

**DEPOSITION OF ZINC OXIDE THIN FILMS BY SPIN COATING AND
EXAMINATION OF THEIR STRUCTURAL, ELECTRICAL AND OPTICAL
CHARACTERISTICS FOR SOLAR CELL APPLICATION**

by

Nubert Mukwakwa

**A dissertation submitted to the University of Zambia in partial fulfillment of the
requirements of the degree of Master of Science in Physics.**

THE UNIVERSITY OF ZAMBIA

LUSAKA

2017

COPYRIGHT

No part of this thesis may be reproduced in any form without the written permission of the author or the University of Zambia

Nubert Mukwakwa

University of Zambia

LUSAKA ZAMBIA

© Copyright reserved

DECLARATION

I **Nubert Mukwakwa** declare that the dissertation, which I hereby submit for the **Master of Science (MSc) in Physics degree** at the **University of Zambia**, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

Signature

Date

APPROVAL

This dissertation of **Nubert Mukwakwa** has been approved as partial fulfilment of the requirements for the award of **Master of Science in Physics** by the **University of Zambia**.

Examiner 1. Name Signature Date

Examiner 2. Name Signature Date

Examiner 3. Name Signature Date

Chairperson Board of Examiners

Name Signature Date

ABSTRACT

This dissertation reports on the deposition of ZnO prepared by sol-gel on substrates by spin-coating, and the characterisation of the resulting thin films. The precursor solution was synthesized using appropriate quantities of aqueous Zinc Acetate dehydrate, 2-Methoxyethanol and Ethanolamine. The mixing was carried out on a hot plated magnetic stirrer for 2 hours at a temperature of 70°C resulting in a clear solution that was allowed to cool down to room temperature before the coating was commenced.

A coating speed of 3000 rpm was applied for 60 seconds with a looping cycle of one which was followed by preheating at 200°C for 2 minutes. The four samples selected in the study were coated at cycles of six, eight, ten and twelve and were all annealed at a temperature of 500°C for two hours.

After annealing, the samples were then characterised. The samples were greyish in colour. They were also found to be largely amorphous when coated on glass substrates. The grain sizes measured using the Scanning Electron Microscopy (SEM) were found to be 45 nm in diameter. X-ray Diffraction (XRD) shows that the thin films are crystalline in nature and their XRD patterns showing enhanced intensities for the peaks corresponding to (002) plane at 2θ depicting a preferential orientation along the c - axis.

The thickness of the films on substrates measured within the range of 1200nm – 1500nm. Specular ultra-violet visible (UV-vis) measurements gave a direct transition optical band gap energy (E_g) of 3.37eV. The highest transmission peak occurred at 95 percent which is within the range of the best solar cell devices of 95 percent transmission.

In this study crystalline ZnO films with a high conductivity at $5.87 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$ and lowest resistivity about $1.7 \times 10^{-3} \Omega\text{cm}$ were obtained. Carrier concentration and Hall Coefficient were to be found $1.26 \times 10^{17} \text{cm}^{-3}$ and $2.01 \times 10^{-3} \text{m}^3/\text{C}$ respectively. These properties are a health indicator that ZnO thin films produced by the sol-gel method can operate as a Transparent Conductive Oxides (TCO).

DEDICATION

Dedicated to my mother **Acquillinah Mukwakwa**, my wife **Cynthia Chitenta Mukwakwa**, and my sons **Jeremiah, Albert and Prince Mukwakwa**.

ACKNOWLEDGEMENTS

For the success of this study, I cannot fully thank the people who made it possible

I thank my supervisor, Dr. S. Hatwaambo and co-supervisor Prof. R. Manyala for their support, guidance and discussions which they tirelessly offered to me throughout my study period.

Dr. M. M. Diale for the guidance and discussion input she rendered to me during my visit at the University of Pretoria.

I want to thank the Dean of the School of Natural Sciences, Dr. H.V. Mweene for affording me an opportunity to pursue my MSc studies after a while.

I also thank Mr. M. Bundala of Physics Department at UNZA for all the assistance he offered to me with the measuring equipment and discussion input in the Solid States laboratory. Mr. Siabbamba of Chemistry Department at UNZA also deserves my appreciation for all the assistance he gave me with the measuring equipment and discussions in the laboratory.

I would also like to extend many thanks to the following members of the Energy and Environment Research Group whose contribution is appreciated; Prof. P.C. Jain, Dr. O. Munyati, Mr. F. Nambala, and Mr. C. Changwe.

I would like to thank my friends: Alfred Madika Illunga, Moono Jambo, Moses Mwale, David Mwale, Sylvester Silungwe and all who always believed in me.

I further wish to thank the International Science Program (ISP) of Uppsala University, Sweden for the financial support without which it would have been very challenging for me to pursue this program.

Lastly, I want to thank my family for their love, support and always believing in me. Above everything else, I thank the Lord; God in heaven whom I believe makes all things possible.

TABLE OF CONTENTS

CHAPTER ONE

INTRODUCTION	1
1.1. Background.....	1
1.2. Statement of the Problem	3
1.3. Aim	3
1.4. Objectives	4
1.5. Research Questions	4
1.6. Significance of the Study	5

CHAPTER TWO

LITERATURE REVIEW	6
2.1. Introduction	6
2.2. Methods of Synthesis of Nano- and Micrometric Zinc Oxide	8
2.2.1. Metallurgical Process	10
2.2.2. Chemical Processes	11
2.2.2.1. Sol-Gel Method	11
2.2.2.2. Solvothermal and Hydrothermal Method	13
2.2.2.3. Using Emulsion or Micro Emulsion Environment.....	14

2.2.2.4. Controlled Precipitation	14
2.2.2.5. Mechanochemical Process	15
2.2.2.6. Other Method of Obtaining Zinc Oxide	15
2.3. Deposition and Fabrication of Zinc Oxide.....	15
2.3.1. Spin Coating	15
2.3.2. Pre-Heating and Post-Heating of Substrates	16
2.4. Characterisation of Zinc Oxide	20
2.4.1. Morphology	20
2.4.2. Structural Characterisation	21
2.4.3. Orientation of Zinc Oxide Thin Films	23
2.4.4. Optical Properties	23
2.4.5. Electrical Properties	24
2.5. Industrial Applications of Zinc Oxide	26
2.5.1. Rubber Industry	27
2.5.2. The Pharmaceutical and Cosmetic	27
2.5.3. The Textile Industry	28
2.5.4. The Electronics and Electrotechnology Industries	28

2.5.5. In Photocatalysis	29
2.5.6. Other Miscellaneous Applications	30
 CHAPTER THREE	
EXPERIMENT AND CHARACTERISATION PROCESSES	32
3.1. Introduction	32
3.2. Sample preparation	32
3.2.1. Substrate Preparation	32
3.2.2. Spin Coater Preparation	33
3.2.2.1. Spin Coating Chamber	33
3.2.2.2. Control Unit	34
3.2.2.3. Power Supply	34
3.2.2.4. Vacuum Pump	34
3.2.2.5. Pressure Pump	34
3.2.2.6. Nitrogen Supply	34
3.3. Thin Film Deposition	35
3.3.1. Preparation of Precursor Solution	35
3.3.2. Solution Deposition on Substrates	36

3.4. Annealing of Coated Substrates	38
3.5. Sample Characterisation	39
3.5.1. XRD Crystal Structure.....	39
3.5.2. Electrical Measurement	40
3.5.2.1. The Four Point Probe	40
3.5.2.2. Hall Effect Measurement	42
3.5.3. Optical Properties	43
3.5.3.1. Transmission Measurement	43
3.5.3.2. Band Gap Measurement	44
3.5.4. Thickness Measurement	45
3.5.5. Measurement of Surface Morphology.....	46

CHAPTER FOUR

RESULTS AND DISCUSSION	48
4.1. Introduction	48
4.2. Physical Appearance	48
4.3. Films Thickness Measurement	49
4.4. Surface Morphology	49
4.5. XRD Patterns of Zinc Oxide	51
4.5.1. Orientation of Zinc Oxide	53
4.5.2. c-Axis Lattice Constants of the Films	54
4.6. Optical Properties and Band Gap	56
4.6.1. Band Gap	58

4.6.2. Optical Transmission	59
4.7. Electrical Properties	61
4.7.1. Four Point Probe	62
4.7.1.1. Sheet Resistance Measurement	62
4.7.1.2. Bulk Resistance Measurement	62
4.7.2. Hall Effect Results	65
 CHAPTER FIVE	
 CONCLUSION AND SUGGESTION FOR FURTHER WORK	70
5.1. Conclusion	70
5.1.1. The Fabrication of Zinc Oxide	70
5.1.2. Characterisation of Samples	71
5.2. Suggestion for Further Work	73
 REFERENCES	74

LIST OF TABLES

Table 3.1 UV-Vis Spectrophotometer Parameters.....	45
Table 4.1 XRD Parameters of (hkl).....	53
Table 4.2 Lattice Parameters and Relative Intensities of (002) Peaks	55
Table 4.3 ZnO Carrier Concentration and Mobility Figures	68

LIST OF FIGURES

Figure 2.1 Examples of Zinc Oxide Structure: Flower (a); Rods (b); Wires (c, d).....	9
Figure 2.2 Overview Showing Two Examples of Synthesis by the Sol-gel Method	13
Figure 2.3 TG–DTA Curves of the Dried ZnO Gel	17
Figure 2.4 Transmittance (a) and Absorbance (b) Spectra of ZnO Thin Films.....	19
Figure 2.5 SEM Micrographs of The ZnO Thin Films	21
Figure 2.6 X-ray Diffraction Pattern of the ZnO Nanostructured Thin Film	22
Figure 2.7 Graph of Conductivity versus Inverse of Temperature for ZnO Thin Films...	24
Figure 2.8 Worldwide Consumption of ZnO	26
Figure 2.9 Schematic Representation all the Application of ZnO	27
Figure 3.1 WS – 400HZ Spin Coater (Physics Department-UNZA).....	33
Figure 3.2 Chart of the Spin Coating Process.....	36
Figure 3.3 The Spin Coating Graph.....	38
Figure 3.4 Annealing Graph.....	39
Figure 3.5 Pictorial Illustration of the Four Point Probe.....	40
Figure 3.6 The Jandell R3000 Four Point Probe	41
Figure 3.7 Illustrative Diagram of the Hall Effect Probe.....	42

Figure 3.8 Peckin Elmer Lambda 19 Spectrophotometer.....	44
Figure 3.9 The UV – Vis Spectrophotometer.....	45
Figure 3.10 Valendor Thickness Gauge	46
Figure 4.1 Samples of ZnO Thin Films on Glass Substrates	48
Figure 4.2 SEM Microstructure of ZnO Films.....	50
Figure 4.3 XRD Patterns of ZnO Thin Films	52
Figures 4.4 UV–vis Absorption Spectra for ZnO Thin Films.....	57
Figure 4.5 Combined UV–vis Absorption Spectra ZnO Thin Films.....	58
Figure 4.6 Transmission Graphs for Each Sample (A, B, C and D).....	60
Figure 4.7 Transmission Graph for all the Samples Combined.....	61
Figure 4.8 Resistivity and Resistivity per Square Graph for Varying Voltage.....	63
Figure 4.9 Resistivity and Resistivity per Square for Varying Current.....	64
Figure 4.10 Hall Voltage Versus Current.....	65

ABBREVIATIONS

AFM	Atomic Force Microscope
Al	Aluminum
Al ₂ O ₃	Aluminum Oxide
CdO	Cadmium Oxide
CdS	Cadmium Sulfide
C ₄ H ₁₀	Butane
C ₂ H ₅ OH	Ethanol
CMOS	Complementary Metal-Oxide-Semiconductor
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
Cu	Copper
°C	Degrees Celsius
DI	De – Ionised
DTA	Differential Data Analyzer
EHP	Exposure Hydrogen Plasma
EP	Extreme Pressure
eV	Electron Volt
FED	Field Emission Displays
Fe ₂ O ₃	Iron (III) Oxide
FPP	Four Point Probe
FTIR	Transform Infrared Spectrometer
H	Hydrogen

H ₂	Hydrogen Ion
HCN	Hydrogen Cyanide
H ₂ S	Hydrogen Sulfide
IEP	Isoelectric Point
ITO	Indium Tin Oxides
ISO	International Standards Organisation
In	Indium
In ₂ O ₃	Indium Oxide
JCPDS	Joint Committee of Powder Diffraction Standards
LCD	Liquid Crystal Display
MEA	Monoethanolamine
Mg	Magnesium
MO	Methyl Orange
MOCVD	Metal Organic Chemical Vapour Deposition
N ₂	Nitrogen
O	Vacancies
OH	Hydroxyl
PEL19	Perkin Elmer Lambda 19
POMs	Polyoxometalates
RhB	Degradation of Rhodamine
ROS	Reaction with characteristic reactive groups
SEM	Scanning Electron Microscopy
SF ₆	Sulfur Hexafluoride

SLG	Soda Lime Glass
Sn	Tin
SnO ₂	Tin Oxide
TCO	Transparent Conducting Oxides
TiO ₂	Titanium Dioxide
TG-DTA	Thermogravimetry – Differential Thermal Analyzer
TGA	Thermogravimetry Analyzer
XRD	X-Ray Diffraction
UV	Ultra Violet
ZABS	Zambia Bureau of Standards
Zn	Zinc
ZnAc	Zinc Acetate
ZnO	Zinc Oxide

CHAPTER ONE

INTRODUCTION

1.1. Background

Due to their unique optical, electrical and semiconducting properties, ZnO thin films are extensively used in various applications. Significant research efforts have been made in recent years for developing highly oriented and transparent ZnO thin films because of their potential application in transparent electrode in display screens, window layers in solar cells, field emitters, ultraviolet laser emission, photodetectors, piezoelectricity, bio-sensors, short wavelength light emitting diode and other uses in information technology. Despite several approaches adopted for making these ZnO thin films; controlling the size, shape, crystallinity and various parameters affecting the size and shape of these materials still need to be investigated. Therefore, it is essential to investigate optimum conditions for deposition of highly oriented and transparent ZnO thin films. The main concern of researcher is to get better quality of material stoichiometry. ZnO thin films are grown by different techniques such as pulsed laser deposition (PLD), magnetron sputtering, Metal Organic Vapour Deposition (MOCVD), spray pyrolysis etc. Spin coating technique is widely adopted due to its comparatively simple procedure as there is no need for costly vacuum system and it has a wide-range advantage of large area of deposition and uniformity of the films' thickness. The Spin coating process also offers other advantages for thin film deposition including outstanding control of the stoichiometry and easy doping. Industrial use of thin films has increased for several reasons amongst them the development of smaller electronic devices. The use of these thin films to produce smaller and thinner

devices is on the increase and as such there is need to understand their characteristics under different conditions of fabrication as well as use. Many aspects need to be probed such as the effect of molecular weight, thermal degradation, and the adhesion properties of the precursor solution.

Currently, Indium Tin Oxide (ITO) is used by over 97 per cent of the TCO market as it possesses a near-ideal combination of high visible-light transparency and high electrical conductivity. The total market for ITOs is estimated to be worth \$26.8 bn by 2016 [1]. However, indium metal is scarce, expensive and has a highly volatile price.

There are currently a number of researches on “The new coatings” which investigates low-cost, earth abundant materials and inexpensive deposition routes which could be used for TCO coatings for products such as solar photovoltaic cells. These coatings are based on silicon-doped zinc oxide and provide an alternative to indium tin oxide.

Zinc has been found to be a much more abundant material than indium, and silicon-doped Zinc Oxide (ZnO) material has electrical conductivities which is around two thirds of ITO, with comparable optical transparency [2]. In addition to solar cells, “our new coating could be used for lighting displays and Liquid Crystal Display (LCD) which are used in smart phones, computers and televisions” [2].

1.2. Statement of the Problem

Environmentally friendly and renewable energy sources have been on the increase as they have proved a better option to non-renewable and hazardous energy sources for achieving sustainability. The most promising environmentally friendly energy sources are wind

power, hydroelectric power and solar energy. In this study the fabrication of ZnO thin films coated on glass substrates was made and a further study of the properties of these films was conducted to investigate the possibility of ZnO becoming a major player in the production of user and environmental friendly renewable energy devices, particularly as a key resource in the production of solar cells.

1.3. Aim

The aim of this research was to produce spin coated ZnO thin films under different deposition conditions and investigate them for their structural, electrical and optical properties as alternatives for the production of good Transparent Conductive Oxides (TCOs) which can be produced cheaply for use in photovoltaic.

1.4. Objectives

This study had two main objectives;

- i. To produce ZnO thin films using the spin-coating method.
- ii. To characterise the spin coated ZnO thin films for their structural, electrical and optical properties.

Thin films have been produced in the Department of Physics of the University of Zambia but not by spin coating. This is also true for characterisation which has been done in a number of studies but most of them concentrated on either electrical or optical characteristics but this study focused on three salient characteristics of ZnO that is structural, optical and electrical characteristics.

1.5. Research Questions

To achieve the above stated objectives, the following questions were addressed;

- i. What are the possible advantages and challenges in the preparation and deposition of ZnO films using the spin coater?
- ii. What are the structural, electrical and optical characteristics of the spin coated ZnO thin films when compared to available literature?

In answering these questions, expected outcome was that most of the possible challenges would be analysed by making a number of trials before eventually running the actual experiment. This implies that starting with the preparation of the precursor solution; many trials were done and tested and the obtained results were compared with other studies. The characterization was done by carrying out one measurement after another and analyzing the results obtained.

1.6. Significance of Study

Fabricating ZnO under different conditions for solar cell application is expected to reveal intrinsic properties, that is, structural, electrical and optical properties which may enhance the quality of ZnO thin films not only for solar cell applications but for other applications as well. If Zambian researchers in the area of solar cell applications are to make any meaningful contributions, there is need to develop expertise by carrying out a number of research activities within the Zambian universities.

This research was an attempt to demonstrate that studies of this nature can be carried out within the Zambian universities and obtain results that are comparable to those obtained through studies carried out in other universities and research institutions outside Zambia. The preparation of zinc oxide thin films by spin coating and examination of their structural, electrical and optical characteristics for solar cell application study was aimed at proving that spin coated ZnO thin films have suitable structural, electrical and optical properties for use as TCO for solar cells. This would be a significant contribution towards the production at lower costs of PV solar cells while ensuring a sustainable supply of the raw material. The production of these solar cells at lower costs will make solar energy a more viable alternative as a replacement for current environmentally unfriendly sources of energy.

