric device fabrication. The lattice mismatch between ZnO and sapphire is 18.4%, while the thermal expansion coefficient of ZnO is $2.9 \times 10^{-6}$ K$^{-1}$, compared with $7.3 \times 10^{-6}$ K$^{-1}$ for sapphire [5]. Furthermore, it is possible for Al to outdiffuse from the sapphire into the ZnO film, resulting in Al donor incorporation and a high background electron concentration, which is undesirable for p-type growth attempts. To solve these problems, a suitable buffer layer with very low background concentration is required. In this work, we investigated the effect of growth temperature on the background electron concentration along with optical properties.

<table>
<thead>
<tr>
<th>Dep. Temp (°C)</th>
<th>n (cm$^{-3}$)</th>
<th>μ (cm$^2$/Vs)</th>
<th>ρ (cm)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>$6.3 \times 10^{18}$</td>
<td>28</td>
<td>0.037</td>
<td>n</td>
</tr>
<tr>
<td>500</td>
<td>$1.5 \times 10^{17}$</td>
<td>4.2</td>
<td>10</td>
<td>n</td>
</tr>
<tr>
<td>700</td>
<td>$3.4 \times 10^{16}$</td>
<td>4.0</td>
<td>47</td>
<td>n</td>
</tr>
<tr>
<td>900</td>
<td>$9.9 \times 10^{15}$</td>
<td>2.7</td>
<td>409</td>
<td>n</td>
</tr>
</tbody>
</table>
The undoped ZnO thin films were deposited on sapphire substrates by rf magnetron sputtering with different substrate temperatures. Table 4.1 shows the room-temperature Hall effect measurement data of the undoped ZnO films deposited at different substrate temperatures. From the table we can see, as the temperature increased, the resistivity of the film increases and the background electron concentration decreases. Higher substrate temperatures lead to reduction of native defects in the ZnO material which are responsible for the background electron concentration. The film deposited at 900 °C has the lowest electron concentration of \(~9.9 \times 10^{15}\) cm\(^{-3}\), which is more than 2 orders lower than the sample grown at 300 °C.

![Photoluminescence spectra](image)

Fig. 4.6. Low-temperature photoluminescence spectra from undoped ZnO films deposited at different substrate temperatures.
In order to explore the reduction of background electron concentration with increased substrate temperature, we performed low temperature PL measurements (12 K) of undoped ZnO thin films deposited at different temperatures and showed in Fig 4.6. This work is done at Youngstown State University. From spectra we can see four emission peaks at 3.361 eV, 3.317 eV, 3.218 eV, and 3.115 eV, respectively. The dominant band edge peak at 3.361 eV is typically assigned to emission from neutral donor-bound exciton (D°X) transition. The intensity of this peak is lowest for the film deposited at 20 °C and highest at 700 °C. The peak at 3.317 eV is more intense for the film deposited at 20 °C. It decreases with increasing substrate temperature, with values of ~1200%, 46%, 8%, 3%, and 5% for the films deposited at 20 °C, 300 °C, 500 °C, 700 °C, and 900 °C, respectively. This peak has been observed in undoped ZnO bulk samples, in ZnO nanostructures, and in films, especially those intentionally doped with group V elements [42, 89, 99, 100]. It has been interpreted as arising from several different origins, including donor-valence band transitions, electron-hole recombination from donor-acceptor pairs, electron-acceptor transitions, recombination of excitons bound to deep neutral acceptors, two-electron satellites of donor-bound excitons, etc [101, 102, 104, 116]. From a detailed study conducted on undoped ZnO films, Schirra et al. as well as Yang et al. determined that this emission line is due to transition of a free conduction-band electron to a hole bound to a neutral acceptor state (e, A°) and emitted exclusively from basal-plane stacking faults in which the acceptors reside [101, 116].

Figure 4.7 (a) and (b) show cross-sectional bright field TEM images of films deposited at 300 and 700 °C, respectively. From the images we can see, the film deposited at 300 °C has more stacking faults compared with the film deposited at 700 °C. This seems to support our PL results that the emission peak at 3.317 eV could possibly be the (e, A°) arising from stacking faults. Luminescence from stacking faults has also been observed in other materials such as GaN [103].
Fig. 4.7. Cross-sectional TEM images of undoped ZnO films deposited at (a) 300 °C (b) 700 °C.
Figure 4.8 shows an Arrhenius plot of the free electron concentration ($n$) of the undoped ZnO film deposited at 900 °C obtained from the temperature-dependent Hall measurements. The linear fit of this plot yields an activation energy of $0.25 \pm 0.02$ eV. A similar plot for the unannealed sample also yields the same value of activation energy, indicating that annealing does not significantly alter carrier concentration of the sample. The activation energy could be related to the luminescence peak at 3.218 eV, originating from a deep donor. Note that the difference between $E_a = 3.437$ eV for ZnO and this deep donor level (3.218 eV) is 0.22 eV, which is close to the value we obtained from the Hall measurements. Based on these results, we believe that the DAP emission peak at 3.115 eV is due to the transition from the deep donor (related to the 3.22 eV emission) to the acceptor (related to the 3.317 eV).
Figure 4.9 shows the XRD data of the annealed and unannealed undoped ZnO films deposited at 900 °C. By comparing the intensities for the ZnO (002) peak we can see there is no significant alteration of the film by post deposition annealing.