CHAPTER TWO

LITERATURE REVIEW

2.1. Introduction

In recent years, the TCOs in thin films are some of the most extensively investigated materials due to their important area of applications in modern solid-state device technology. Pure and doped ZnO polycrystalline thin films are also used for a large number of acoustical, electronic and optical devices, because they are characterized by excellent piezoelectric properties, and varistor effect to mention but a few [3]. The main technological interest for polycrystalline ZnO thin films based devices lies on their very low cost. Transparent conductive ZnO thin films have been prepared by a variety of deposition technologies but mostly sputtering, spray pyrolysis, chemical vapour deposition, and pulsed laser deposition. The conventional transparent conductive films of Tin Oxide (SnO_2), Indium Oxide (In_2O_3), ITO (Indium Tin Oxide), Cadmium Oxide (CdO), and others in this family, were found to reduce to their metallic characteristics by Exposure Hydrogen Plasma (EHP) technique [4]. The excess of metallic Tin (Sn) or Indium (In) atoms in SnO_2 and In_2O_3 thin films respectively leads to a decrease of the transmission coefficient especially in the blue spectral domain. For this reason, the respective films become unsuitable for application in amorphous and polycrystalline silicon solar cells [5]. The photovoltaic devices based on Zinc Oxide (ZnO) thin films are characterized by a stable structure in the presence of hydrogen plasma.

ZnO is a well-known group II-IV semiconductor with a direct wide-band-gap of 3.37 eV and a large excitonic binding energy of 60 meV at room temperature. The direct wide-band-gap of the ZnO enables the semiconductor to be a good candidate for optoelectronic

applications and the large exciton energy helps to employ the excitonic recombination process as a lasing mechanism [6]. ZnO exists mostly as n-type, whose conductivity is supposedly due to the existence of native point defects, such as O vacancies and Zn interstitials [7]. Some other impurities, such as Al, Mg, H, are also claimed to contribute to the n-type conductivity in ZnO [8]. Many wide-band-gap semiconductors exist as doping asymmetry i.e., easy to get n-type ZnO, but rather difficult to produce p-type ZnO [9].

ZnO is a polar semiconductor material with two crystallographic planes that have opposite polarity and different relaxation energies, which lead to a higher growth rate along the c-axis i.e., the formation of nanorods-like vertical structures [10]. ZnO exists in zinc blende, cubic rock salt and wurtzite crystal structures. However, at ambient temperature and pressure, ZnO crystallizes normally in a wurtzite structure with a hexagonal lattice that has two interconnecting sub-lattices of Zn^{2+} and O^{2-} with the Zn ion surrounded by tetrahedral O ions and vice versa [11]. This tetrahedral coordination gives rise to a polar symmetry along the hexagonal axis, which is responsible for a number of the chemical and physical properties of ZnO, which include the piezoelectricity and spontaneous polarization. The structure of ZnO is a key factor in crystal growth, etching and defect generation [12].

It has been clearly established that structural, electronic transport and optical properties of ZnO films are very sensitive to preparation method and deposition conditions [13]. In this regard, it is worthy of mention here that so many studies have been conducted around ZnO ranging from preparation methods to characterization for its various properties as a semiconductor with potential use in solar cells. Other studies have also touched on how the properties offered by ZnO can be enhanced by using it as a coating layer on other semiconductors like Silicon, Gallium, Tin and others for which uniform crystals form [14].

As compared to other preparation methods, the spin coating method for deposition of ZnO films has some important advantages such as technological simplicity and low cost of the used materials and equipment [15].

Recently, significant progress in ZnO crystal quality has been made [16]. Besides the nanostructures like nanotubes, nanorods, nanowalls and nanofibers, high-quality undoped and doped ZnO thin films have been grown with plasma-assisted molecular beam epitaxy vapor transport deposition method vacuum arc deposition Metal Organic Chemical Vapour Deposition (MOCVD), sol–gel process and spray pyrolysis. Such nanotubes, nanowires, nanoribbons and nanofibers have attracted attention for their potential applications in applied fields such as Field Emission Displays (FED), optical waveguides, solar cells, ultraviolet photo detectors, optical switches, and gas detectors [17].

The spin coating method has distinct advantages such as cost effectiveness, deposition of multicomponent oxide layers of many compositions on various substrates, simplicity, excellent compositional control, homogeneity and lower crystallization temperature. There are no studies on the optical constants of spin coated ZnO nanostructured thin films in available literature.

2.2. Methods of Synthesis of Nano- and Micrometric Zinc Oxide

The variety of structures of nanometric zinc oxide means that ZnO can be classified among new materials with potential applications in many fields of nanotechnology. Zinc oxide can occur in one- (1D), two- (2D), and three-dimensional (3D) structures. One-dimensional structures make up the largest group, including nanorods [18–20], -needles [21], -helixes, -springs and -rings [22], -ribbons [23], -tubes [24–26] -belts [27], -wires [28–30] and -

combs [31]. Zinc oxide can be obtained in 2D structures, such as nanoplate/nanosheet and nanopellets [32, 33]. Examples of 3D structures of zinc oxide include flower, dandelion, snowflakes, coniferous urchin-like, etc. [34–37]. ZnO provides one of the greatest assortments of varied particle structures among all known materials as shown in Figure 2.1 [37].

Preparation has mainly dealt around the composition of the precursor materials which would subsequently be fabricated in a preferred way to end up with either nanoparticles or a thin film of ZnO coated on a substrate of choice. The nanoparticles have either been studied in a standalone basis or as precursor to further processing while various methods have also been exploited to come up with thin films of coating which are then subject of characterization.

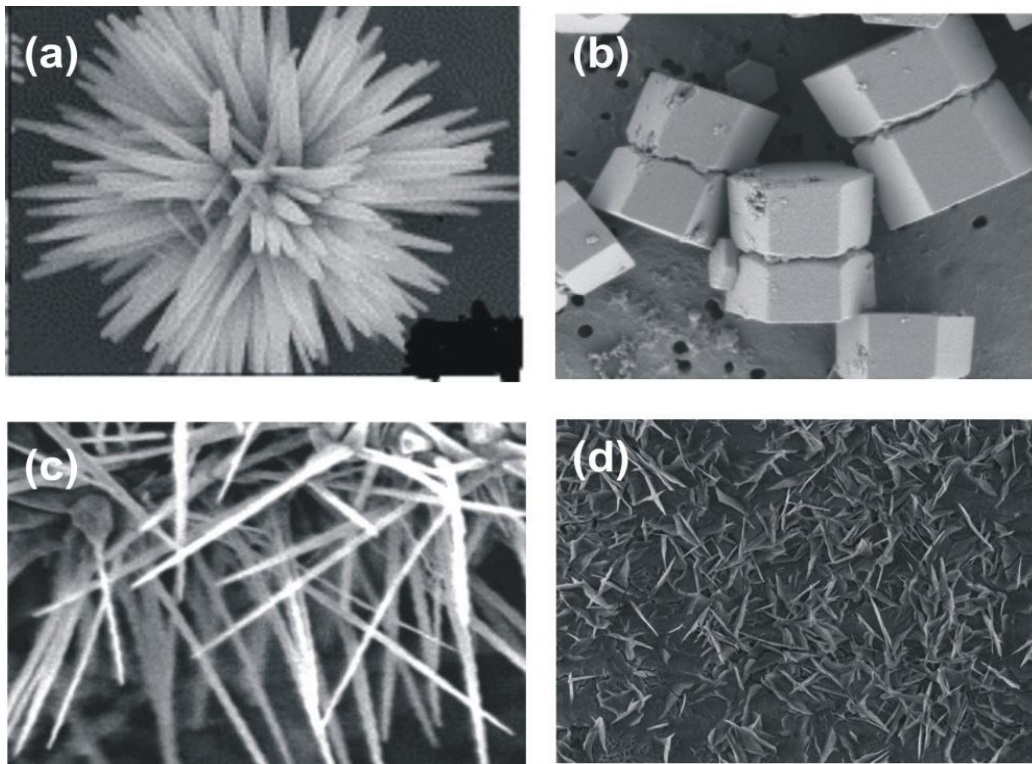


Fig. 2.1. Examples of zinc oxide structure: flower (a); rods (b); wires (c, d) [37]

The zinc oxide occurs in a very rich variety of structures and offers a wide range of properties. The variety of methods for ZnO production, such as vapour deposition, precipitation in water solution, hydrothermal synthesis, the sol-gel process, precipitation from micro emulsions and mechanochemical processes, makes it possible to obtain products with particles differing in shape, size and spatial structure.

These methods are generally categorized in two groups; one, *Metallurgical Processes* which can be described as the processes for obtaining zinc oxide are based on the roasting of zinc ore. The second method is called, *Wet Chemical Processes* which is the process of obtaining ZnO through a chemical process with the only unfortunate part being that not all methods that work in the laboratory can be applied on an industrial scale. The chemical process will be of particular interest in this study.

2.2.1. Metallurgical Process

According to the ISO 9298 standard [38], zinc oxide is classified either as type A, obtained by a direct process (the American process); or type B, obtained by an indirect process (the French process).

The direct (American) process involves the reduction of zinc ore by heating with coal (such as anthracite), followed by the oxidation of zinc vapour in the same reactor, in a single production cycle. This process was developed by Samuel Wetherill [38], and takes place in a furnace in which the first layer consists of a coal bed, lit by the heat remaining from the previous charge. Above this bed is a second layer in the form of zinc ore mixed with coal. Blast air is fed in from below, so as to deliver heat to both layers and to carry carbon monoxide for zinc reduction. The resulting zinc oxide (of type A) contains impurities in

the form of compounds of other metals from the zinc ore. The resulting ZnO particles are mainly needle-shaped, and sometimes spheroidal. To obtain a product with a permanent white color, the oxides of lead, iron and cadmium that are present are converted to sulfates. Increasing the permanence of the color is linked to increasing the content of water-soluble substances, and also increasing the acidity of the product. Acidity is desirable in the case of rubber processing technology, since it lengthens prevulcanization time and ensures the safe processing of the mixtures [39].

In the indirect (French) process, metallic zinc is melted in a furnace and vaporized at about 910 °C. The immediate reaction of the zinc vapour with oxygen from the air produces ZnO. The particles of zinc oxide are transported via a cooling duct and are collected at a bag filter station. The indirect process was popularized by LeClaire in 1844, and since then has been known as the French process. The product consists of agglomerates with an average particle size ranging from 0.1 to a few micrometres [40]. The ZnO particles are mainly spheroidal in shape. The French process is carried out in vertical furnaces, with an original vertical charge, vertical refining column, vaporizer with electric arc, and rotary combustion chamber [41]. Type B ZnO has a higher degree of purity than type A.

2.2.2. Chemical Processes

Under the chemical processes, there are several methods that are used in synthesizing ZnO and these are the subject of discussion in this subsection.

2.2.2.1. Sol-Gel Method

The obtaining of ZnO nanopowders by the sol-gel method enables the surface modification of zinc oxide with selected organic compounds. This changes its properties and extends its

range of applications. The favourable optical properties of nanoparticles obtained by the sol-gel method have become a common topic of research, as reflected in numerous scientific publications [42]. Figure 2.2 shows two examples of synthesis by the sol-gel method: films from a colloidal sol (Figure 2.2a), and powder from a colloidal sol transformed into a gel (Figure 2.2b).

In a related study where the sol-gel method was used, Zinc acetate dehydrate ($\text{Zn}(\text{COOCH}_3)_2 \cdot 2\text{H}_2\text{O}$), was used as the starting salt material to prepare ZnO thin films by sol-gel method. The flow chart of the preparation of ZnO thin films is shown in Figure 2. The zinc acetate dehydrate was first dissolved in isopropanol ($(\text{CH}_3)_2\text{CHOH}$)-Monoethanolamine (MEA: $\text{HOCH}_2\text{CH}_2\text{NH}_2$) solution at room temperature. The concentration of zinc acetate was 0.3 mol/l and molar ratio of MEA to ZnAc was kept to 1.0. The mixture was stirred by a magnetic stirrer at 70 °C until a clear and homogeneous solution formed [43]. The precursor solution prepared in this way did not produce any precipitates after 2 weeks of storage which gives it the preferred characteristics for spin coating and subsequent processing.

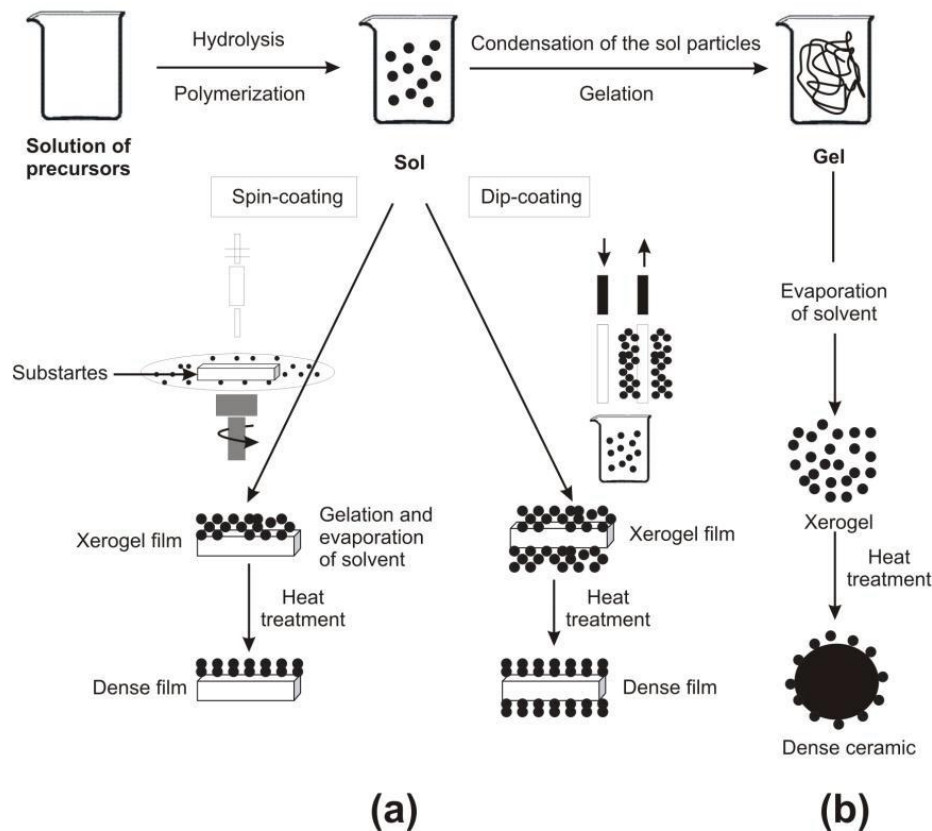


Fig. 2.2. Overview showing two examples of synthesis by the sol-gel method: (a) films from a colloidal sol; (b) powder from a colloidal sol transformed into a gel (created based on [44] with permission from Elsevier Publisher).

2.2.2.2. Solvothermal and Hydrothermal Method

The hydrothermal method does not require the use of organic solvents or additional processing of the product (grinding and calcination), which makes it a simple and environmentally friendly technique. The synthesis takes place in an autoclave, where the mixture of substrates is heated gradually to a temperature of 100–300 °C and left for several days. As a result of heating followed by cooling, crystal nuclei are formed, which then grow. This process has many advantages, including the possibility of carrying out the synthesis at low temperatures, the diverse shapes and dimensions of the resulting crystals

depending on the composition of the starting mixture and the process temperature and pressure, the high degree of crystallinity of the product, and the high purity of the material obtained [45,46].

2.2.2.3. Using an Emulsion or Micro Emulsion Environment

This is another method used to obtain ZnO. The classic definition of an emulsion is a continuous liquid phase in which a second dispersed and discontinuous, immiscible liquid phase is far from complete. One very convenient way to classify emulsions is first to divide them into two large groups based on the nature of the external phase. The two groups are usually called *oil-in-water* (O/W) and *water-in-oil* (W/O) emulsions. The terms “oil” and “water” are very general; almost any highly polar, hydrophilic liquid falls into the “water” category in this definition, while hydrophobic, nonpolar liquids are considered “oils” [47, 48].

2.2.2.4. Controlled Precipitation

Controlled precipitation is a widely used method of obtaining zinc oxide, since it makes it possible to obtain a product with repeatable properties. The method involves fast and spontaneous reduction of a solution of zinc salt using a reducing agent, to limit the growth of particles with specified dimensions, followed by precipitation of a precursor of ZnO from the solution. At the next stage this precursor undergoes calcination, followed by milling to remove impurities. It is very difficult to break down the agglomerates that form, so the calcined powders have a high level of agglomeration of particles. The process of precipitation is controlled by parameters such as pH, temperature and time of precipitation.

2.2.2.5. Mechanochemical Process

The mechanochemical process is a cheap and simple method of obtaining ZnO nanoparticles on a large scale. It involves high-energy dry milling, which initiates a reaction through ball–powder impacts in a ball mill, at low temperature. A “thinner” is added to the system in the form of a solid (usually NaCl), which acts as a reaction medium and separates the nanoparticles being formed [49].

2.2.2.6. Other Methods of Obtaining Zinc Oxide

There also exist many other methods of obtaining ZnO, including growing from a gas phase, a pyrolysis spray method, a sonochemical method and synthesis using microwaves [49].

2.3. Deposition and Fabrication of Zinc Oxide Thin Films

There are so many ways of depositing ZnO but of interest to this study is the deposition of ZnO prepared by sol-gel method in which spin coating process is used.

2.3.1. Spin Coating

Different spin coaters have been used over time ranging from basic and homemade ones to modern and state of the art spin coaters which are programmeable. The challenge is to find a fine balancing amount of solution applied, spin speed and time taken so as to end up with a smooth, coherent and adhesive coat.

Smirnov et al [50] established experimentally that the composition of coating solution plays an important role in preparing high quality ZnO thin films. It was found that the ratio 10 ml to 1 g of ethanol to acetate in mixture solution results in stoichiometric and

homogenous films. Increasing this ratio lowers the ability of the coating solution to form films onto glass substrates (the solution is not able to adhere to the substrates).

The film thickness increases with increasing number of cycles for a determined spinning speed. Therefore it is possible to produce films with controlled thickness given that the relationship has been found to be linear [50]. The average thickness was found to be about 33 nm per coating cycle. Generally, the thickness of the coating depends on the speed at which solution level falls, concentration and viscosity of the respective solution, surface tension of the solution, temperature and relative humidity [50].

The thickness of the films is in principle a multiple of the thickness of one coating. For a certain value of deposition time and cycle number, the film thickness decreases slowly with increasing of rotation speed to about constant value. A similar behaviour was also found for many semiconducting films deposited by spin coating [50].

2.3.2. Pre Heating and Post Heating of Substrates

In a study by Davood Raoufi and Taha Raoufi [43] on the effect of heat treatment on the physical properties of sol–gel derived ZnO thin films, various effects of pre heating and post heating temperatures on the films were observed. The study used three samples which, after each coating, the films were dried at 250 °C for 5 min on a hot plate and then after the deposition of the last layer, the resulting thin films were annealed at 300 °C, 400 °C and 500 °C in air for one hour.

Firstly, their results showed that there were three weight losses in temperature regions 30–60 °C, 100–210 °C and 220–270 °C. The first weight loss may be from the evaporation of isopropanol. The second and the third weight losses are due to the evaporation of water and the decomposition of residual organics and Monoethanolamine (MEA), respectively. The endothermic peak at 100 °C in (Differential Thermal Analyzer) DTA curve results from the evaporation of the solvent. The mass loss is about 85% of the initial weight as seen in (Thermogravimetry Analyzer) TGA curve. The broad exothermic peak results from the decomposition of residual organics and crystallization of ZnO. These results are shown in Figure 2.3 which were obtained from the (Thermogravimetry – Differential Thermal Analyzer) TG – DTA [43].

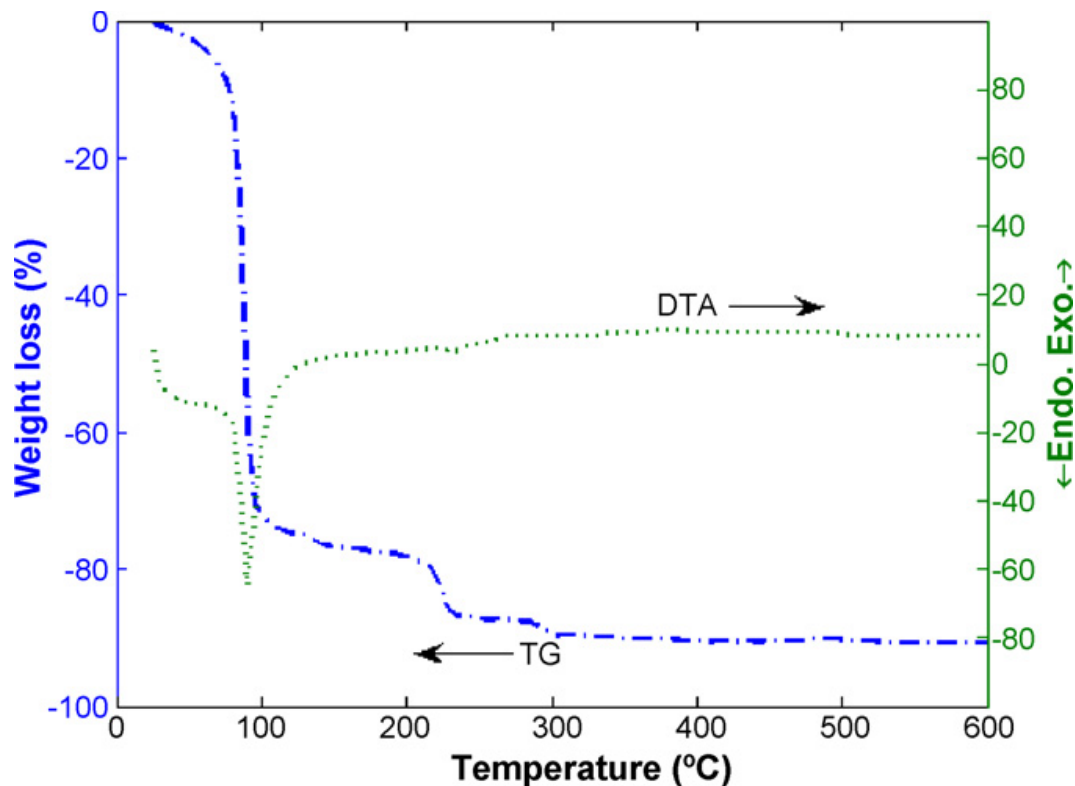


Fig. 2.3. TG–DTA curves of the dried ZnO gel [43]

Secondly, from the XRD data, it was found that the average grain size increased with increasing annealing temperature. The average grain size was estimated as 14 nm for 300 °C, 19 nm for 400 °C, and 28 nm for 500 °C.

Thirdly, as can be inferred from Figure 2.4 [51], it was deduced that all ZnO thin films annealed at different annealing temperatures were highly transparent in the visible range (400–700 nm) with a transmittance of more than 80% with sharp absorption edges observed in the ultraviolet region. Figure 2.4(b) shows the UV–Vis absorption spectra of the samples annealed at different temperatures. The exciton absorption is at about 379 nm. The film annealed at 500 °C shows lower absorption at lower wavelengths and the tail height decreases with increasing annealing temperature from 300 °C to 500 °C.

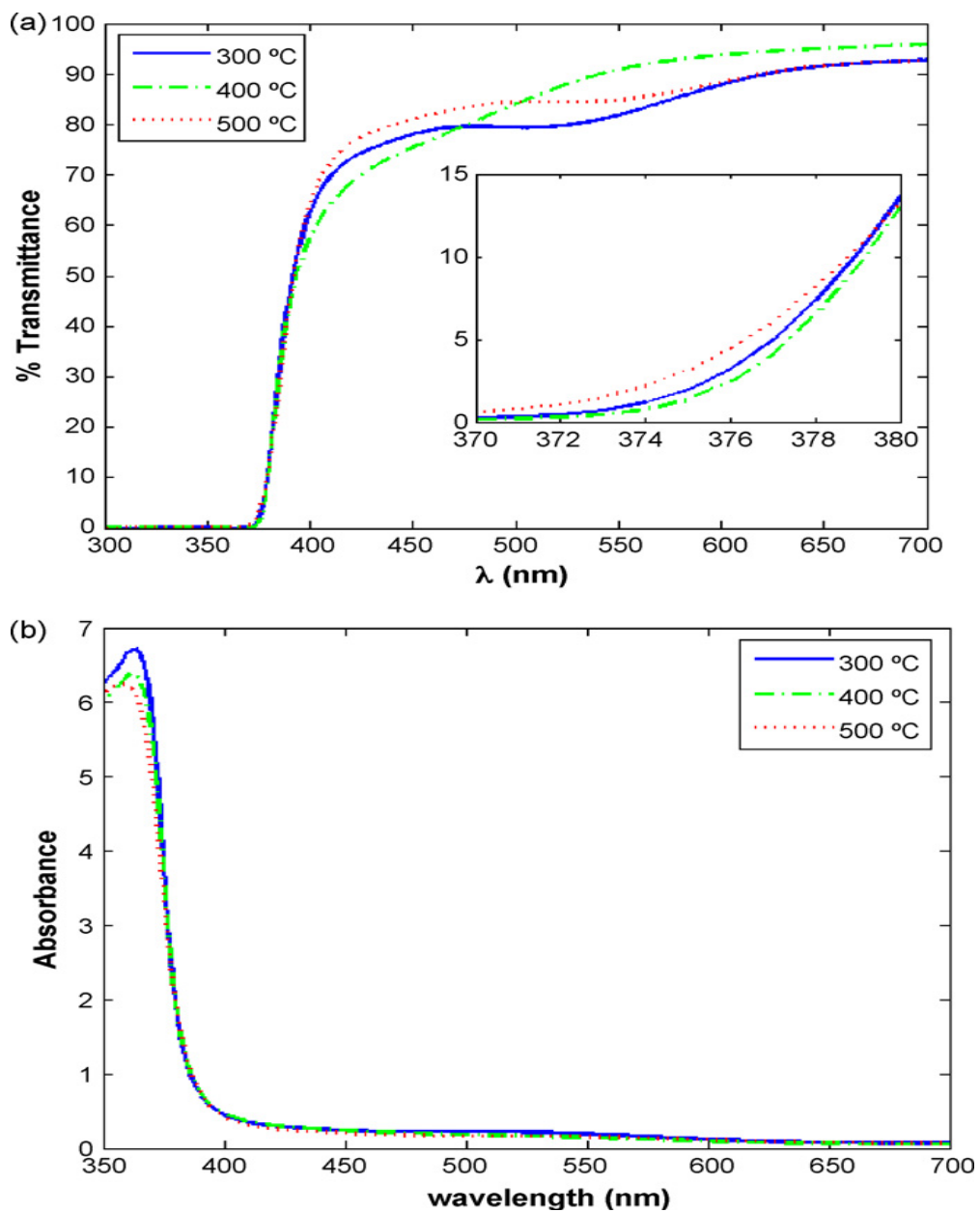


Fig. 2.4. Transmittance (a) and absorbance (b) spectra of ZnO thin films annealed at different temperatures [51]

Fourthly, it was observed from the Scanning Electron Microscope (SEM) photos shown in Figure 2.5 that the surface of the thin film annealed at 300 °C contained some cracks while no cracks were observed after annealing at 400 °C, and 500 °C. As the annealing

temperature of ZnO films increased from 300 °C to 500 °C, the crystallite size increased and the films became denser. As a result, the measured resistivity decreased from 68 Ωcm to 23 Ωcm. Usually, the grain boundary caused a larger effect on the electrical properties. The grain boundary decreased with increasing crystallization of thin films and the electrical resistivity decreased by reason of the increase in crystallization and orientation with increasing heat-treatment temperature [51, 52].

2.4. Characterisation of ZnO

Piezo- and pyroelectric properties of ZnO can be used as a sensor, converter, energy generator and photocatalyst in hydrogen production [53, 54] while its hardness, rigidity and piezoelectric constant makes it an important material in the ceramics industry whereas its low toxicity, biocompatibility and biodegradability makes it a material of interest for biomedicine and in pro-ecological systems [55–57].

While much has already been established in the characterisation of ZnO and put to good use headway is yet to be made in as far as its utility in solar cells is concerned and this subsection will focus on the many findings from this point of view.

2.4.1. Morphology

Figure 2.5(a)–(c) [58, 59] shows the Scanning Electron Microscopy (SEM) micrographs of the surface of 8-layer ZnO thin films annealed at 300 °C, 400 °C and 500 °C, respectively. From these Figures, it can be seen that the ZnO thin films are porous and the average crystallite size of the films is about 15–30 nm, which is in acceptable agreement with XRD data [43].

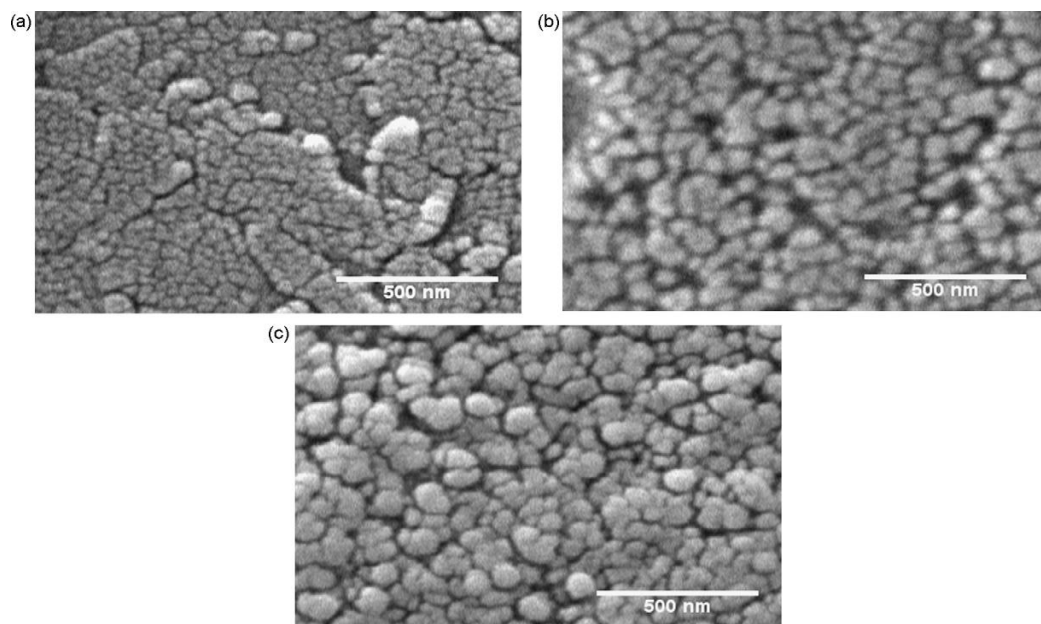


Fig. 2.5. SEM Micrographs of the ZnO Thin Films Annealed at (a) 300 °C, (b) 400 °C and (c) 500 °C [58, 59].

In addition the film was reported to exhibit a porous nanostructure and the spherical crystalline particle size is approximately 40 nm which is still supported by other literature showing ZnO nanostructures having 9–250 nm have been reported [58, 59].

2.4.2. Structural Characterisation of the ZnO Gel Powder

Smirnov *et al* [50] showed that XRD pattern for a ZnO films prepared by six cycle spin-coating of ZnO films followed by post-deposited heat treatment are polycrystalline and have a hexagonal (wurtzite) structure. The deposited films have an amorphous phase. The film crystallites are preferentially oriented with (0 0 2) planes parallel to the substrate surface, in addition to other (1 0 0), (1 0 1) prominent reflections. The lattice parameters calculated from XRD, were in good agreement with those indicated in Joint Committee of Powder Diffraction Standards (JCPDS) data for ZnO crystals. This behaviour indicated

that the quality of ZnO films improves when they are annealed at higher temperatures [60]. This is shown in figure 2.6 [60].

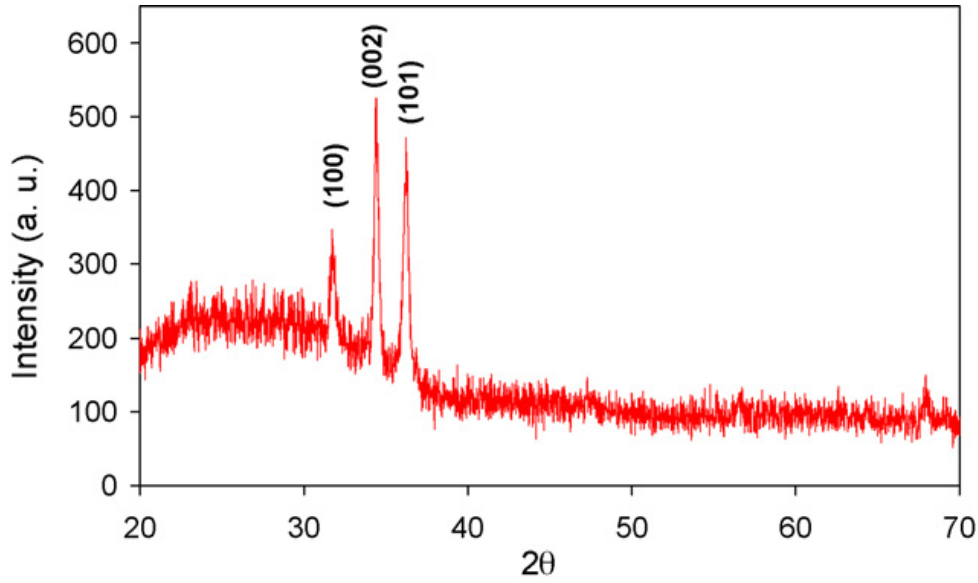


Fig. 2.6. X-ray diffraction pattern of the ZnO nanostructured thin film [60].

The lattice constants for hexagonal ZnO film are reported in 36-1451 Joint Committee on Powder Diffraction Standards (JCPDS) standard data $a = 3.24982\text{\AA}$ and $c = 5.20661\text{\AA}$ [25]. Lattice constants are obtained by use of the equation,

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + k^2 + hk}{a^2} \right) + \frac{l^2}{c^2} \quad (1)$$

Smirnov *et al* [50] calculated the lattice constants by using equation (1) and found that $a = 3.25452\text{\AA}$ and $c = 5.20980\text{\AA}$ which are in good agreement with 36-1451 JCPDS standard data [61].

2.4.3. Orientation of ZnO thin Films

Compared to powder diffraction data of zincite (wurtzite) structure (JCPDS 36-1451), the XRD patterns of all the films indicated enhanced intensities for the peaks corresponding to (0 0 2) plane, indicating preferential orientation along the c-axis as shown in Figure 2.6. In view of the fact that c-axis oriented ZnO films were also obtained by using other fabrication methods such as chemical deposition [59], RF sputtering [62] and laser ablation [63], this fact could be a common aspect in all ZnO thin films. It is believed that the preferential orientation is due to the minimization of surface energy and internal stress [51]. Also, the c-orientation might be as a result of the facilitated growth of the film along the c-axis due to the highest atomic density found along the (0 0 2) plane [64].

2.4.4. Optical Properties

Yang *et al* [65] reveals that ZnO thin films prepared under different conditions produce similar transmission spectra with close optical transmittance values. The optical transmittance of ZnO thin films is high in visible range (between 75% and 95%) within spectral domain of 450–1300 nm [66]. This is important for applications of these films as transparent conductive electrodes and solar cell windows. It has been observed that the transmittance of ZnO thin films decreases with increases in number of coating cycles [66]. Other studies have also shown that the transmittance of ZnO thin films increases with increase in annealing temperature. The increase in transmittance with the increasing of the annealing temperature may be due to decreasing optical scattering caused by densification of the ZnO film.

It is known, that pure compounds like ZnO are characterized by a sharp transmission edge at a photon energy corresponding to the forbidden energy band gap of the respective

intrinsic semiconductor material. In the lower wavelength range (300–370 nm) the values of the transmission coefficient are determined by the polycrystalline structure of the films (crystallite shape and size, roughness of the film, characteristics of grain boundaries [67].

2.4.5. Electrical Properties

The plot of conductivity (σ) versus the reciprocal of temperature ($1000/T$, 1/K) of ZnO nanostructured thin film is shown in Figure 2.7 [68]. The conductivity curve of the film indicates different three regions (I, II and III). The regions I and III corresponds to different conduction mechanisms. In I and III regions, electrical conductivity increases with increasing temperature. As the temperature is increased more charge carriers in turn overcome the activation energy barrier and participate in the electrical conductivity.

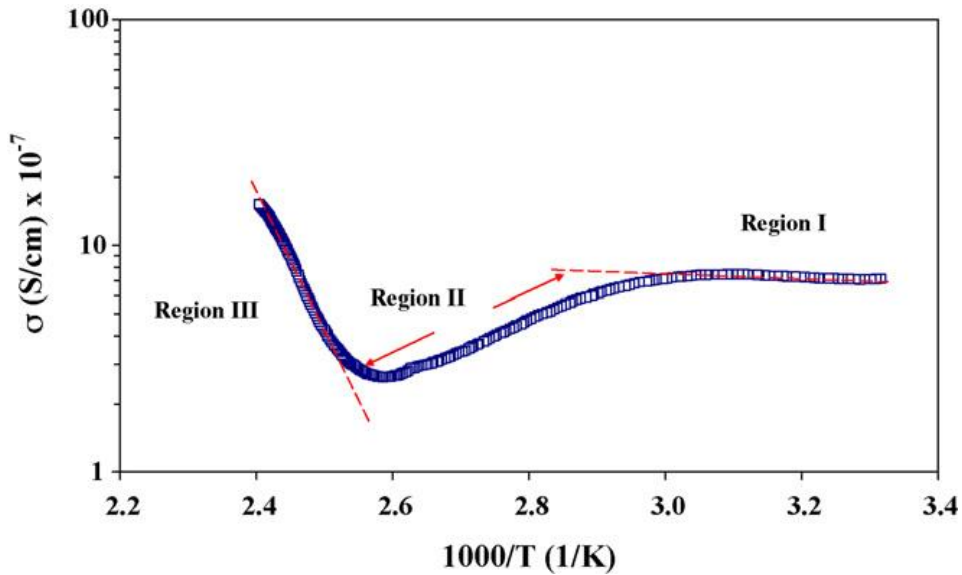


Fig. 2.7. Graph of Conductivity versus Inverse of Temperature of the ZnO Thin Films [68].