In conclusion, higher substrate temperatures lead to reduction of native defects in the ZnO material, which are responsible for the background electron concentration. The film deposited at 900 °C has the lowest electron concentration of $\sim 9.9 \times 10^{15}$ cm$^{-3}$ and apparently a greatly reduced amount of stacking faults, as discussed above. Reducing the background electron concentration is the first requirement to achieve p-type conductivity. Based on these observations, we determined a substrate temperature of 900 °C is the optimum condition for depositing ZnO buffer layers.
4.2 TEM investigation of threading dislocation in Aluminum Nitride thin films

Aluminum nitride (AlN) that has a direct band gap ~ 6.1 eV, has emerged as a promising deep ultra violet (DUV) material with the demonstration of AlN-based light emitting diode (LED) and photo detector [117, 118]. AlN possesses outstanding properties such as high temperature stability, hardness and high thermal conductivity that makes it a good candidate for high temperature/power/radiation devices [119]. Because of the piezoelectric property, it has also application in surface acoustic wave (SAW) devices [120]. Due to the growth of AlN epilayers on foreign substrates such as sapphire, it suffers from a high density of threading dislocation (TD). AlN with low defects and dislocation density is sought to improve the device performance as well as to design advanced devices such as avalanche photodiodes. High quality, low dislocation density AlN/sapphire can also be used as templates to grow nitride based device structures. Thus, the characterization of threading dislocations and techniques to reduce the threading dislocations are crucial. We reported structural analysis of AlN epilayers grown by the three step method by metal organic chemical vapor deposition (MOCVD). The samples were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), DUV photoluminescence (PL), and transmission electron microscopy (TEM).

The AlN samples were grown on c-plane sapphire substrates by MOCVD at Kansas State University. The schematic layer structure of AlN epilayers grown by three-step method is shown in the inset of Fig 4.10. An intermediate AlN layer was inserted between the buffer and high temperature AlN epilayers. This additional layer is a key difference compared to the conventional two-step method. The growth process started with the thermal cleaning of the substrate in hydrogen ambience prior to the growth in a horizontal reactor. In an optimized
growth process, the growth was initiated with a thin AlN buffer layer at 950 °C. An intermediate AlN of thickness ~120 nm was then grown at 1100 °C. The top high temperature layer was grown at 135 °C which was limited by the system. Growth pressure throughout the process was 40 Torr. Trimethylaluminum (TMAI) and blue ammonia were used as the aluminum (NH₃) and nitrogen sources, respectively. Hydrogen was used as the carrier gas. The flow rates for TMAI and NH₃ were about 20 mL/min and 2 L/min, respectively. Growth rate of about 1.2 mm/h was obtained under these conditions. AlN epilayers with thickness ranging from 1 to 4 mm were grown without cracks. A typical *in situ* optical reflectance curve of AlN epilayer grown by three-step method is shown in Fig. 4.10.

**Fig 4.10.** A typical *in situ* optical reflection curve during the growth of AlN epilayer by three-step method. Inset: Schematic layer structure of three-step growth method. An intermediate layer is inserted between the buffer and high temperature layer.
A small signal can be seen during the buffer growth. Significant reflectance is observed during the growth of intermediate layer and high temperature layer. The reflectivity is higher during the growth of the high temperature layer than that of the intermediate layer. Average reflectance intensity is almost constant during the high temperature layer growth indicating a smooth surface. The reflection curve is different from a typical GaN growth process in which the reflectivity drops to its minimum in the beginning of high temperature growth and it recovers as thickness increases [121, 122]. In the AlN growth, we found that if the average reflectance intensity dropped, it is very difficult to recover the reflectance signal which ultimately leads to a rough surface. An AlN buffer does not smear by annealing while ramping up the growth temperature as in GaN. Growth of AlN epilayer on sapphire substrates using the two-step method often leads to a rough surface. With the insertion of intermediate layer between the buffer and high temperature layer, a smooth surface is routinely obtained.

Fig. 4.11. (a) PL spectrum of AlN epilayers grown on sapphire substrates measured at room temperature. (b). AFM image taken in 1 mm × 1 mm scan size. RMS surface roughness is about 0.5 nm.
Atomic force microscopy images of AlN epilayers showed very smooth surface. Figure 4.11(b) shows an AFM image with root mean square roughness about 0.5 nm in 1 μm × 1 μm scan size. With the insertion of intermediate layer, the band edge (impurity) emission intensity in PL measurement has significantly increased (decreased) in our samples. A typical room temperature PL spectrum of AlN epilayer grown by the three-step method is shown in Fig. 4.11(a). The PL measurement was also done at Kansas State University. The samples have a strong band edge emission peak at 5.98 eV with very low impurity emissions at room temperature, ensuring excellent optical quality of the material. At 10 K, the band edge emission peak is at 6.06 eV. Detailed optical properties of AlN epilayers grown on sapphire substrates are also reported elsewhere [118].