The electrical conductivity of the ZnO film can be analyzed by the well-known Arrhenius relation,

$$\sigma = \sigma_0 e^{-E/k_B T} \quad (2)$$

where σ_0 is the pre-exponential factor, k_B is the Boltzmann constant T is the temperature in Kelvin and E is the activation energy. E_I and E_{III} activation energy values for I and III regions were calculated from the linear portions of Figure 2.7, respectively. The obtained E_I and E_{III} values were found to be 25.8 meV and 1.32 eV, respectively. The magnitude of the activation energy $E_{III} = 1.32$ eV obtained from conductivity data is small in comparison with optical band gap energy ($E_g = 3.30$ eV). This confirms that while the activation energy corresponds to the energy required for conduction from one site to another, the optical band gap corresponds to another transition. These activation energies at different temperature regions (I and III) indicate the presence of two donor levels. These levels are the shallow and deep donor levels in the band gap of the ZnO semiconductor. The value of 25.8 meV corresponds to the shallow donor level, while the value of 1.32 eV corresponds to the deep donor level. Thus, it can be concluded that in region III, the electrical conductivity of the ZnO thin film is thermally activated from the deep donor level to the conduction band. The region II is a transition region, in which more charge carriers are ionized from the shallow donor level and then the charge carriers are depleted and in turn, the electrical conductivity decreases with increase of temperature until the activation of charges in the deep donor level starts. Room temperature electrical conductivity value was found to be 7.261×10^{-7} S/cm. This conductivity value is higher than that of nanophase zinc oxide prepared by precipitation method [68]. Lee *et al.* [69] reported that the conductivity for nanophase ZnO having particle size of 60 nm is in the range 2×10^{-6} to 2×10^{-4} S/cm at 450 - 600 °C. The increase in conductivity of nanostructured ZnO thin film is attributed to the trapping of electrons in the grain boundaries. The grain size (28 nm) of the nanostructured ZnO studied is less than the Debye length (~30 nm for nano ZnO) and this suggests accumulation of

electrons at grain boundary and in turn, increases conductivity. The film obtained is an n-type semiconductor material due to the presence of intrinsic defects such as oxygen vacancies and Zn interstitials [70].

2.5. Industrial Applications of ZNO

Because of its diverse properties, both chemical and physical, zinc oxide is widely used in many areas. It plays an important role in a very wide range of applications, ranging from tyres to ceramics, from pharmaceuticals to agriculture, and from paints to chemicals. Figure 2.8 shows worldwide consumption of zinc oxide by region [71]

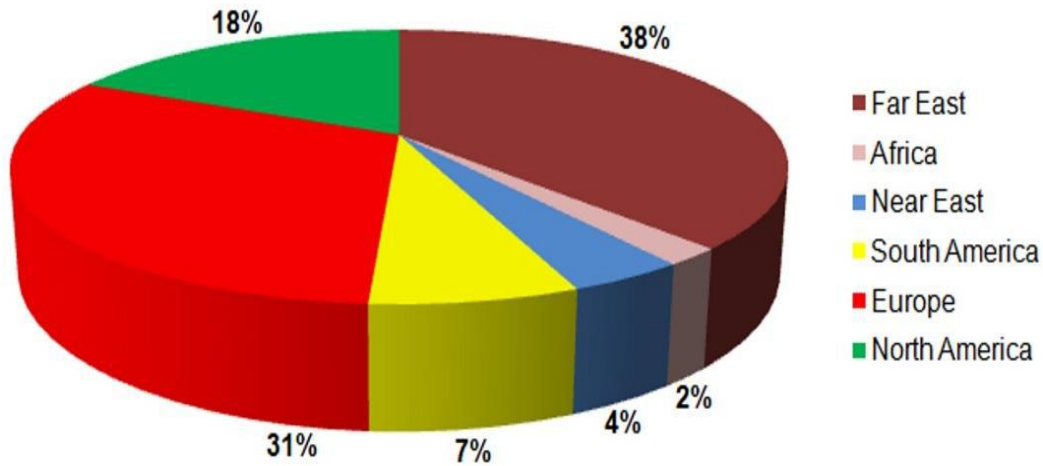


Fig.2.8. Worldwide consumption of zinc oxide [71].

In Figure 2.9 [71] summarized application paths of ZnO are presented. However, the focus of the research by Kolodziejczak – Radzimska and Jesionoski [71] concentrated on the Electronics and Electrotechnological industries as well as Photocatalysis.

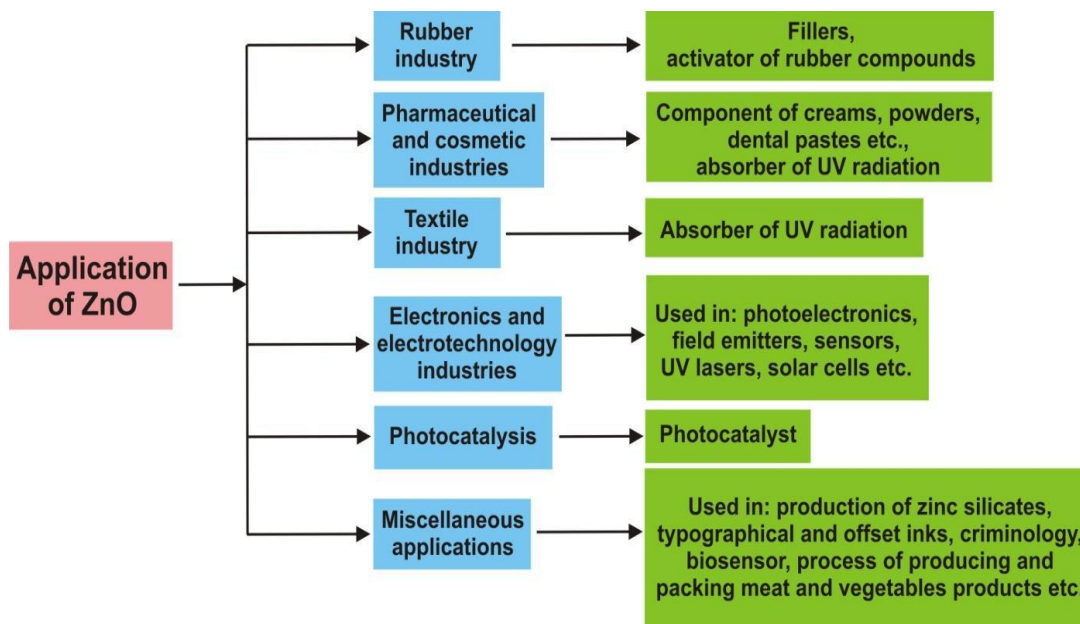


Fig.2.9. Schematic representation all the application of ZnO mentioned in the text [71].

2.5.1. Rubber Industry

Global production of zinc oxide amounts to about 105 tons per year, and a major portion is consumed by the rubber industry to manufacture various different cross-linked rubber products [72]. These rubber products include car tyres.

2.5.2. The Pharmaceutical and Cosmetic Industries

Due to its antibacterial, disinfecting and drying properties [73, 74], zinc oxide is widely used in the production of various kinds of medicines. It was formerly used as an orally administered medicine for epilepsy, and later for diarrhoea. Currently it is applied locally, usually in the form of ointments and creams, and more rarely in the form of dusting powders and liquid powders. ZnO has properties which accelerate wound healing, and so it is used in dermatological substances against inflammation and itching. In higher concentrations it has a peeling effect. It is also used in suppositories. Additionally it is used in dentistry, chiefly as a component of dental pastes, and also for temporary fillings. ZnO

is also used in various types of nutritional products and diet supplements, where it serves to provide essential dietary zinc [75].

2.5.3. The Textile Industry

For textile applications, not only is zinc oxide biologically compatible, but also nanostructured ZnO coatings are more air-permeable and efficient as UV-blockers compared with their bulk counterparts [76]. Therefore, ZnO nanostructures have become very attractive as UV-protective textile coatings. Different methods have been reported for the production of UV-protecting textiles utilizing ZnO nanostructures. For instance, hydrothermally grown ZnO nanoparticles in SiO₂-coated cotton fabric showed excellent UV-blocking properties [77]. Synthesis of ZnO nanoparticles elsewhere through a homogeneous phase reaction at high temperatures followed by their deposition on cotton and wool fabrics resulted in significant improvement in UV-absorbing activity [78]. Similarly, ZnO nanorod arrays that were grown onto a fibrous substrate by a low-temperature growth technique provided excellent UV protection [79].

2.5.4. The Electronics and Electrotechnology Industries

Of particular interest to this study is the understanding of ZnO as a semiconductor and an important semiconductor for that matter which, as already noted earlier, has a range of applications in electronics and electrotechnology.

These properties mean that it can be used for the production of light-permeable electrodes in solar batteries. It also has potential uses as a transparent electrode in photovoltaic and electroluminescent equipment and is a promising material for UV-emitting devices [71].

Zinc oxide is also used in gas sensors. It is a stable material whose weak selectivity with respect to particular gases can be improved by adding other elements. It is most commonly used to detect CO and CO₂ (in mines and in alarm equipment), but can also be used for the detection of other gases (H₂, SF₆, C₄H₁₀, C₂H₅OH). The zinc oxide used in the production of such equipment is obtained by a variety of methods (chemical vapour deposition, aerosol pyrolysis or oxidation of metallic zinc); it is important to control the process temperature, since this determines the properties of the product [80].

One of the most important applications of ZnO in electronics is in the production of varistors. These are resistors with a non-linear current-voltage characteristic, where current density increases rapidly when the electrical field reaches a particular defined value.

2.5.5. Photocatalysis

Intensive scientific work has taken place in recent years on photocatalysis. In this process, an electron-hole pair is produced below the intensity of light by means of oxidation or reduction reactions taking place on the surface of the catalyst. In the presence of a photocatalyst, an organic pollutant can be oxidized directly by means of a photogenerated hole or indirectly via a reaction with characteristic reactive groups (ROS), for example the hydroxyl radical OH·, produced in solution [71]. The most commonly used catalysts are TiO₂ and ZnO. TiO₂ exhibits photocatalytic activity below the intensity of UV light. ZnO provides similar or superior activity to that of TiO₂, but is less stable and less sensitive to photocorrosion [82]. Better stability, however, is provided by zinc oxide of nanometric dimensions, which offers better crystallinity and smaller defects [80]. The photocatalytic activity of ZnO can be further improved, and the range of the visible spectrum for zinc oxide can be extended, by adding other components [83].

Other studies by numerous researchers prove that ZnO offers unique photocatalytic properties, making it possible for it to be used as a photocatalyst in the process of degradation of various substances [88].

2.5.6. Other Miscellaneous Applications

Apart from the applications mentioned in previous sections, zinc oxide can also be used in other branches of industry, including for example concrete production. The addition of zinc oxide improves the process time and the resistance of concrete to the action of water. Also, the addition of ZnO to Portland cement slows down hardening and quenching (it reduces the gradual evolution of heat), and also improves the whiteness and final strength of the cement [49].

ZnO is also used for the production of typographical and offset inks. It imparts good printing properties (high fluidity). The addition of ZnO means that the inks have better covering power, pure shade and high durability, and prevents darkening. Zinc oxide is also used in pigments to produce shine.

Zinc oxide also has uses in criminology such as in mechanical fingerprint analysis. It is also an ingredient in cigarette filters, as it selectively removes certain components from tobacco smoke. Filters are made of charcoal impregnated with ZnO and Fe₂O₃, which remove significant quantities of HCN and H₂S from tobacco smoke without producing a smell. It also removes Sulphur and its compounds from various liquids and gases, particularly industrial waste gases. ZnO also removes H₂S from hydrocarbon gas, and desulphurizes H₂S and other Sulphur components.

ZnO and its derivatives are also used as an additive to car lubricating oils, reducing consumption and oxygen corrosion. Zinc oxide has also been used in various types of lubricants, such as those with EP additives, vibration-resistant lubricants and solid lubricants. In the future, advantage may also be taken of the adhesive properties of ZnO [90].

CHAPTER THREE

EXPERIMENT AND CHARACTERISATION PROCESSES

2.6. Introduction

In this chapter the experimental procedure that was followed in preparation and characterization of spin coated ZnO thin films is described. In Section 3.2 the description of the equipment (Spin Coater) and its parts used in sample preparation are given. Substrate cleaning procedure is also included in this section. Section 3.3 gives film deposition and annealing process. Electrical, structural and surface morphology of spin coated ZnO thin films obtained in this study are described in section 3.4 while optical properties of spin coated ZnO thin films are presented in section 3.5.

3.2. Sample Preparation

3.2.1. Substrates Preparation

In this study Soda Lime Glass (SLG) slides were used as substrate. These substrates were thoroughly cleaned by first degreasing using Trichloroethylene sonification. They were then placed in 2-propanol followed by immersing them in methanol, each of these processes lasting for 5 minutes. The glass substrates were then rinsed with de-ionised (DI) water before being dried by blowing them with pure Nitrogen (N_2) gas. Then the SLG slides were stored in desiccators containing blue silica gels. This kept the substrates dry and dust-free ready for use.

3.2.2. Spin Coater

WS – 400 BZ Spin Coater was used for deposition of spin coated ZnO thin films. The system contains the following parts spin coating chamber, control unit, power supply, vacuum pump, pressure pump and the nitrogen supply unit.

A schematic diagram of the spin coater in question is as shown in Figure 3.1.



Fig.3.1. WS – 400 BZ Spin Coater (Department of Physics -UNZA)

3.2.2.1. Spin Coating Chamber

Spin Coating Chamber contains a motor, Aluminum Chuck/CD cake box and Plexiglas base. The chamber is roofed with chamber cover which prevents escape of dangerous fumes generated during coating process.

3.2.2.2. Control Unit

The control unit is composed of a small screen and soft touch control keys at the bottom which are used for programming of the deposition. Once the program is completed the 'Start' is used to run the program and the 'Pause' or the 'Stop' key are used to stop the program from running.

The Control Unit can also be connected to a computer through an extension cable and through this connection programming can be done via the computer as well as running the program through the computer. This can also enable Blue Tooth operation of the spin coater once the software installation have been made.

3.2.2.3. Power Supply

An AC power supply was used to run the spin coater, the pressure pump and the vacuum pump.

3.2.2.4. Vacuum pump

The Spin Coater must be connected to a vacuum pump which provides vacuum suction to the substrates to keep in place during deposition.

3.2.2.5. Pressure pump

The pressure pump is used to supply pressure on the deposition syringes to enable them release the solution to be deposited on the substrates.

3.2.2.6. Nitrogen supply

The nitrogen supply is used to create a clean dry environment in the deposition chamber which is needed in order to control the humidity in the said chamber.

3.3. Thin Film Deposition

3.3.1. Preparation of Spin - Coated ZnO Thin Films Precursor Solution

The precursor solution was synthesized using appropriate quantities of aqueous Zinc Acetate dehydrate, 2- Methoxyethanol and Ethanolamine. The mixing was done on a hot plated magnetic stirrer for 2 hours at a temperature of 70 °C. A clear solution was obtained and allowed to cool down to room temperature before the coating was commenced.

The diagram on Figure 3.2 shows the spin coating process from the preparation of the precursor solution, coating on glass slides and preheating up to the annealing process. For the samples in question four glass slides were chosen and prepared in the manner described in subsection 3.2.1. This was followed by cleaning the spin coater chamber, ensuring that all the components were connected and setting the program to the required parameters. Then program was run as set.

The first glass slide was run through six coating cycles, the second one through eight coating cycles, the third one through ten coating cycles and the fourth was treated to twelve coating cycles. Each slide was coated and placed in a sample tray labeled from A to D to avoid mixing up during other processes. There were no labels placed on the slides themselves.

Drying was done by placing the sample in an Ashing Oven with a fixable thermostat to maintain the temperature at 200°C. The temperature was maintained at the same level and the door to the oven was opened and closed at the minimum for the entire sample to avoid heat losses.

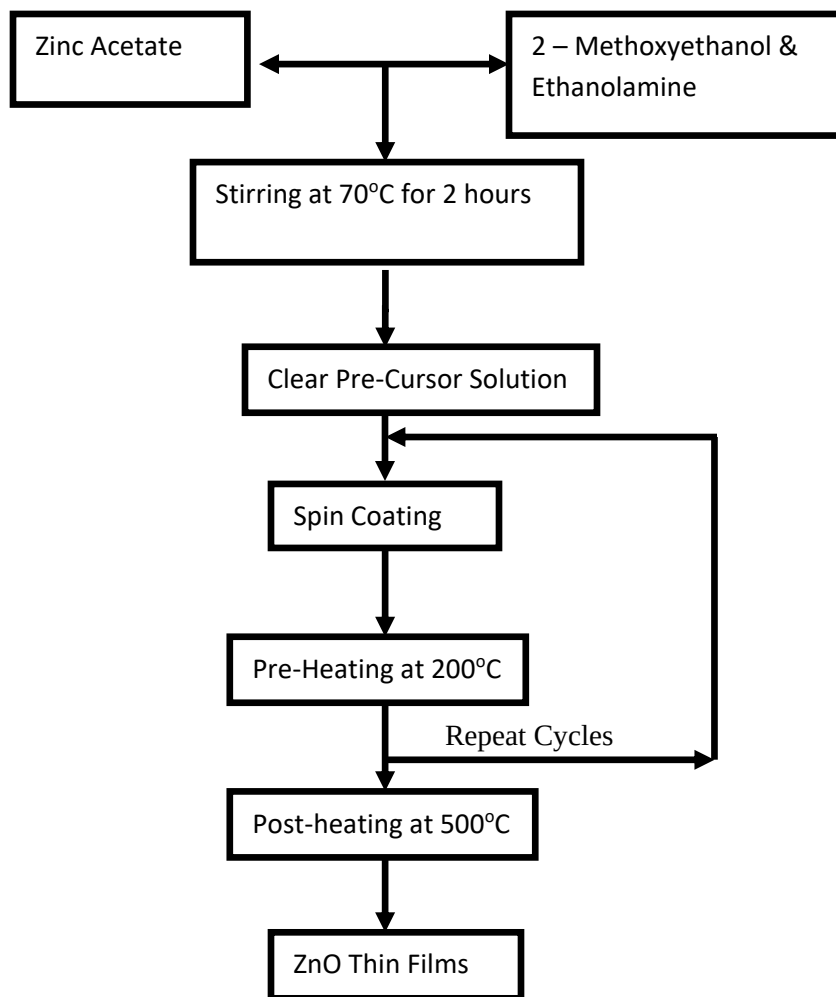


Fig. 3.2. Flow chart of the spin coating process

3.3.2. Films Deposition

The following procedure was maintained when preparing Spin - Coated ZnO thin films;

- (i) Substrate was positioned at the centre of the chuck.
- (ii) The deposition syringe was filled with the precursor solution and set in the right position.
- (iii) The pressure and nitrogen gauges were set and readied for operation.
- (iv) The program was set on the Control Unit, the spinning speed set at 3000 rpm for 60 seconds, the number of loops set at 1, the vacuum requirement turned on and all the connections secured.
- (v) The vacuum pump, the pressure pump and nitrogen supply unit were turned on and the program was ready to run.
- (vi) Once the spinning chuck came to a stop, the vacuum pump, the pressure pump and the nitrogen gas supply were turned off, and the substrate was removed using stainless tweezers.
- (vii) Lastly, solvent deposited on the substrate was dried at the temperature of 200°C for 2 minutes in the Ashing oven
- (viii) The procedure was repeated to get the desired number of coating cycles for each respective sample.

Shown in Figure 3.3 is the graphical expression of the spin coating process which shows the time taken for the spinning chuck to reach the required speed.

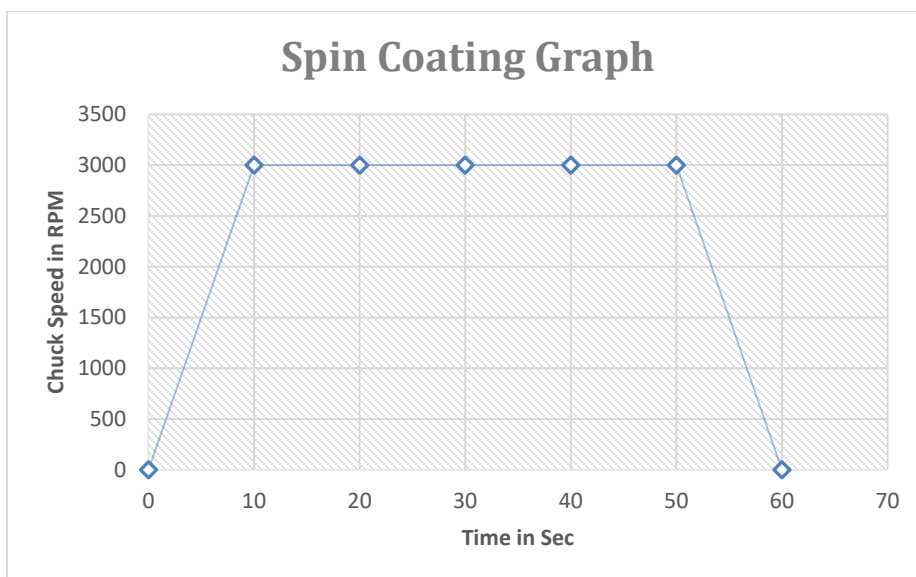


Fig. 3.3. The Spin Coating Graph

3.4. Annealing of Spin - Coated ZnO Thin Films

After drying of the sample in the oven the films were taken for annealing using the CVD XD-1200NT Rapid Tube Gas Annealing oven. The general steps during annealing were as follows;

1. The chamber was opened and a glass tube was replaced with a clean dry ceramic tube which is able to withstand temperatures of over 500 °C.
2. The samples were placed inside at the centre of the tube in direct alignment with the furnace thermocouple and the tube was left open on the ends to allow for inflow of air
3. The chamber was then closed and annealing program was set as indicated in Figure 3.4. The temperature was to rise from 0 °C to 500 °C in 30 min and stay at 500 °C for the next 50 min and reduce to 0 °C in 30 min.

4. The Furnace was then turned on for a specified period of time.
5. The furnace was allowed to cool down to room temperature
6. The samples were then removed using steel tweezers and placed respectively in small plastic containers labeled A, B, C and D in readiness for characterisation.

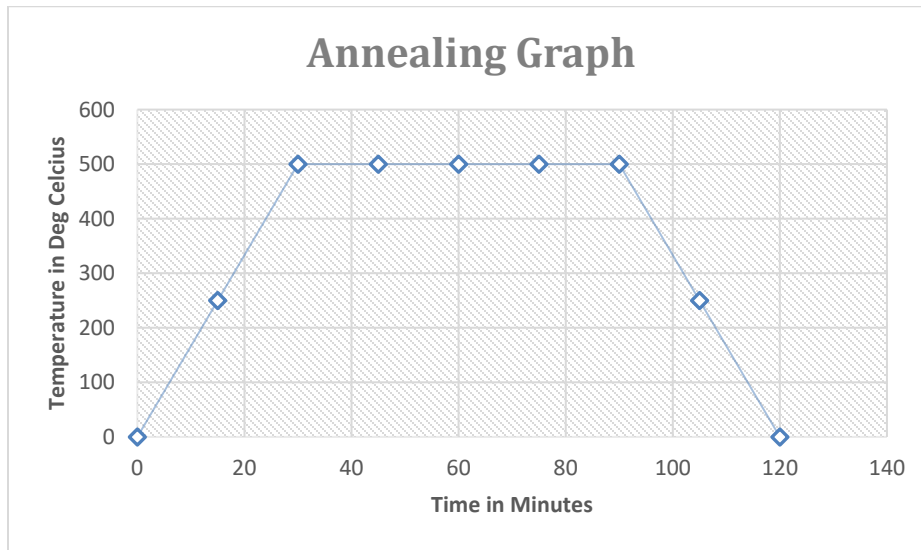


Fig. 3.4. Annealing Graph

3.5. Sample Characterization

This section discusses the characterization techniques which were used as well as the equipment used are presented.

3.5.1. XRD – Crystal Structure

The samples were pressed into sample holders specially designed for solid blocks and were then analysed using Rigaku smart Lab XRD instrument operated in out-of-plane mode,

with Cu K α 1 radiation wavelength of 1.54 Å, in theta/2-theta configuration with a Sc-70 detector. The XRD was set to the following operational parameters: voltage was set at 45 kV, current was set at 200 mA and the scan speed was set to 2 deg/min.

3.5.2. Electrical Measurement

3.5.2.1. Four Point Probe (FPP)

Measuring the Voltage through the inner probes allows the measurement of the substrate resistivity. The Four Point Probe (FPP) used in this study is the Jandell Model RM3000 which has a digital screen which displays the current and the voltage from the sheet. The pictorial illustration of the FPP is shown in Figure 3.5.

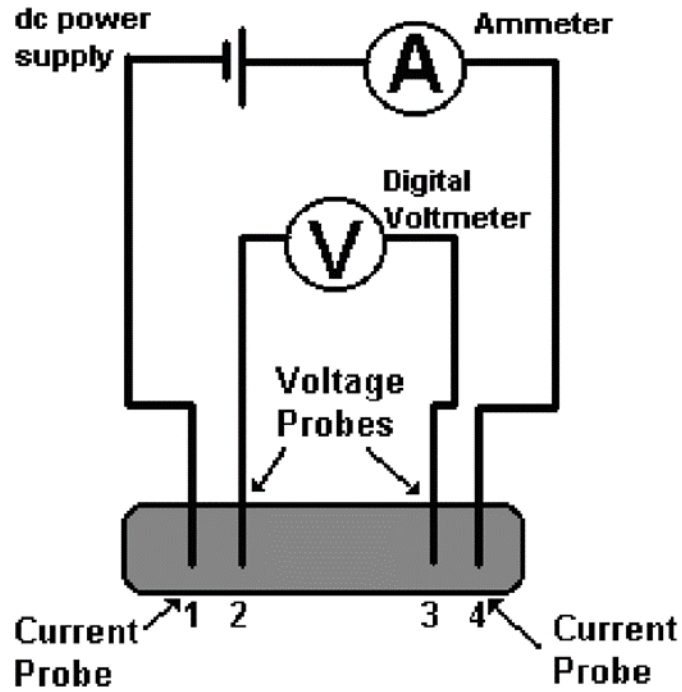


Fig. 3.5. Pictorial illustration of the Four Point Probe [95]

A current was passed through the outer probes which induced a voltage in the inner voltage probes. The junction between the n and p -type materials acted as an insulating layer and the casing kept the cell in the dark. The FPP used is shown on Figure 3.6.

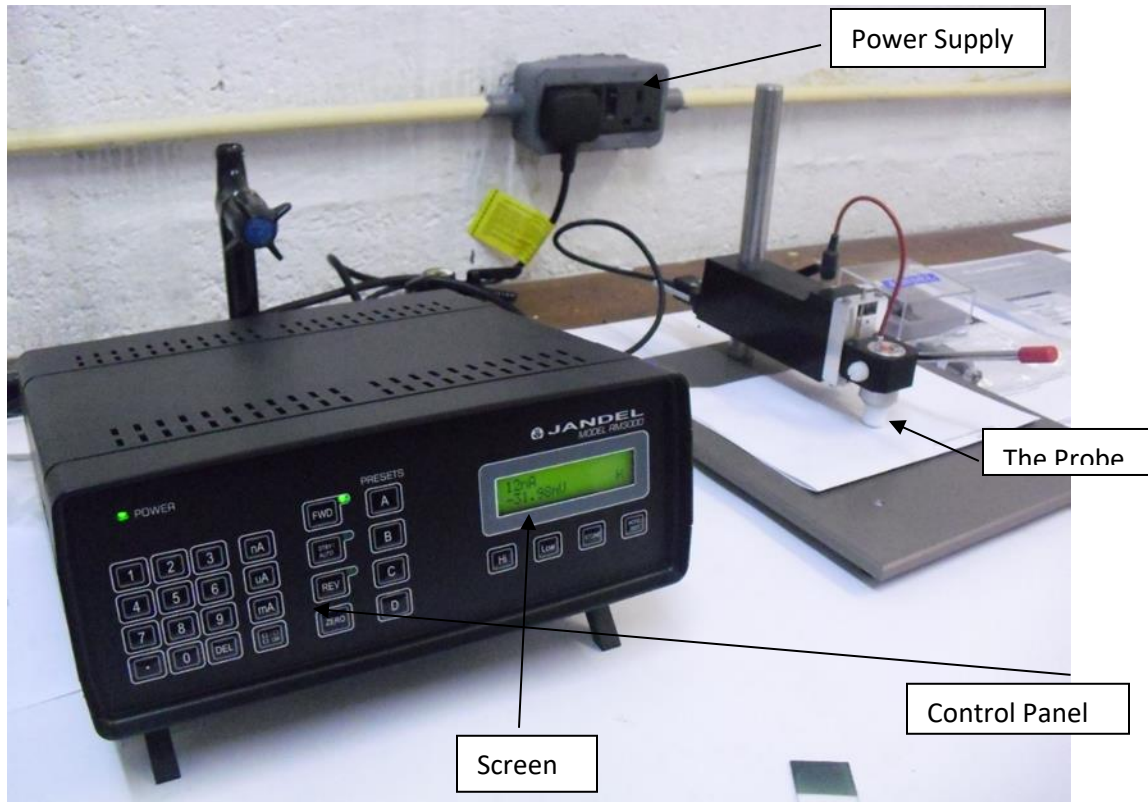


Fig.3.6. The Jandel Model RM3000 Four Point Probe (Dept. Chemistry, UNZA)

Before the measurements, the FPP was cleaned and pretested before introducing the samples. The pretesting was done to ensure that all the parameters of the probe were operating normally. Once this was done the samples were introduced one at a time into the sample chamber and a current value was selected and the corresponding resistivity obtained. The next current value was selected and then corresponding value of the resistivity obtained. This was done for a total set of six current values and their corresponding resistivity for all the four samples. The resulting values were tabulated and

used to produce graphical representations which are discussed in the results and analysis section.

3.5.2.2. Hall Effect Measurement

The measuring system illustrated in Figure 3.7 shows how measurements utilizing permanent magnet or electromagnet were possible and how suitable they are for the determination of the influence of disturbances on the measured mobility. Special feature of the equipment used was that it was possible to generate a magnetic field due to the air-cooled magnet with fast switching magnetic pole. This had the advantage of minimising excessive heat generation in the samples. It also exhibited lower false thermal voltages in sample contacts.

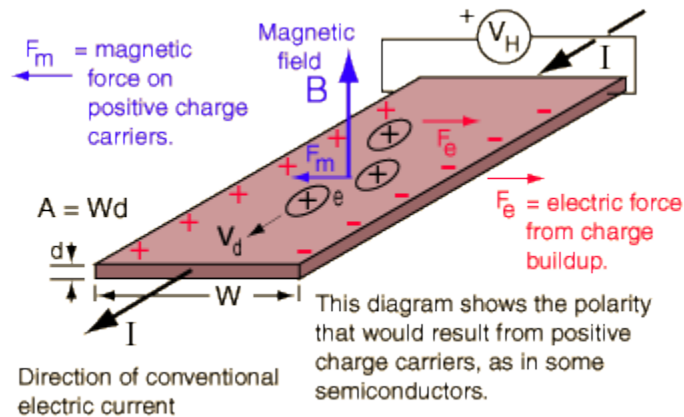


Fig. 3.7. Illustrative diagram of the Hall Effect Probe [96]

In this study, the measurement of large magnetic fields in the orders of Teslas was done by making use of the Hall Effect [97, 98]. A thin film Hall probe was placed in the magnetic field and the transverse voltage (on the order of microvolts) is measured.

The experiment was conducted by allowing a constant flow of the magnetic field B through the thin films in which a current I was allowed to flow through the contacts which were made at the edges of the films. The contacts were made using two metal electrodes spring clips at each end of the sample and marked a and b .

The current used was less than 0.80 A to avoid damaging the sample through overheating as well as ensuring reliable results. The expected Hall voltage was generally small and needed a highly sensitive instrument to measure and in this case a Philips Microvoltmeter Model PM2434 was used. When using this instrument special care was provided and note was taken to measure the deflection before each measurement. This was done to take note of possible drifts caused by thermal voltages in the circuit because the thermal voltage drift can affect the Hall voltage reading for zero fields and zero current.

3.5.3. Optical Properties

This subsection details the characterization methods and equipment which were used to analyse the ZnO thin films for their optical properties. The areas covered include the transmission properties, the absorption cut off frequency which was used to calculate the band gap and finally determination of the thickness of the coating.

3.5.3.1. Transmission Measurement

Perkin Elmer Lambda 19 Spectrophotometer shown in Figure 3.8 was used to determine the transmission spectra of the spin coated ZnO thin films. Spectrophotometry measurements were carried out in the wavelength range $300 \leq \lambda \leq 3200nm$.

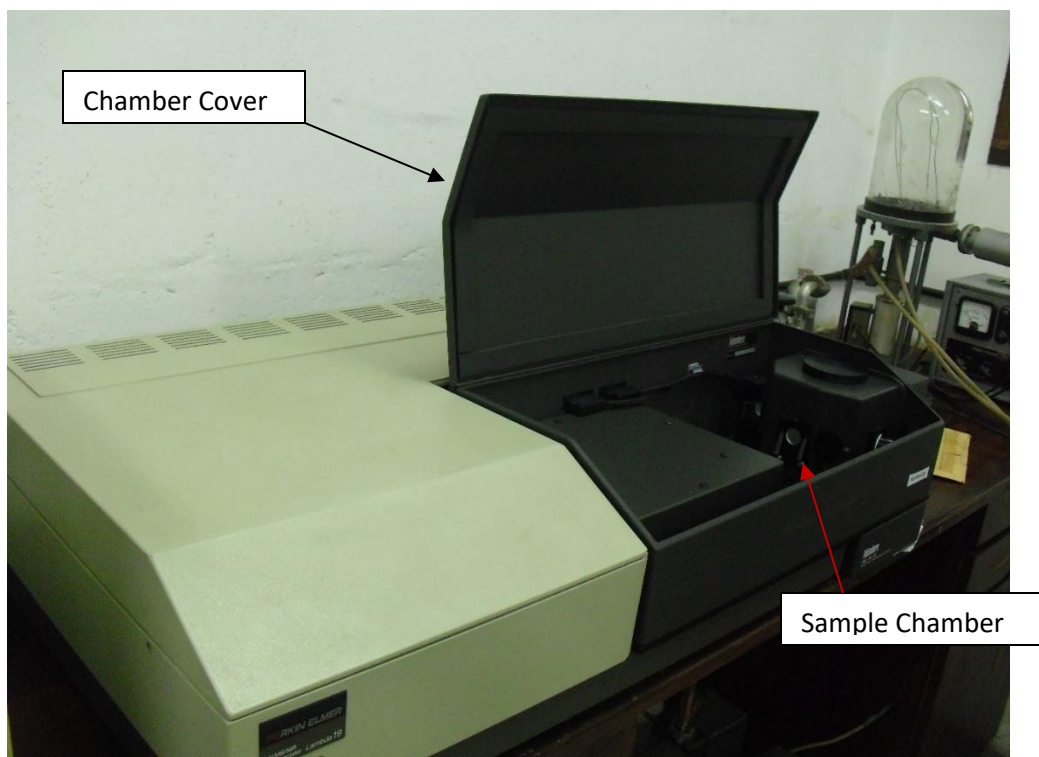


Fig. 3.8. Perkin Elmer Lambda 19 Spectrophotometer (Dept. Physics, UNZA)

The Spectrophotometer was connected to a computer on which operational software was installed which can two different modes, reflectance and transmission.

3.5.3.2. Band Gap Measurement

The band gap measurement was carried out using a UV-2600 Shimadzu UV-Vis spectrophotometer along with 150-mm integrating sphere as shown in Figure 3.9. The spectrophotometer was connected to a computer and has operational software which manages the scanning process. The software was used to generate and manage the obtained data. The sample was run using the parameters listed in Table 3.1.



Fig. 3.9.The UV – Vis spectrophotometer (Dept. Physics, UNZA)

The holder, Figure 3.10 with powder sample in is clamped on the external port of the integrating sphere. A low volume powder sample press was used.

Table 3.1. UV- Vis spectrophotometer parameters

Wavelength range	250-800 nm
Spectral Band Wavelength	2 nm
Data interval	1 nm

The entrance port of the integrating sphere was kept open to minimize the specular reflection component which can cause fringes or noise at the extreme end of the range. The spectra were recorded in absorbance versus wavelength and reflectance versus wavelength modes. It was possible to place a second sample in the second compartment where the integrating sphere was mounted without interfering with the main sample compartment.

The samples were placed one at a time in the sample holder and once they were held in place, the scan was done by running the scan program on the computer screen. Once the scan was completed then the computer generated the graphs. The process was repeated for all the four samples and a graph produced for each one of them was plotted.