Fig. 4.12. (a) Bright field plan view TEM images of AlN epilayer taken with g = 11\bar{2}0 and tilted at 18° from [0001] zone axis and.(b) Plan view diffraction pattern.

In order to investigate the growth process of AlN epilayers grown by the three-step method, TEM samples for both cross-section and plan view TEM imaging were prepared. The TEM samples were prepared by using Fischione ultrasonic disk cutter, mechanical grinding, and
polishing followed by dimple grinding, and Ar+ ion milling. The TEM characterization was
carried out using a JEOL 2010 TEM system operating at 200 kV. Figure 4.12 shows a typical
bright field plan view TEM image of an AlN epilayer taken with \( g = 11\bar{2}0 \) with the specimen
tilted at \( \sim 18^\circ \) from [0001] zone axis. All three types of dislocations – edge, screw, and mixed can
be detected by tilting the sample in the plan view image using \( g = 11\bar{2}0 \) [123]. Here it should be
noted that the dominant threading dislocations observed are edge type. The screw and the mixed
dislocations were seldom observed. Based on the plan view images the average total dislocation
density is \( \sim 2\times10^9 \) cm\(^{-2}\). Our results agree well with the dislocation densities estimated from the
analysis of XRD rocking curves [124].

Figure 4.13(a) shows a representative bright field cross section TEM image of an AlN
epilayer sample. The image was taken near zone axis \([2\bar{1}10]\). Threading dislocations are
generated at the interface of AlN and sapphire. We did not observe distinct interfaces of the
intermediate layer and high temperature layer. The dotted line in the Fig. 4.13(a) indicates the
region where the growth of HT-AlN starts. In the beginning of HT-AlN growth, the threading
dislocations start bending and annihilating. From the TEM images, we observed that most of the
threading dislocations are annihilated within the thickness of \( \sim 300 \) nm. Figure 4.13(b) and (c)
shows the dark field cross-section images taken with \( g = 0001 \) and \( 1\bar{1}00 \), respectively. Under the
two-beam condition \( (g\cdot b) \), screw and edge type threading dislocations with Burgers vectors \( b = <0002> \) and \( b = 1/3<1\bar{2}10> \) are visible with \( g = 0001 \) and \( 1\bar{1}00 \), respectively [125]. Although
dislocations can be seen in the beginning of the growth, they annihilate, leaving the screw type
threading dislocation almost clean in the HT-AlN region as shown in Fig. 4.13(b). Edge type
threading dislocations are dominant as shown in Fig. 4.13(c). This is consistent with the plan
view TEM images with dominant edge type threading dislocations. The edge type threading
Fig. 4.13. (a) Bright field cross-section view TEM image of AlN epilayer taken near zone axis [2\bar{1}0]. (b) Dark field cross-section TEM image under tow beam condition with $g = 0001$. (c) Dark field cross-section TEM image under two beam condition with $g = 1\bar{1}00$. (d) Cross-section diffraction pattern.
dislocations are annihilated as the thickness increased forming loops. However, some dislocations propagate vertically.

Fig 4.14. High resolution cross-section TEM image taken near zone axis [2\bar{1}0] near the interface of AlN and sapphire substrate.

Figure 4.14 shows a high resolution TEM image taken near zone [2\bar{1}0] near the interface of AlN and sapphire substrate. At the interface of AlN and sapphire, the contrast modulations due to the strain near misfit dislocations (MD) can be observed. It is believed that the formation of periodic arrays of MD is due to the slip causing strain relaxation in the region without threading dislocations [126]. Some regions the strain is relaxed by generating threading dislocations. In the high resolution cross-section image, well-aligned basal planes can be clearly observed indicating very low staking fault. The reduced staking fault is consistent with the small FWHM of XRD rocking curve measured at symmetric peak at (0002). Screw dislocations are
normally generated from the stacking faults tilting the symmetric planes which broaden the FWHM of rocking curves measured at symmetric planes such as (0002) plane [127].

The AlN structure has the highest stacking fault energy among all nitride-based wurtize materials [128]. We found that AlN epilayers grown with buffer temperature around 950 °C have much smaller FWHM of XRD rocking curve measured at symmetric peak at (0002) compared to the samples grown with buffer temperature around 550 °C (GaN reference). Similar results were reported for AlN directly grown on sapphire substrate using high temperature growth condition [129]. However, the FWHM of rocking curves measured at asymmetric plane [1012] are normally more than one order in magnitude larger than the FWHM measured at symmetric plane (0002). FWHM of rocking curves measured at asymmetric planes such as [1012] plane are related to the density of edge dislocations [127]. AlN epilayers grown on sapphire substrate thus, suffer from the large density of edge dislocations. Edge type threading dislocations are generated mainly from MD due to the intrinsic lattice mismatch of AlN with sapphire. Reducing edge type threading dislocations is a major challenge in AlN growth. Edge type threading dislocations can be reduced by annihilation by forming a loop with similar neighboring dislocations having opposite Burger vectors [130].