3.5.4. Thickness measurement

The thickness of the ZnO film was measured using the Valendor (Mitutoyo Corp) Thickness Gauge with sensitivity readings in nanometers.

The thickness was obtained by measuring the step between the coated and uncoated parts. The readings were recorded and used in the subsequent analysis of the samples. Figure 3.10 shows the key functional features of the Valendor.

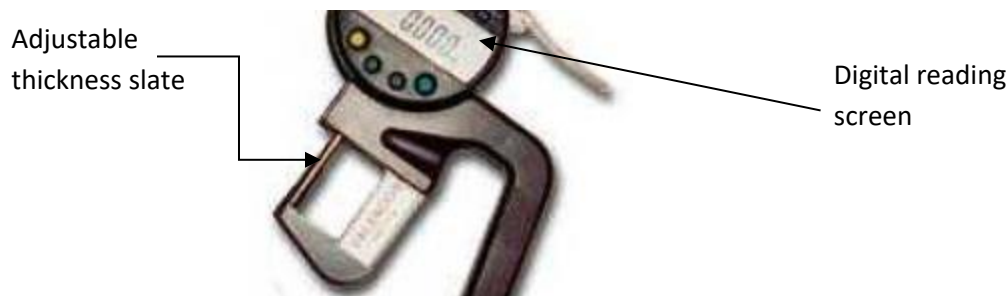


Fig. 3.10. Valendor thickness gauge (Laboratory Dept., ZABS)

The thickness readings were obtained by placing the samples on the adjustable thickness slate which immediately reflects any difference to the digital screen in micrometers. The measurements were taken by moving the gauge slate along the coated and uncoated areas of the thin films and noting the difference. The recorded differences were tabulated and the

average of all the figures collected was evaluated and used in a number of calculations requiring the thickness of the films.

3.5.5. Measurement of Surface Morphology

The surface morphology or topography was done using the SEM which uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. Samples were placed in a retractable sample holder. Data was collected over a selected areas of the surface of the samples through a scanning probe. A 2-dimensional image was generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width were imaged in a scanning mode using conventional SEM techniques which produced magnification ranging from 20X to approximately 30,000X and spatial resolution of 50 to 100 nm. The images were collected in soft copy form for analysis

CHAPTER FOUR

RESULTS AND DISCUSSIONS

3.6. Introduction

In this chapter the experimental results are discussed. The influences of deposition conditions of the spin coating on electrical, optical and structural properties of ZnO are also discussed. The parameters used include precursor concentration, annealing conditions and film thickness. Optical properties studied include transmittance, reflectance, absorption, and the band gap of ZnO. The investigated electrical properties include electrical resistivity, carrier concentration, charge mobility, and sheet concentration. Surface morphology and film composition of spin coated ZnO thin films are also investigated in this study.

3.7. Physical Appearance of Spin Coated ZnO Thin Films

The spin coated ZnO thin films shown in Figure 4.1, appeared grayish-brown in colour, after drying and annealing. Some film surfaces were smooth and uniform while others were not, but with good adherence to the SLG substrate.



Fig. 4.1. Samples of ZnO thin films on Glass substrates

3.8. Film Thickness Measurement

The ZnO film thickness measurements were carried out and the readings were in the range between 1.2 μm to 1.5 μm . These readings were used in subsequent calculations and other workings

3.9. Surface Morphology of ZnO Thin Films

The surface topography of thin films is a very important tool in investigating the microstructure of the films. The SEM micrograph of ZnO thin films annealed at 500 $^{\circ}\text{C}$, is shown in Figure 4.2. The micrograph depicts the presence of tightly packed grains. The SEM image was taken at 25, 000X magnification. The image showed that ZnO crystals are spherical in shape with smooth surface and the size of the grains averaging 45 nm.

From Figures 4.2 and 4.3, it can be seen that the ZnO thin films are porous and the average crystallite size of the films is about 45 nm which is in acceptable agreement with XRD data [58, 59].

The surface of the thin film coated with six layers or coated six times, contained some cracks which can be alluded to atoms not being tightly packed in fewer layered films while no crack were observed for higher layered films because several layers filled the existing gaps left in previous coating. The thickest film was layered twelve times. Thus the morphological differences of the ZnO thin films affect their optical absorption edges, as can be seen in Figure 4.2. As the layers of coating increased from six to twelve, the crystallite size increased and the films became denser. These results are in good agreement with what has been obtained in similar studies [99].

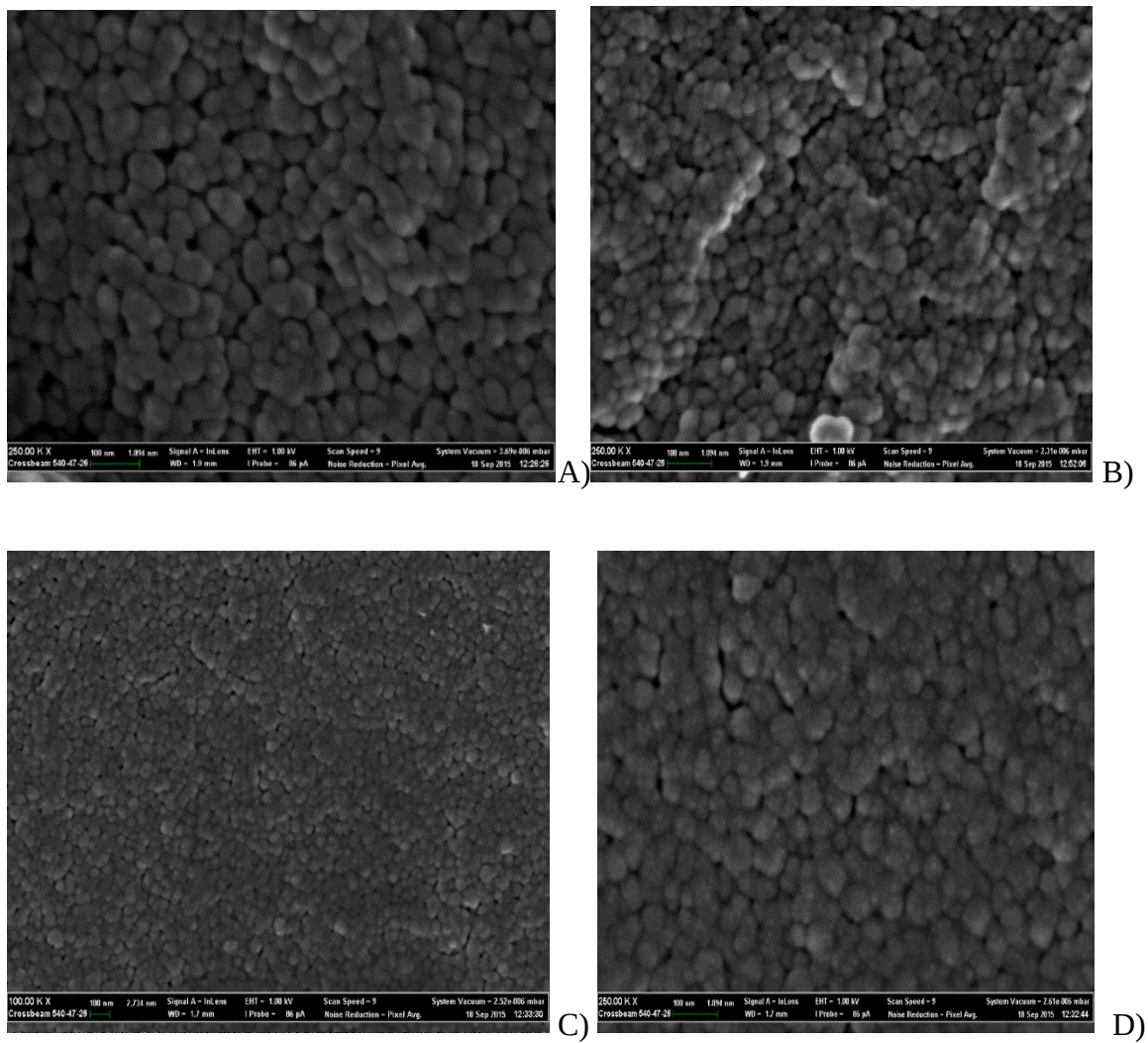
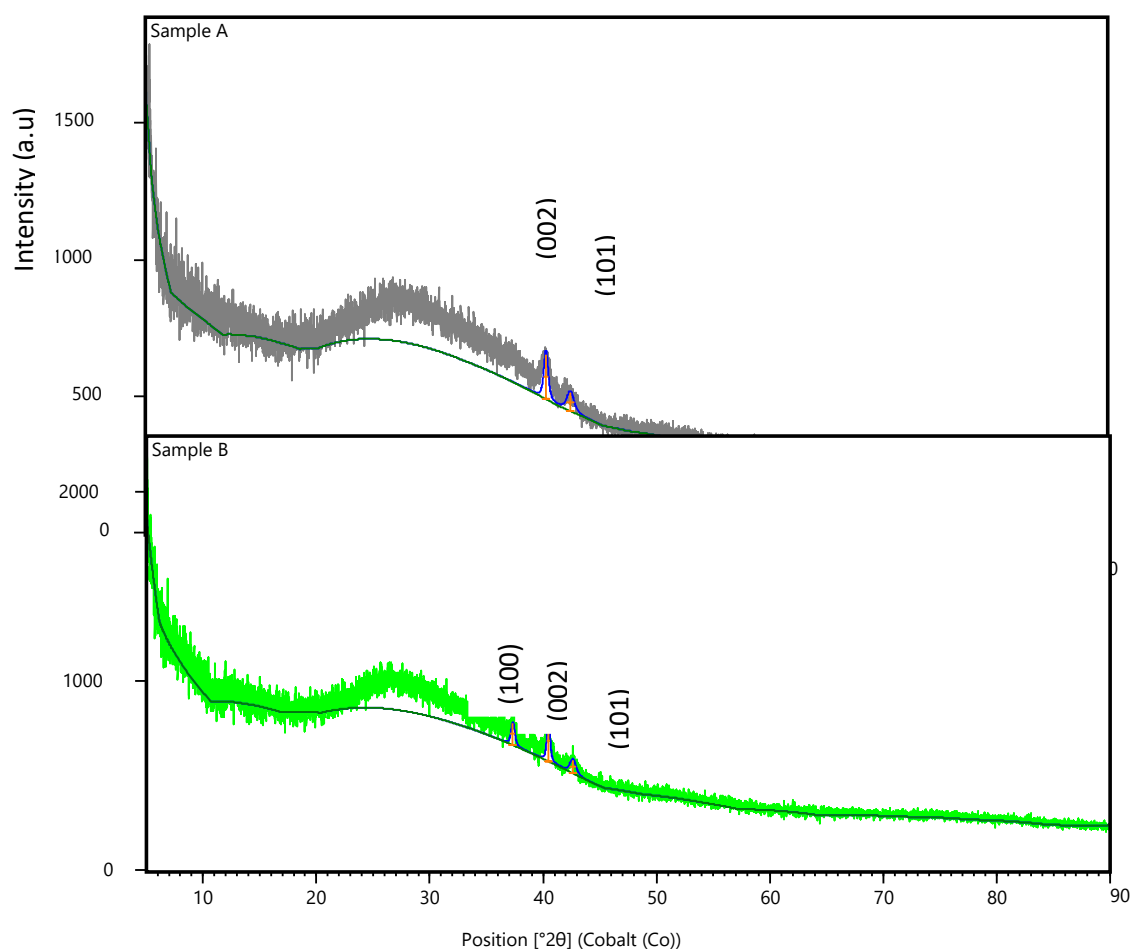


Fig.4.2. SEM microstructure of ZnO films (A-D)

3.10. XRD Patterns of ZnO Thin Films

The XRD pattern of the dried gel powder of ZnO annealed at 500°C for one hour is shown in Figure 4.3 (A-D). From these figures, the well-crystallized diffraction peaks were observed in the graphs and they are labeled (100), (002) and (101). The XRD parameters of ZnO dried gel powder annealed at 500°C for one hour are displayed in Table 4.1. The data in Table 4.1 shows that the calculated d-values are in good agreement with those taken from the Joint Committee of Powder Diffraction Standards (JCPDS) card file data for ZnO powder [100, 101]. This is in a situation where the prepared material has crystallized in a hexagonal wurtzite ZnO.



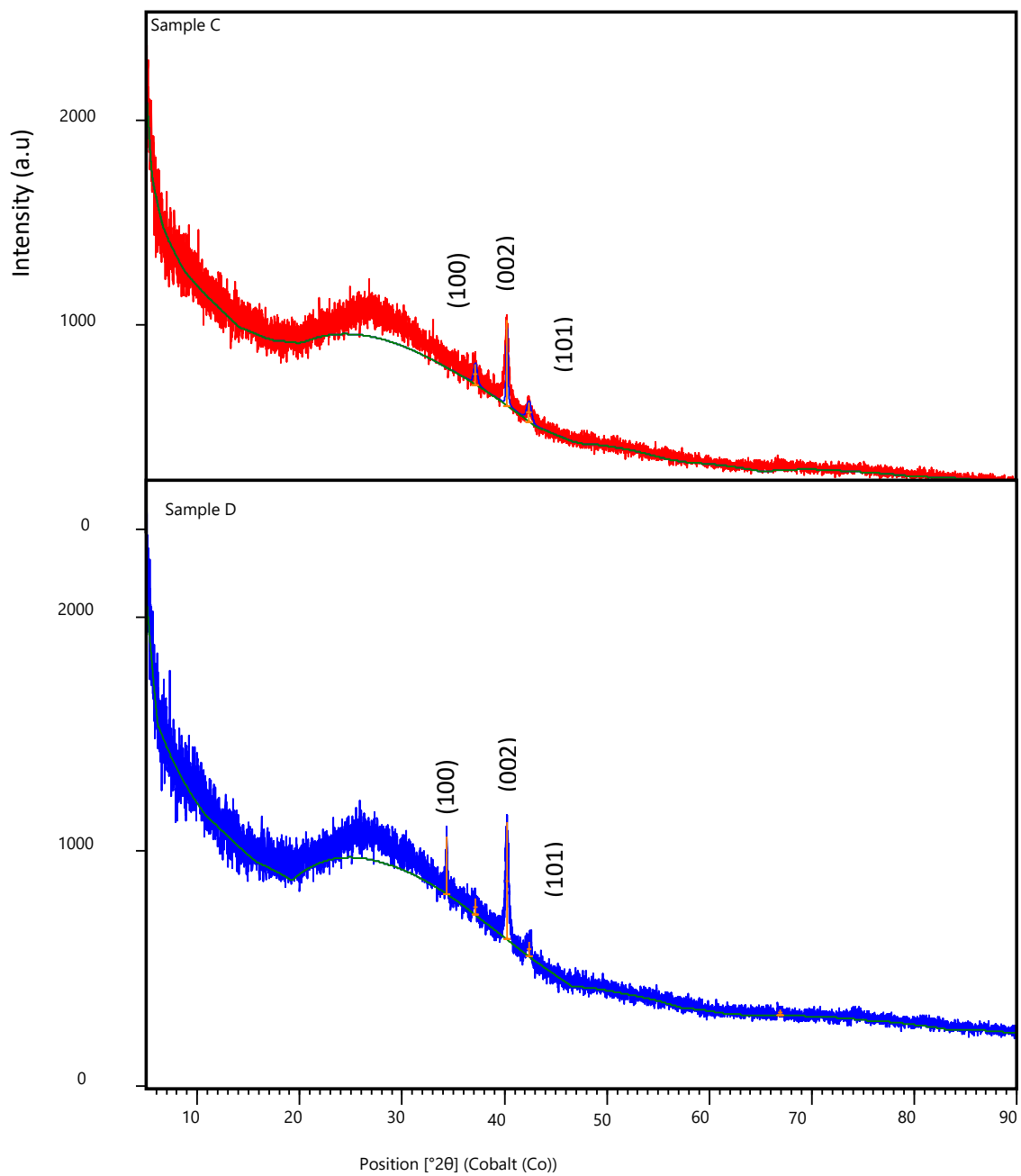


Fig. 4.3. XRD Patterns for the ZnO Thin Films

Table 4.1: The XRD Parameters of (h k l),

h k l	ZnO Prepared in this Work		JCPDS 36-1451	
	2 θ°	d-Value ($\text{\AA}^\circ$)	2 θ°	d-Value ($\text{\AA}^\circ$)
1 0 0	35.720	2.8186	35.770	2.8143
0 0 2	39.320	2.6108	39.422	2.6033
1 0 1	42.120	2.4847	42.253	2.4759

3.10.1. Orientation of ZnO Thin Films

Annealing was done for 1 hour so that the quality of the films and their crystallisation was influenced more by heating rather than by the heating time. When compared to powder diffraction data of Wurtzite structure (JCPDS 36 – 1451), the XRD patterns of all the films showed enhanced intensities for the peaks corresponding to (002) plane depicting a preferential orientation along the c - axis. The relative intensity of peaks corresponding to the (002) can be said to increase with temperature [102].

In view of the fact that c-axis oriented ZnO films have also been prepared by using other fabrication methods such as chemical deposition [103], RF sputtering [104] and laser ablation [105], this fact could be a common aspect in all ZnO thin films. It is believed that the preferential orientation is due to the minimization of surface energy and internal stress [106]. Also, the c-orientation might be as a result of the facilitated growth of the film along the c-axis due to the highest atomic density found along the (0 0 2) plane [107].

3.10.2. c-Axis Lattice Constants of ZnO Thin Films

The lattice parameters were calculated by using the following formula:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + k^2 + hk}{a^2} \right) + \frac{l^2}{c^2} \quad (3)$$

where a and c are the lattice parameters and d_{hkl} is the crystalline surface distance for $h k l$ indices. Firstly the values of lattice parameters from the X-ray diffraction data were calculated followed by the values of strain along the c-axis (ε_{zz}) by using the formula [108]:

$$\varepsilon_{zz} = \frac{c - c_0}{c_0} 100\% \quad (4)$$

where c is the lattice parameter of the strained ZnO films calculated from XRD data and c_0 (5.207) is the unstrained lattice parameter of ZnO. At the same time, the strain can be negative (compressive) or positive (tensile). The lattice parameters of ZnO thin films, yielded a hexagonal unit cell which was very close to the parameters of $a_0 = 3.250 \text{ \AA}$ and $c_0 = 5.207 \text{ \AA}$ (JCPDS 36-1451). As can be seen from Table 4.2 the heat-treated thin films give smaller c values than the ZnO powder [109].