We believe that three-dimensional island growth dominates in buffer and two-dimensional growth dominates in HT-AlN. The transition from three-dimensional to two-dimensional growth occurs during the growth of I-AlN. This layer promotes bending of the propagation and annihilation of threading dislocations during the growth. We found that the thicknesses of the buffer and I-AlN layers are critical for reducing FWHM of rocking curves measured at (1012) planes and hence edge dislocation density. Threading dislocations with large deviation angles annihilated faster whereas threading dislocations with small deviation
angles annihilate forming large loops as thickness was increased. The use of high temperature buffers and insertion of I-AlN promote bending of threading dislocations in various angles (as high as 45° from the growth direction), and releasing the strain induced by lattice and thermal mismatch. This could be the reason that we could grow thick AlN epilayers up to 4mm without any cracks. Threading dislocation density could be further reduced by using higher growth temperature for HT-AlN layer [131]. The three-step method could be transferred to grow AlN epilayers on other substrates and other growth techniques.

In conclusion, we have investigated AlN epilayers grown by three step growth method by MOCVD. From the cross section view images, the threading dislocations are significantly diminished within 300 nm thickness. Screw dislocations are reduced by using high temperature buffer. Edge type dislocations are reduced by inserting an intermediate layer between the buffer and high temperature AlN layers. From plan view TEM images, the average threading density is \( \sim 2.7 \times 10^9 \text{ cm}^{-2} \), which agrees well with the dislocation density estimated by XRD rocking curve analysis. The threading dislocations further decreases with increasing the thickness. Thus, a thick AlN/sapphire template could be used to grow DUV optoelectronic device structures for improved performance.
4.3 Electro-optical effects and temperature-dependent electrical properties of LuFe$_2$O$_4$ thin films

Recently, LuFe$_2$O$_4$ (LFO) compound has attracted extensive research interest due to its unique multiferroic properties [6, 59]. LFO belongs to the RFe$_2$O$_4$ family (R=Y, Dy to Lu) which has a layered rhombohedral structure with space group R3m. RFe$_2$O$_4$ is considered a spin- and charge-frustrated system of triangular lattices, occupied by the mixed valence states of Fe with an equal number of Fe$^{2+}$ and Fe$^{3+}$ ions. While ferroelectricity in LFO is believed to be induced by the Fe$^{2+}$ - Fe$^{3+}$ charge ordering (CO) mechanism, the magnetism is induced by the spin ordering of the Fe$^{2+}$ and Fe$^{3+}$ ions in the frustrated lattice [6]. Because of unique geometrical and charge frustrations, LFO undergoes several charge and magnetic transitions: three-dimensional (3D) CO transition at ~330 K, two dimensional (2D) CO transition at ~ 500 K, a glassy transition at ~ 80 K, a first order magnetic transition at ~170 K, and a ferromagnetic transition at ~240 K [57-59, 61].

Although LFO has been known as a high temperature (T ~ 240 K) multiferroic for some time, its ferroelectricity and high dielectric properties have been controversial in recent years. In particular, ferroelectricity and high dielectric properties of LFO have been linked to the Maxwell–Wagner effects at the contact interfaces. The authors of the papers in Refs [132] argue that ferroelectric and dielectric measurements on LFO samples could very well be influenced by the space charge effects at the metal–insulator interfaces, thus associating the ferroelectricity of LFO with the extrinsic effects rather than the intrinsic charge-ordering mechanism. In order to further explore and understand ferroelectricity and multiferroic properties of LFO, a detailed systematic study is essential.
Various aspects of the properties of LFO have been reported in the last few years, such as the giant and tunable dielectric properties of single crystal LFO [6], low frequency magneto-electric effects [133], the sensitivity of lattice vibration to the charge, magnetic and structural transitions in single crystal [134], electric-field induced magnetization [135], and structural properties [136]. Li and Cao et al. have reported nonlinear electrical transport properties of bulk LFO samples, and they associate the nonlinear behavior with the electric field induce changes of the CO state in LFO [137]. Despite extensive studies on single crystal LFO, the properties of LFO thin films have rarely been investigated. Transport properties of thin films, which are important for their device applications, have not been reported so far. In our previous studies, we investigated the spin–charge–orbital coupling in LFO thin films using temperature dependent optical absorption studies [56]. Because of the strong spin–charge–orbital coupling in the LFO thin films, electrical transport properties of the thin films are expected to be interesting for the development of LFO based multifunctional devices.

The LFO thin films samples in investigation were prepared at SUNY Buffalo State College. We first mixed Lu₂O₃ and Fe₂O₃ powders in a stoichiometric ratio. Subsequently, we ground and heated the mixture at 1000 °C. The mixture was then pressed into pellets and sintered at 1100 °C. Before starting deposition, we slowly heated the target pellet to its melting point. We deposited 300 ± 30 nm LFO films on (001) sapphire at 750 °C by electron beam deposition. During the deposition process, the base pressure was 2×10⁻⁶ Torr and the oxygen partial pressure was 4×10⁻⁴ Torr. The substrates were preheated at 600 °C for 30 min, and the film deposition rate was maintained at 50 Å/min. All the thin films were annealed at 600 °C in the mixture of oxygen and air for about 3 h.
Fig 4.15. (a) An SEM image of the surface of a 300 nm LFO thin film, grown on (001) sapphire substrate, (b) an AFM image of the LFO thin film taken in a 2 µm × 2 µm scan size by tapping mode and (c) the X-ray diffraction pattern of the LFO thin film grown on sapphire.
Figure 4.15(a) shows the SEM image of the surface of an LFO sample imaged by Hitachi TM-1000 under operating voltage of 15 kV. For the most part, surface is smooth, as shown in Fig. 4.15(a). However few pits and grains like features can be seen in a few regions on the surface. A typical AFM image taken by Digital Instrument's multimode AFM is shown in Fig. 4.15(b) by using tapping mode. The surface roughness is ~5 nm in a 2 μm×2 μm scan size. XRD pattern of the LFO thin films on sapphire substrates, shown in Fig. 4.15(c), was scanned by Philips X'Pert-MPD system in θ–2θ mode. The XRD pattern has two peaks showing (006) and (107) planes as preferred planes.

Fig. 4.16 Representative absorption spectra of the LFO thin film on sapphire at 78 and 300 K, extracted from the transmittance data. The arrows indicate the electronic transitions. The inset shows the Fe$^{2+}$ (d$^6$) crystal-field splitting scheme.
Figure 4.16 shows representative absorption spectra of LFO film on (001) sapphire as a function of photon energy at 78 and 300 K. The absorption coefficients ($\alpha$) were extracted from the transmittance data using $\alpha = -\ln (T)/d$, where $T$ is the transmittance and $d$ is the film thickness. The LFO absorption spectra show an insulating character with several electronic transitions in the energy range of 1–6 eV. We assigned the observed electronic transitions in the LFO thin film based on the single crystal optical data [63] and the first principle calculations [66, 138]. The first two transitions centered at 1.60 and 2.40 eV are assigned to Fe$^{2+}$ d to d on-site transitions. Weak oscillator strengths of these two transitions are consistent with the fact that these Fe$^{2+}$ d to d on-site transitions are normally parity forbidden. However, the theoretical calculations report a strong hybridization between O 2p and Fe 3d states in the building block FeO$_5$ [66, 138], relaxing the selection rules for the d to d electronic transitions in LFO. In addition, the local structural distortion and the spin-lattice coupling, as reported by Xu et al.[139], in this system further relax the selection rules. Similarly, a broad and strong peak centered at 3.30 eV is attributed to O 2p to Fe 3d charge transfer electronic transition. The electronic peaks at energies greater than 3.30 eV arise from O 2p to Fe 3d, Lu 6s, and Lu 5d charge-transfer transitions.

The inset in Fig. 4.16 shows the crystal-field splitting of the Fe$^{2+}$ 3d orbitals in a FeO$_5$ trigonal bipyramidal environment. The five-coordinated oxygen ligand fields in FeO$_5$ split the originally degenerated Fe d states into three groups: (dxy, dx$^2$-y$^2$), (dxz, dyz), and dz$^2$. Since the Fe$^{2+}$ (d$^6$) ions are in a high spin state, all five d-states are singly occupied except the lowest one which is doubly occupied by two electrons with antiparallel spins. Therefore, with the given electronic configuration, there are two possible spin-allowed electronic transitions in Fe$^{2+}$ (d$^6$): dxy → (dxz, dyz) and dxy → dz$^2$. 
Fig. 4.17. Electro-optical effects in applied dc voltages up to 200 V, and the absorption coefficient of the LFO films in the photon energy range of 1-2.75 eV at (a) 78 K and (b) 170 K.
Figure 4.17(a) and (b) shows the optical absorption spectrum and electro-optical effects of the LFO thin film in the photon energy range of 1 – 2.75 eV at 78 and 170 K, respectively. To investigate the effect of the applied fields on the optical properties, we measured the absorption coefficient ($\alpha$) of the LFO thin film in applied dc voltages up to 200 V. The voltages were applied to the thin film through two copper wires, approximately 5 mm apart. The wires were attached to the film surface using silver paste. Interestingly, the LFO thin film displays the electric field-induced changes in the absorption spectra at low temperatures. In Fig. 4.17(a) and (b), we show the electro-optical effects, i.e., the ratio of the relative change of $\alpha$ in applied voltages [$\alpha(V) - \alpha(0)$] to $\alpha$ in the zero voltage $\alpha(0)$: $[\alpha(V) - \alpha(0)]/\alpha(0)$, at 78 and 170 K, respectively. The observed high-energy electro-optical effects are positive and negative depending on the photon energy, and these effects are reproducible. As shown, the field-induced changes are found to be stronger around the rising slope of the 1.60 eV peak. Similarly, these effects are stronger at low temperatures, which vary from +4% to −5% at 78 K, and from +3.5% to −1.5% at 170 K. At temperatures above 240 K, we observed very small (<1%) electro-optical effects. Stronger electric-field-induced effects below the magnetic transition at 240 K suggest that LFO has a strong spin–charge coupling.