Table 4.2: Lattice Parameters and Relative Intensities of (0 0 2) Peaks of ZnO Thin Films

Sample	T (in °C)	<i>a</i>	<i>c</i>	I(002)/[I(100) + I(002) + I(101)]
A	500	3.230	5.171	0.6839
B	500	3.231	5.201	0.6820
C	500	3.231	5.170	0.6842
D	500	3.229	5.170	0.6842
JCPDS 36-1451 –		3.250	5.207	0.2189

Zhang *et al.* [110], have also reported smaller *c* values for nanocrystalline ZnO thin films prepared on p-type Si (1 0 0) substrates by a sol–gel method followed by heat-treatment. Other researchers have reported higher *c* values for ZnO thin films prepared on quartz glass substrates by a sol–gel method [111]. The difference in *c*-axis lattice parameter has to be attributed to the occurrence of stress in the thin films. Under compression (parallel to the surface), the *c*-axis lattice parameter will decrease, leading to a somewhat larger interplanar distance for the (0 0 2) planes [112]. The mechanism of formation of the *c*-axis preferentially oriented ZnO thin film suggested that the value of the surface free energy is minimum for the ZnO (0 02) plane at growth stage [113]. Grain size (*D*) was calculated using Debye–Scherrer formula given by [114]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (5)$$

where $\lambda = 0.154$ nm is the wavelength of the X-ray radiation used, θ the Bragg diffraction angle of the XRD peak and β is the measured broadening of the diffraction line peak at an angle of 2θ , at half its maximum intensity in radian. It was found that the average grain size increased with increasing annealing temperature. The average grain size was estimated at 28 nm for a 500°C annealed sample. The XRD peak can be widened by internal stress and defects, so the average grain size calculated by this method is normally smaller than the actual value [115].

3.11. Optical Properties and Band Gap

In this sub section the results of the optical absorbance (A), transmittance (T) and the band gap values, (E_g) of ZnO thin films are reported. Figure 4.4 and 4.5 shows the UV–Vis absorption spectra of the samples coated to different cycles. The exciton absorption is at about 389 nm. As shown in Figure 4.4 and 4.5, the ZnO thin films were highly transparent in the visible range (400–700 nm) with a transmittance of more than 80% and sharp absorption edges were observed in the ultraviolet region. The film with fewer coating layers showed lower absorption at lower wavelengths. The tail height decreased with increasing layers of coating.

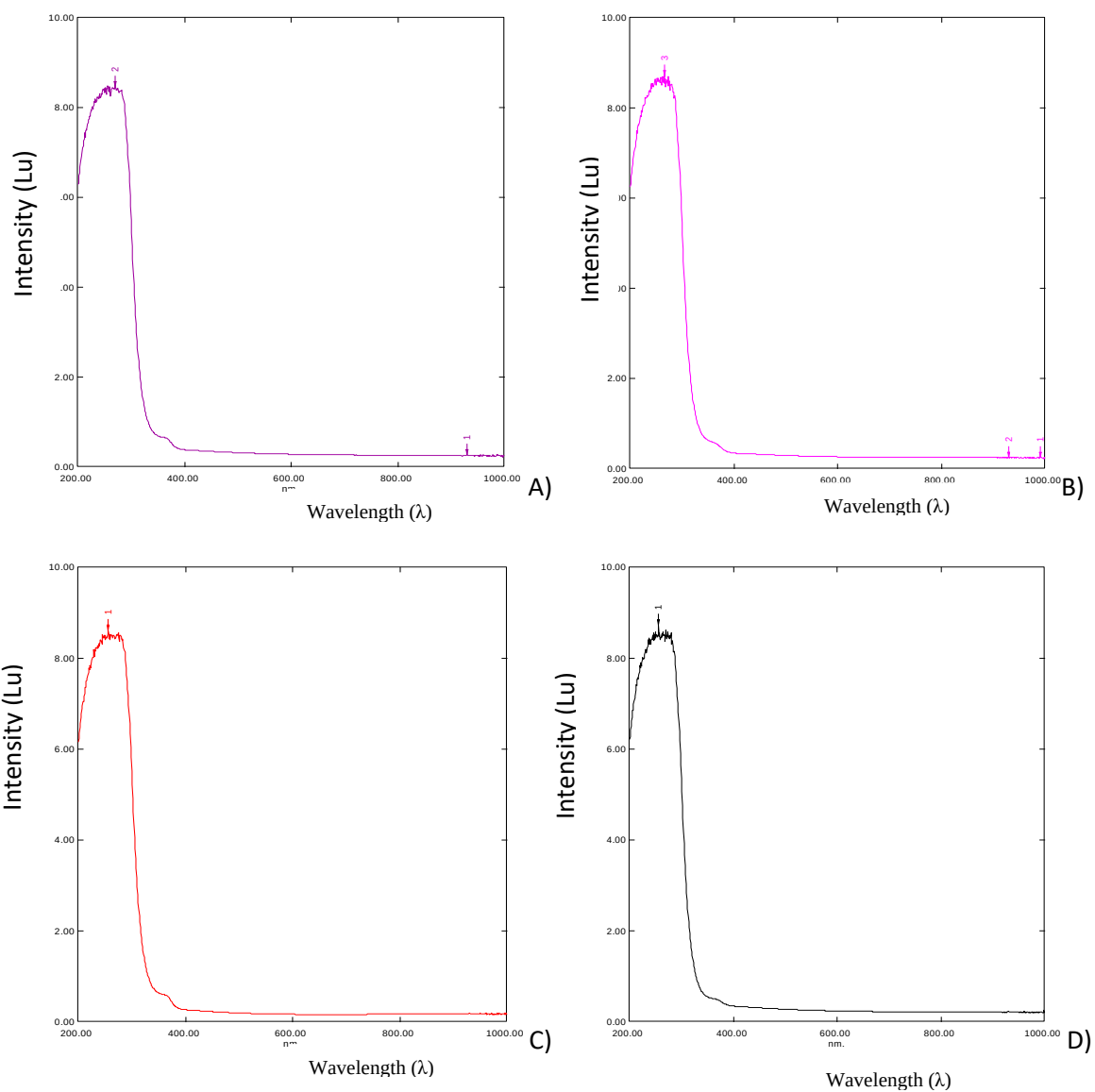


Fig.4.4.UV–vis Absorption Spectra for Each Sample (A, B, C and D)

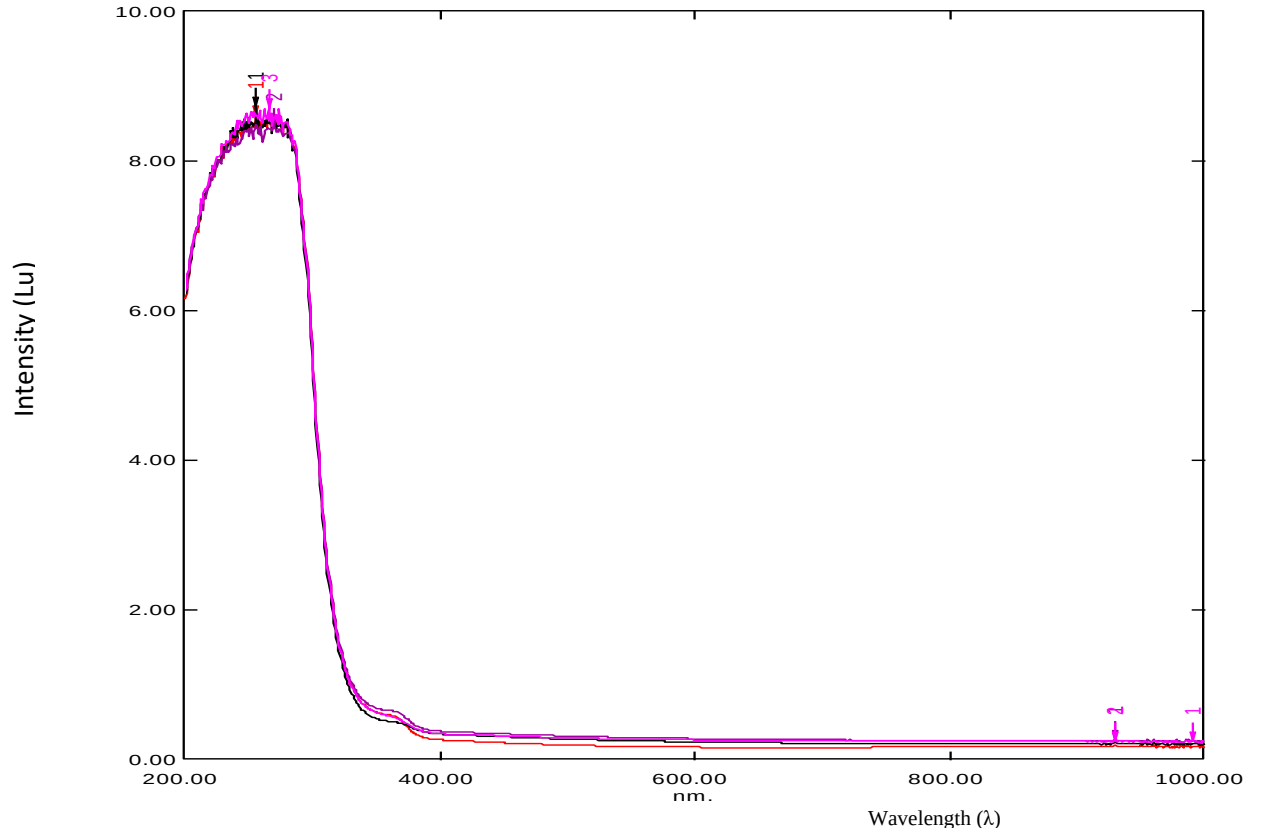


Fig. 4.5. UV–Vis Absorption Spectra ZnO Thin Films for all Samples

4.5.1. Band Gap

The resulting spectrum obtained from the UV – Vis Spectrophotometer on ZnO is shown in Figure 4.4 (A-B) and the combined spectra in Figure 4.5 shows the existence of a strong cut off frequency at 389.0 nm; where the absorbance value is at its minimum. Band gap energy of the obtained ZnO thin films was calculated using;

$$E = \frac{hc}{\lambda} \quad (6)$$

where E is the band gap energy, h is the Planks' constant which is equal to 6.626×10^{-34} Js, C is the speed of light which is equal to 3.0×10^8 m/s and λ is the cut off wavelength approximated to 389.0×10^{-9} m from the graph in Figure 4.4. The band gap energy was found to be 5.245×10^{-19} J or 3.37 eV, where 1.6×10^{-19} J is used as a conversion factor from joules to electron volts. The Figure obtained is in agreement with that obtained in other studies [116].

The UV – Vis absorption spectra results showed that ZnO thin films are optically transparent in the wide wavelength ranges from about 400 nm to 1 μ m. The performed measurements also revealed the edge of light absorption to be around 379 nm.

3.11.2. Transmission

Investigation of the optical properties of the spin coated ZnO thin films was performed by the Perkin Elmer Lambda 19 Spectrophotometer and the results are shown in Figures 4.6 (A-D) and for the combined spectra in Figure 4.7.

The measured transmission spectra in the range 350 nm to 2500 nm for all the ZnO thin film samples indicate that the thin films are rather transparent in the visible region. However, transmission is seen to drop drastically in the ultra violet region for the films studied. This drop which occurs at 380 nm can be attributed to band gap absorption. In addition, this sharp edge at 380 nm when used to calculate band gap energy yields 3.37 eV obtained earlier which is very close to the intrinsic band gap of ZnO (3.3eV) [117]. It was also observed that the highest transmission peak gives a transmission of 95 percent which is in agreement with results obtained for the best solar cell devices that require 95 percent transmission [118].

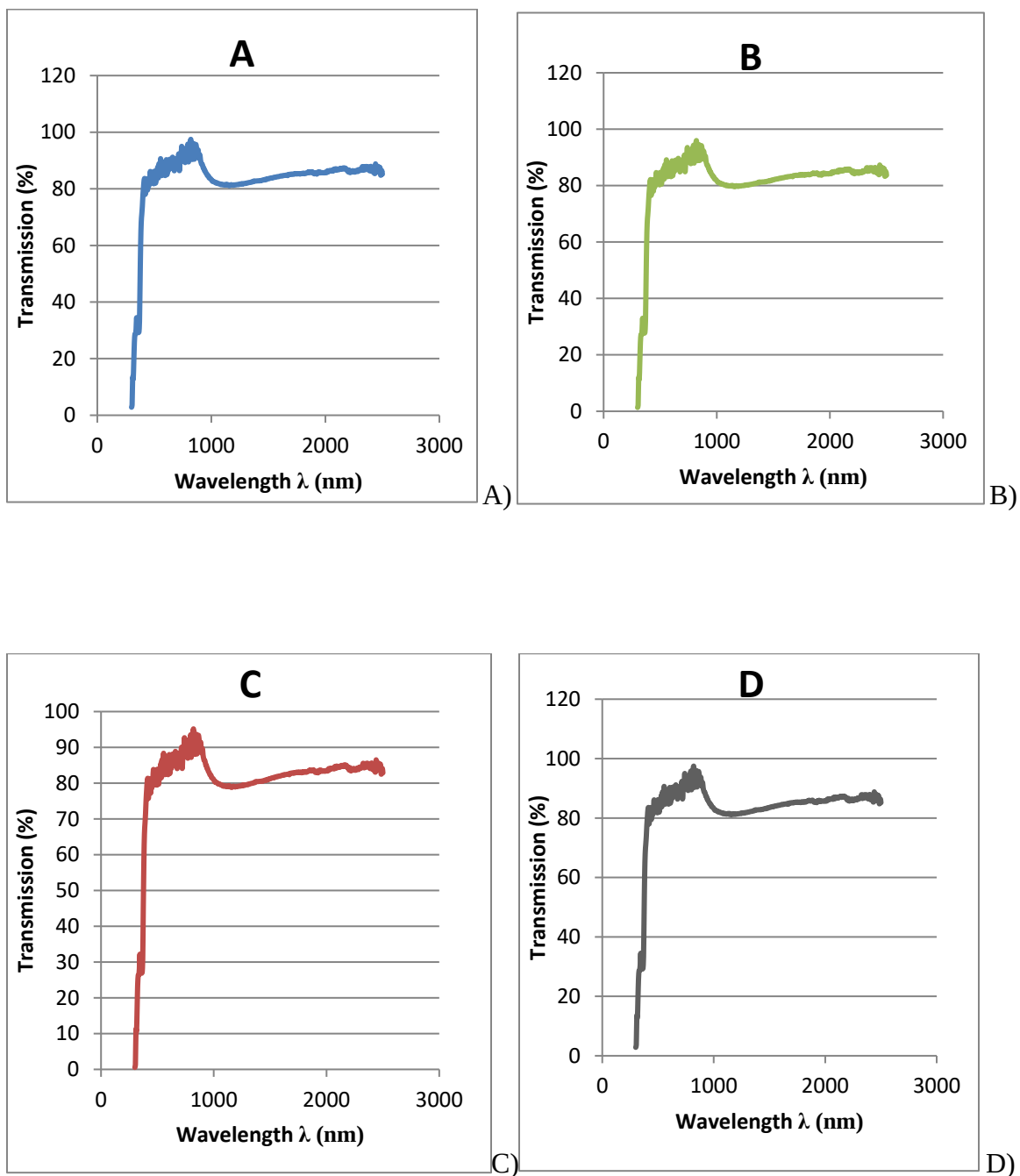


Fig. 4.6. Transmission Graphs for Each Sample (A, B, C and D)

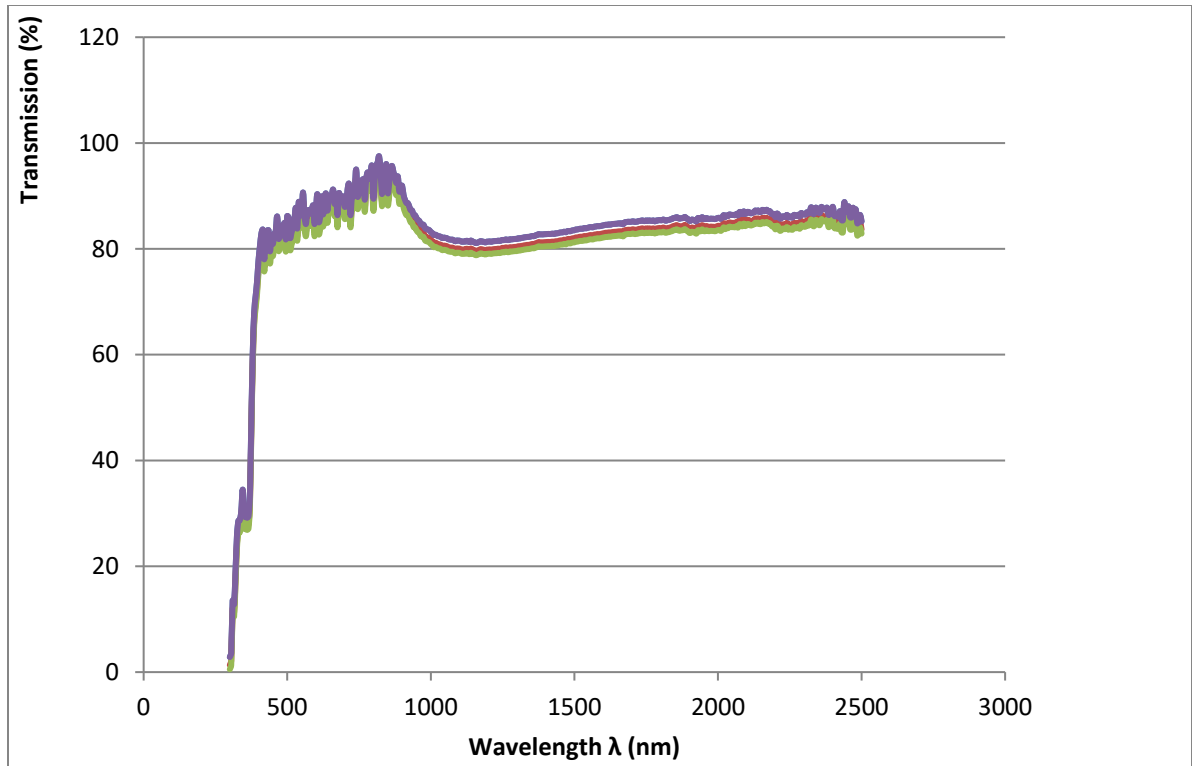


Fig. 4.7. Transmission Graphs for all Samples Combined

In the visible region of solar spectrum, transmission spectra of ZnO thin films show sinusoidal behaviour; this may be due to the layered structure of thin films.

3.12. Electrical Properties

ZnO can be regarded as a material of the future, because it has unique electrical properties. These properties are of great interest for fundamental research, but also for the possible development of new technologies. This section discusses the electrical properties of ZnO thin films as obtained in this study.

3.12.1. Four Point Probe

3.12.1.1. The Measurement of Sheet Resistivity

The voltage and current readings from the probe were used in the formula to obtain the sheet resistance per square unity (ρ_{sq}) which was used to make plot the graph in figure 4.8.

$$\rho_{sq} \left(\frac{\Omega}{sq} \right) = \frac{\pi V}{\ln 2 I} \quad (7)$$

Where V is the Voltage and:

$$\frac{\pi}{\ln 2} = 4.53 \quad (8)$$

The typical emitter sheet resistivity of silicon solar cells lies in the range 30-100 Ωcm .