To understand the relationship between the electro-optical effects and applied voltages, we measured the size of the signals for the photon energy of 1.20 eV at 78 K and 1.40 eV at 170 K, respectively, where the effects are the strongest. The inset in Fig. 4.17(b) shows that the electro-optical response varies approximately linearly with the applied voltages, indicating a linear electro-optical effect in LFO. In addition, the electro-optical data at 78 K display the signal oscillation as a function of photon energy with the periodicity of ~0.25 eV, which may be linked to the electric field dependent changes in the surface thickness of the sample. We note that these
electro-optical measurements are not affected by the contact effects at all, and thus, they are intrinsic property of the LFO thin films. There has been a recent report of the low-energy (~60 meV) electro-optical effects of single crystal LFO, and the effects are believed to be associated with the correlated phases of LFO [140]. The electro-optical effects in the perovskite-type ferroelectrics, such as BaTiO3, KNbO3, and LiNbO3, are well studied in literature and the effects are induced by the relative displacements of the central metal ion in the TiO6 or NbO6 octahedron in applied electric fields [141-143]. The electro-optical effects in LFO, however, are driven by a different mechanism. The cause of the high-energy electro-optical in the LFO thin film can be interpreted by considering the direct coupling process between Fe d electrons in the CO state and applied electric fields. In particular, the applied fields directly affect the d-electrons in the Fe sites, and thus the spin-allowed Fe2+ d to d electronic transitions at 1.6 eV display the observed electro-optical effects. Further, the electro-optical effects are stronger below the magnetic transition which suggests that the field-induced changes could be mediated by the spin–charge coupling process. There is a possibility that a small part of the effects could be associated with the heating effect. However, the temperature-induced changes are expected to be small and spread over the whole spectrum range, as reported in Reference [140]. The fact that the measured high-energy electro-optical effects are localized around the 1.6 eV electronic transition means that the effects are indeed field-induced changes associated with the CO state rather than the temperature-induced effects.

The Hall-effect measurement system was used to measure the basic transport properties of the LFO thin films. At 500 K, resistivity, mobility and carrier concentration of the sample were measured to be ~1400 $\Omega$·cm, 5 $\text{cm}^2/\text{V}·\text{s}$ and $8.9 \times 10^{14}$ $\text{cm}^{-3}$, respectively. Resistivity increases and mobility decreases upon cooling, a typical property of an insulator. It is interesting
to note that the majority charge carriers are holes in the LFO thin film at temperatures above 440 K. Thus, LFO behaves as a p-type semi-insulating material at high temperatures. The p-type character might be related to the 2D charge ordering of Fe$^{2+}$ and Fe$^{3+}$ ions in the triangular lattice. Based on the p-type nature of the LFO thin films, the charge involved in the polar arrangement could be dominated by holes at high temperatures. Although a stoichiometric LFO has equal number of Fe$^{2+}$ and Fe$^{3+}$ ions [6], LFO could be either n-type or p-type if the numbers of Fe$^{2+}$ and Fe$^{3+}$ ions are not equal. For example, if the number of Fe$^{3+}$ ions is greater than the number of Fe$^{2+}$ ions in the lattice, then LFO behaves as a p-type insulator. The type of the majority carrier, however, could not be confirmed below 440 K as the two resistance parameters in the Van der Pauw measurements had unacceptable differences in their values. Such a difference between the parameters indicates an unsymmetrical electrical behavior of LFO, arising from a 3D CO transition at temperature ~330 K [62].

In order to investigate the temperature dependent electrical properties of the LFO thin film, we carried out V–I characteristic measurements using a linear four-probe method, as shown in the schematic circuit diagram in Fig. 4.18(a). In the four-probe method, the outer probes were used to apply current to the sample and the inner probes were used for voltage measurements, eliminating the possible contact effects. Voltage and current were measured simultaneously while sweeping the current from negative to positive and vice versa. Figure 4.19(b–d) shows the representative V–I curves for the polycrystalline LFO thin film at different temperatures.

In Fig. 4.18(b), the linear V–I characteristic was measured with the resistance value of around $0.9 \times 10^9 \Omega$ at 340 K. Similarly, we observed linear V–I curves at temperatures above 340 K (not shown here). On the other hand, as shown in Fig. 4.18(c, d), we observed a hysteresis effect in the V–I curves for increasing (red) and decreasing (blue) currents at temperatures below
Fig. 4.18. Representative V-I characteristics of a 300 nm LFO thin film at different temperatures. (a) Schematic of a linear four-probe VI measurement on a thin film sample, (b) a linear V-I relationship between current and voltage at 340 K, (c) the hysteresis effect in the V-I at curve for increasing and decreasing currents at 300 K, and (d) a strong hysteresis in the V-I curve at 80 K. The up-arrow (red) and down-arrow (blue) represent the increasing and decreasing current sweeps.
340 K, indicating that the hysteresis could be associated with the CO state. While the V–I characteristic stays symmetric, the hysteresis effect becomes stronger at low temperatures. The observed V–I hysteresis effects are reproducible on different LFO samples, and are very likely associated with the CO state of LFO. We note that the surface charge effects, also known as the Maxwell–Wagner effects, at the electrical contacts do not affect our data because these measurements were carried out using a linear four-probe method in the thin film surface of ~2 mm length. The surface charge effects become a big issue in the parallel-plate capacitance measurements in which ultrathin films (thickness <100 nm) are sandwiched between two metal electrodes. In such cases, the surface charge effects could dominate the dielectric and electrical transport properties of ultrathin films [144]. We note two reasons that the observed hysteresis in the V–I curves could be intrinsic property of LFO: (1) the V–I measurements are made on the sample surface (length ~2 mm) in linear four-probe geometry rather than in the capacitance geometry to eliminate the contact effects, and (2) measured resistance (~10^9 Ω) of the sample is consistent with the reported values for LFO [144, 145].

Next, we performed dynamic V–I measurements on the LFO thin films at temperatures ranging from ~240 to 400 K in order to evaluate the transient behavior of the voltage under current. Positive and negative current pulses of duration 100 s were applied to the sample in the interval of 100 s in a linear four-probe configuration. The voltage limit for the current source was set at 10 V to minimize the heating effects. In Fig. 4.19(b, c), we show representative transient behaviors in voltage signals under the applied current pulses [Fig. 4.19(a)] of the sample at temperatures 340 and 280 K, respectively. At 340 K [Fig. 4.19(b)], the measured voltage signal follows the applied current pulse, indicating a linear behavior of the material, which is consistent
Fig. 4.19. Transient behaviors in voltage signals of the LFO thin film at temperatures 340 and 280 K (b, c) under the applied current pulse (a). At low temperatures, the LFO thin film starts to exhibit nonlinear transient behaviors.
with the V–I measurement [Fig. 4.19(b)]. In Fig. 4.19(c), the nonlinear transient behavior starts to appear in the voltage data at 280 K. In particular, the voltage changes are peculiar when the direction of the applied current pulse changes. The low temperature responses below 240 K (not shown here) were, in general, similar to the 280 K data. We believe that the observed nonlinear transient behaviors are due to the interactions of the applied field with the CO state of LFO. Although it is possible that the heating effect could have partially affected the observed transient behaviors, our electro-optical data are consistent with our assumption that the observed nonlinearity is an intrinsic property of the sample. Non-linear V–I curves for single crystal and polycrystalline LFO bulk samples have previously been reported [146, 147]. Nagata et al. have recently reported the nonlinear electrical conductivity of single crystal YbFe$_2$O$_4$ in which the self-heating effect was eliminated by measuring the temperature of the sample with a small thermocouple mounted right on the sample surface [148].

We attribute the observed V–I characteristics of the LFO thin films to the effects of the applied field on the CO state. In polycrystalline LFO thin films, we expect to have randomly oriented CO domains caused by grain boundaries, impurities, and defects. Further, these CO domains are sensitive to temperature because the spin, charge, and lattice degrees of freedom are strongly coupled in LFO [6, 61]. Consequently, the net polarization of all the CO domains in the polycrystalline LFO thin films changes with temperature, resulting in the temperature-dependent hysteresis effects and non-linear V–I behaviors. Further, we recall from our earlier report the temperature dependent band gap of the LFO thin film shows the ferromagnetic transition at ~ 240 K [56]. While the electrical properties of the material are greatly influenced by the charge carriers and the band gap rather than the spin orientation, our findings clearly show that the magnetic ordering and a strong spin–charge coupling significantly influence the electrical
properties. Such a strong coupling in the system could lead to the spintronic applications of LFO thin films.

In summary, the LFO thin films show the linear electro-optical effects of size up to 5% near Fe$^{2+}$ d to d on-site electronic transition. The thin film behaves as a p-type semi-insulator material at temperatures above 440 K. Temperature dependent voltage–current and transient response of voltage under current pulse measurements showed hysteresis and a nonlinear relationship below 340 K. The complex electrical behaviors and electro-optical properties of LFO thin films could be attributed to the interaction of the applied fields with the CO domains in the polycrystalline LFO thin films.
CHAPTER 5

CONCLUSIONS AND OUTLOOK

In this thesis work, we characterized three different thin films materials, ZnO, AlN and LFO. For ZnO thin films, we have investigated the transport properties of ZnO heavily doped by P and As. The samples were grown on sapphire substrates by RF magnetron sputtering. We used variable temperature Hall effect measurements in a wide range of temperature from 80 to 800 K. These samples exhibited n-type conductivity throughout the temperature range with carrier concentration of 3.85 × 10^{16} \text{ cm}^{-3} and 3.65 × 10^{17} \text{ cm}^{-3} at room temperature for P-doped and As-doped ZnO films, respectively. The Arrhenius plots of free electron concentration of the doped samples showed double thermal activation processes with a small activation energy of about 0.04 eV due to shallow donors and a large activation energy of about 0.8 eV due to deep donors. We also performed low temperature PL measurements for detailed understanding of energy levels involved. Based on our PL measurements and theoretical calculation, the deep donor level observed in the Hall effect measurements could be related to oxygen vacancy. We also investigated undoped ZnO buffer layer in an effort to prepare ZnO buffer layer with low background concentration. Undoped ZnO thin film samples were grown at different substrate temperatures. Hall Effect measurements showed that the resistivity and background electron
concentration of the thin films decrease as the substrate temperatures increase. The film deposited at 900 °C has the lowest electron concentration of \( \sim 9.9 \times 10^{-15} \text{ cm}^{-3} \) which is more than 2 orders reduced background concentration compared to the sample grown at 300 °C. Additional measurement with PL and TEM images showed that the reduced background concentration is also related to the reduced amount of stacking faults.

Next, we did TEM investigation of AlN epilayers grown on sapphire substrate using three-step growth method by MOCVD. TEM images were taken from plan view and cross section of the samples. From the cross section view images, the threading dislocations are significantly diminished within 300 nm thickness. Screw dislocations are reduced by using high temperature buffer. Edge type dislocations are reduced by inserting an intermediate layer between the buffer and high temperature AlN layers. From plan view TEM images, the average threading density is \( \sim 2.7 \times 10^9 \text{ cm}^{-2} \), which agrees well with the dislocation density estimated by XRD rocking curve analysis. The threading dislocations further decreases with increasing the thickness. Thus, a thick AlN/sapphire template could be used to grow DUV optoelectronic device structures for improved performance.

Last, we investigated the electro-optical and temperature-dependent electrical-transport properties of LuFe\(_2\)O\(_4\) (LFO) thin films. The LFO thin films at 78 K showed the electro-optical effects of size up to 5% near the Fe\(^{2+}\) d to d on-site electronic transition. In the three-dimensional charge-ordered state of LFO, we observed hysteresis in dc voltage–current measurements and nonlinear voltage–current relationship in transient response of voltage under current pulses. The electro-optical and electrical properties of LFO thin films are interpreted in terms of the field-induced changes of the charge-ordered state mediated by the spin–charge–lattice coupling effect.
We also discuss possible mechanisms of the complex electrical properties and electro-optical effects in conjunction with the Maxwell–Wagner effects.

**Future direction:**

Despite the difficulties in achieving p-type conductivity, ZnO remains a promising material for electronic and optoelectronic device applications. If reliable and reproducible p-type doping can be achieved, it would hugely boost the applications of ZnO. The quality and availability of ZnO substrates have dramatically improved recently, the search for a p-type dopant must continue with the highest priority. Advanced growth techniques such as delta doping could be employed in order to achieve p-type conductivity in ZnO. Further other dopants such as Li can be employed.

AlN is an interesting, challenging, and technologically important material for deep UV application. For these reasons we need to keep working on improving crystalline quality of the materials especially for thick layer growth. After that doping for both n-type and p-type need to be addressed in order to develop AlN based DUV optical devices.

Although LFO is a promising multifunctional material, many aspects of its multiferroic properties are still not well understood. So far the thin films are polycrystalline. Much effort need to done to improve the crystalline quality of thin films. Additionally, magneto-electric of thin films of LFO can be done for device applications.
List of Publications

1. **Electro-optical Effects and Temperature-dependent Electrical Properties of LuFe$_2$O$_4$ Thin Films.**
   Thin Solid Films 562(0): 490-494 2014

2. **Properties of ZnO Thin Films Co-doped with Lithium and Phosphorus.**
   T. N. Oder, A. Smith, M. Freeman, M. McMaster, B. Cai and M. L. Nakarmi.
   Journal of Electronic Materials (online first in March issue) 2014

3. **Elevated Temperature Dependent Transport Properties of Phosphorus and Arsenic Doped Zinc Oxide Thin Films.**
   Journal of Applied Physics 114: 223709 2013

4. **Properties of Sputter Deposited ZnO Films Co-doped With Lithium and Phosphorus.**
   T. N. Oder, A. Smith, M. Freeman, M. McMaster, B. Cai and M. L. Nakarmi.

5. **Elevated Temperature Dependence of Energy Band Gap of ZnO Thin Films Grown by E-Beam Deposition.**

6. **TEM Analysis of Microstructures of AlN/Sapphire Grown by MOCVD.**
   B. Cai and Mim L. Nakarmi.

7. **Spin-Charge-Orbital Coupling in Multiferroic LuFe$_2$O$_4$ Thin Films.**

8. **Three-step Growth Method for High-quality AlN Epilayers.**

9. **Optical and Electronic Properties of NiFe$_2$O$_4$ and CoFe$_2$O$_4$ Thin Films.**
   Applied Physics A 104. 2011
Appendix

I-V Curve Measurement Labview Program:
Van der Pauw Measurement Program:
Hall-effect Measurement Program:
Bibliography