In typical usage the current is set to 4.53 mA so that the resistivity is simply the voltage reading in mV.

3.12.1.2. The Measurement of Bulk Resistivity

The measurement of bulk resistivity is similar to that of sheet resistivity except that a resistivity in cm^{-3} is used with wafer thickness, t . The film thickness for the ZnO thin films in this study was obtained Valendor thickness gauge discussed earlier. The voltage and current readings from the FFP probe were again used in the formula to obtain the sheet resistivity (ρ).

$$\rho = \frac{\pi}{\ln 2} t \left(\frac{V}{I} \right) = 4.523 t \left(\frac{V}{I} \right) \quad (9)$$

where t is the film thickness in cm.

Equation 9 is used when the wafer thickness is less than half the probe spacing ($t < s/2$)

[119]. For thicker samples the equation is:

$$\rho = \frac{V}{I} \frac{\pi t}{\ln\left(\frac{\sinh\left(\frac{t}{s}\right)}{\sinh\left(\frac{t}{2s}\right)}\right)} \quad (10)$$

where s is the probe spacing [51].

The FPP measurements for variation of voltages are shown on Figure 4.8.

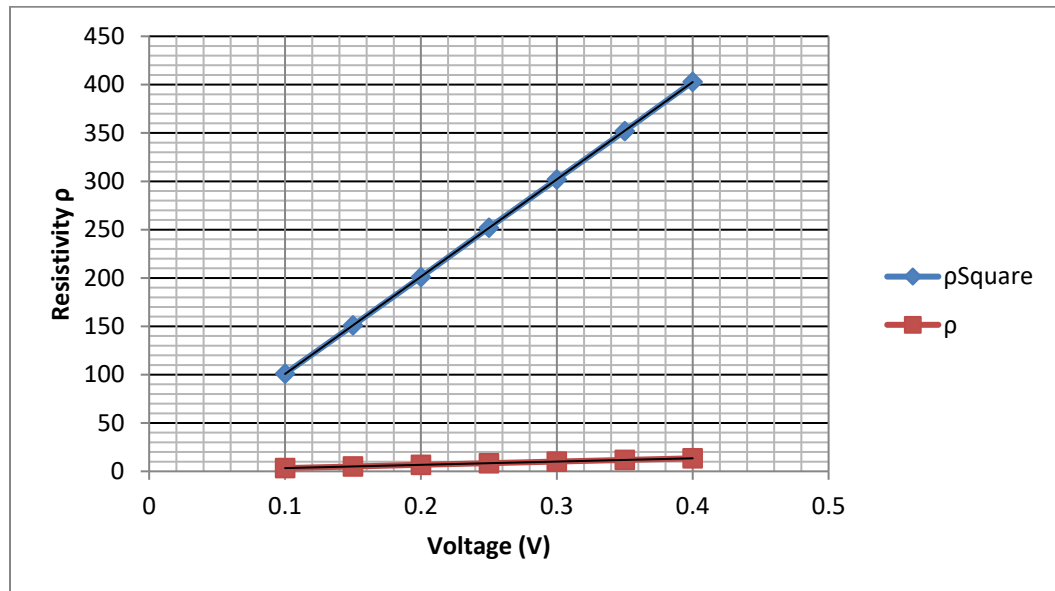


Fig. 4.8. Resistivity and Resistivity per Square Graph for Varying Voltage

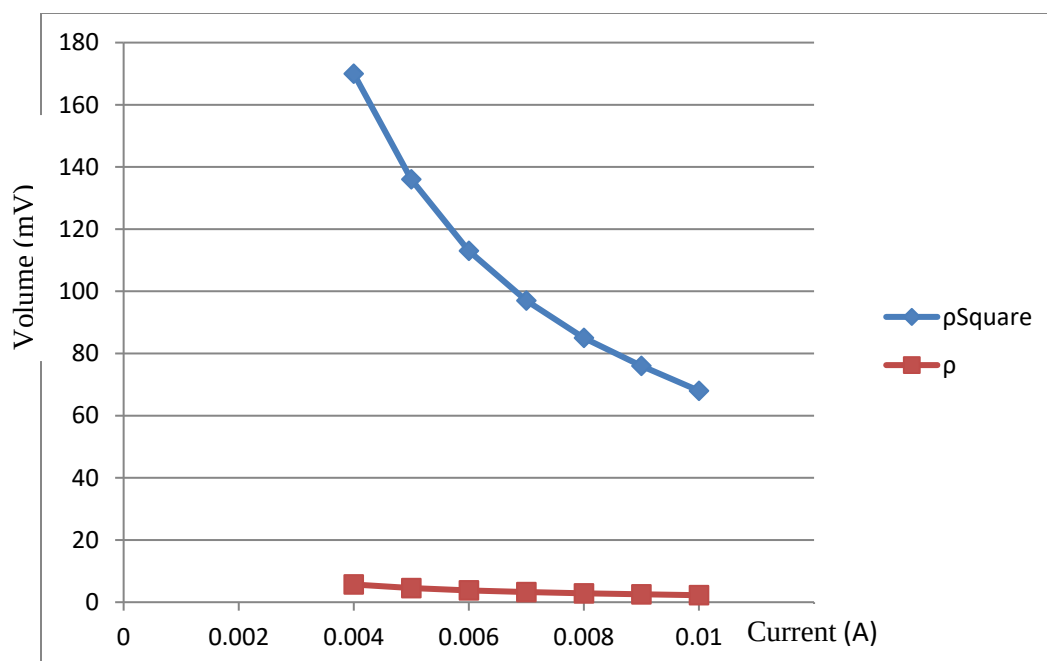


Fig. 4.9. Resistivity and Resistivity per Square for varying Current

Measurements of resistivity Figure 4.9 provides more information TCO. ZnO represents attractive alternative of TCO for solar cell applications. Resistivity of TCO is one of the most important parameters significantly affecting the performance of solar cells, thus need to be controlled.

In this study it was found that ZnO a material which, under ordinary circumstances, has a small oxygen deficiency can still be of great use. This lack of oxygen makes ZnO an n-type semiconductor with a typical resistivity of 1–100 Ωcm . The high resistivity is thought to result from a decrease in the normal oxygen deficiency of ZnO. Three mechanisms are likely to be involved in the enhanced oxygen incorporation. Although quantitative data are not available at this time it is clear that the effect of oxygen atoms is large.

4.6.3. Hall Effect

The Hall measurement, carried out in the presence of a magnetic field, yields the sheet carrier density n_s and the bulk carrier density n or p (for n -type or p -type material) if the conducting layer thickness of the sample is known. The Hall voltage for thick, heavily doped samples can be quite small (in the order of microvolts).

The difficulty in obtaining accurate results is not merely the small magnitude of the Hall voltage since good quality digital voltmeters on the market today are quite adequate. The more severe problem comes from the large offset voltage caused by none symmetric contact placement, sample shape, and sometimes none uniform temperature.

Figure 4.10 shows a plot of the current and the corresponding Hall Voltage for the selected current values. The graph confirms the existence of the Ohmic laws and the conductivity of the ZnO thin Films.

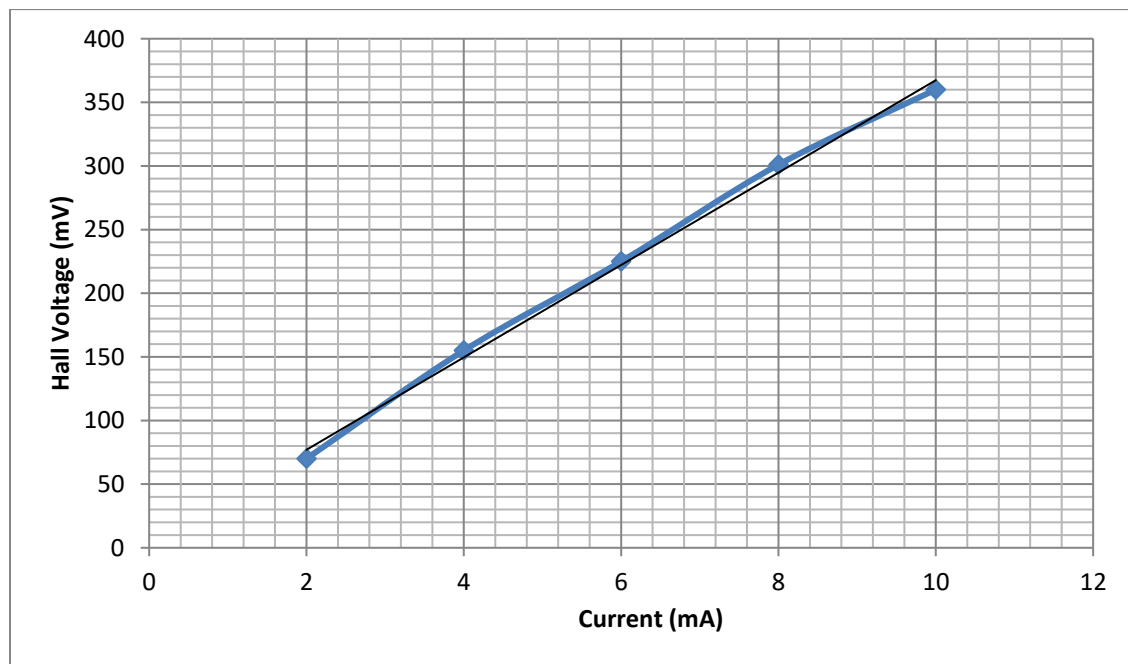


Fig. 4.10. Hall voltage Versus Current

Regarding the mobility, the values are relatively large compared with the intrinsic ZnO, except when measurements were taken with a very large voltage. The sheet carrier density and carrier concentration varies by two orders of magnitude. An interesting result is obtained regarding the carrier type, whereas at lower electric field strength material appears to be of N-type, at higher electric fields strength it is of P-type.

The transverse voltage (Hall Effect) measured in a Hall Probe has its origin in the magnetic force on a moving charge carrier. The following parameters were used in coming up with the hall voltage measurements.

The magnetic force was expressed as

$$F_m = ev_d B \quad (11)$$

where v_d is the drift velocity of the charge.

The current expressed in terms of the drift velocity was given as

$$I = neAv_d \quad (12)$$

where n is the density of charge carriers. Then

$$F_m = \frac{eIB}{neA} \quad (13)$$

At equilibrium this expression was applied

$$F_m = F_e = \frac{V_H e}{w} \quad (14)$$

after substitution this expression was obtained

$$V_H = \frac{IB}{ned} \quad (15)$$

In this study the conductivity of the sample was calculated using

$$\sigma = \left(\frac{\pi t R_{ab}}{\ln 2} f \right)^{-1} \quad (16)$$

where t is the sample thickness and R_{ab} is the resistance which is defined as

$$R_{ab} = \frac{V_{ab}}{I_{ab}} \quad (17)$$

The function f is defined by the equation [119] as

$$\cosh \left(\left[\frac{x-1}{x+1} \right] \frac{\ln 2}{f} \right) = \frac{1}{2} \exp \left(\frac{\ln 2}{f} \right) \quad (18)$$

These computations yielded a higher conductivity at $5.87 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ and lower resistivity of about $1.7 \times 10^{-3} \Omega \text{cm}$.

With a magnetic field B the Hall coefficient R_H is calculated by

$$R_H = \frac{d}{2B} [R_{ab}(+B) - R_{ab}(-B)] \quad (19)$$

where $R_{ab}(+B)$ and $R_{ab}(-B)$ are the resistances of R_{ab} measured at positive and negative magnetic field B respectively. For n-type semiconductors the condition $R_{ab} < 0$ is satisfied and thus carrier concentration n and mobility μ are given by

$$n = \frac{1}{eR_H}, \quad \mu = \sigma R_H \quad (20)$$

Computations carried out using the equations number 11 to 20 yielded the results in Table 4.3.

Table 4.3. Carrier Concentration and Mobility for ZnO Thin Films

<u>Sample</u>	<u>Carrier Concentration (cm⁻³)</u>	<u>Carrier Mobility (cm²/Vs)</u>
A	1.21×10^{17}	52.21
B	1.30×10^{17}	53.52
C	1.25×10^{17}	53.01
D	1.32×10^{17}	53.28

The Hall Coefficient was found to be $2.01 \times 10^{-3} \text{ m}^3/\text{C}$. These results were found to be within the experimental error ranges as obtained in other studies [120].

From the Hall Effect studies, it is observed that the conductivity and carrier mobility are linearly related while the carrier mobility are an inverse of the carrier density. The Hall coefficient and carrier concentration have been determined from Hall voltage measurements at constant magnetic field. Obtained results are in good agreement with literature [120].

The quick switch combination is especially an advantage for a sample with low Hall voltage (less than $50\mu\text{V}$). The potential of developed tool was attested by measurement on various types of semiconductor samples and structures.

It should be added that the measurements point to the non-uniformity of the sample's electrical properties. This is due to spatial anisotropy in the internal structure of the sample, which is confirmed by SEM results discussed earlier [120].

CHAPTER FIVE

CONCLUSION AND SUGGESTION FOR FURTHER WORK

5.1. Conclusion

This section summarises the final results gathered from the deposition of ZnO prepared by sol-gel method and applied to the substrates by spin-coating. The characterisation of the resulting thin films will also be addressed.

5.1.1. Fabrication of ZnO

This subsection is a conclusion on the fabrication process of ZnO on glass substrates and also addresses the first objective of this study. The challenges encountered during the fabrication process are also discussed.

During the preparation of the precursor solutions and the eventual spin coating, challenges were observed on obtaining correct ratios of aqueous Zinc Acetate dehydrate, 2-Methoxyethanol and Ethanolamine to obtain a colourless and homogenous solution with the required adhesiveness. However, these challenges were surmounted by ensuring that correct proportions are used to obtain a clear homogenous solution which was used for the subsequent procedures in the study.

The coating at a speed of 3000 rpm for 60 seconds with a looping cycle of one which was applied and was followed by preheating at 200 °C was the right choice as it gave a good adhesiveness on the four samples which were selected for the study and were coated to different cycles, six, eight, ten and twelve for samples A, B, C, and D respectively.

The selection of the coating speed was carefully made at 3000 rpm while the required vacuum pressure for holding the sample in place at this speed was applied. The pressure from the Nitrogen gas chamber had to be carefully selected while also balancing the pressure from the pressure pump.

The coating of ZnO on glass substrates was followed by annealing at a temperature of 500°C for two hours whose resulting effects on the samples shows that this was a very good choice of the gradient of temperature rise, constant temperature and the eventual cooling gradient.

5.1.2. Characterisation and Results

This subsection gives a conclusion on the results obtained from the characterisation and compares these results with the aim and second objective of this study. The discussion will spell out whether the set objectives were met. Any suggestions to improve these results will be given.

The samples in this study were clear in appearance after annealing. This result is in line with the expected results for TCOs and the results from the Lambda 19 Spectrophotometer of a transmittance of 95% is a good argument for the accuracy of the preparation of the precursor solution, the coating speed and the annealing process.

The micrograph obtained from the SEM depicted the presence of tightly packed grains. These images shown on Figure 4.2 were taken at a magnification of 25,000X and they also show that ZnO crystals are spherical in shape with smooth surface. The images also revealed that the ZnO thin films are porous and with an average crystallite size of about 45

nm which is in acceptable agreement with XRD data and results from other studies [58, 59].

The structure of the ZnO powder in the films as obtained from the XRD data was analysed in comparison with other studies and compared to the expectations of this study. XRD showed the presence of several peaks in all the films and the peaks are indication of a random orientation of the crystallites. When compared to powder diffraction data of Wurtzite structure (JCPDS 36 – 1451), the XRD patterns of all the films showed enhanced intensities for the peaks corresponding to (002) plane depicting a preferential orientation along the c - axis. The relative intensity of peaks corresponding to the (002) can be said to increase with temperature [102]. Table 4.1 showed that the obtained lattice parameters of the ZnO thin films, yielded a hexagonal unit cell which was very close to the parameters of $a_o = 3.250 \text{ \AA}$ and $c_o = 5.207 \text{ \AA}$ (JCPDS 36-1451) [109].

The UV- Vis Spectrophotometer results. The UV – Vis absorption spectra results showed that zinc oxide ZnO thin films are optically transparent in the wide wavelength ranges from about 400 nm to 1 μm . The performed measurements also revealed the edge of light absorption to be around 379 nm. Using these results, the thicknesses of the layers and using formula 10 it was possible to obtain the band gap energy of 3.27 eV which is a necessary property for TCOs.

Finally a conclusion is made on the results of from the FPP and Hall Effect Measurements. The measurement in this study from the FPP showed a positive correlation of the voltage and resistivity as well as the sheet resistivity. The high resistivity is thought to result from a decrease in the normal oxygen deficiency of ZnO.

The Hall Effect results showed that the annealed ZnO thin films are a p-type conductivity while measured Hall Voltage was in a wide-ranging of between 2.3 V and 6.1 V. This implies that the annealed ZnO thin films behaved like the semiconductor materials which they really are.

The Hall Coefficient found in this study was $2.01 \times 10^{-3} \text{ m}^3/\text{C}$ and is within the experimental error ranges as obtained in other studies [120]. A carrier concentration of averaging $1.27 \times 10^{17} \text{ cm}^{-3}$ with a carrier mobility giving an average of $53.01 \text{ cm}^2/\text{Vs}$. The electrical measurement showed a high conductivity at $5.87 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ and lowest resistivity about $1.7 \times 10^{-3} \Omega \text{ cm}$ were obtained.

A closer analysis of the results obtained in this study showed that while ZnO has the required properties for use in solar cells, it is still difficult to conclude that ZnO alone is sufficient to produce the required conductivity whilst maintaining a low resistivity. However, a further optimization of the ZnO thin films will improve the optical properties and electrical properties which in turn will allow employment of low cost sol - gel ZnO in the thin film solar cell devices.

5.2. Suggestions for Further Work

As the author of the present study, the following are suggestions for future studies;

- I. Role of substrate and annealing temperature on the structure of ZnO thin films for solar cell applications
- II. Spectral Transmittance of ZnO thin films in a multilayer environment

REFERENCES

- [1] D. Raoufi, A. Kiasatpour, H.R. Fallah, A.S.H. Rozatian, *Applied Surface Science*, 253, (2007), 9085.
- [2] The Engineer Energy News, Zinc Based Transparent Coating Could Cut Cost of Solar Cells UK press (2015).
- [3] J.L. Vossen, in G. Hass, M.H. Francombe and R. W. Hoffmann (eds.), *Physics of Thin Films*, Academic Press, New York, (1977), p. 1.
- [4] Z. K. Tang, G.K. L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma and Y. Segawa, “Room Temperature Ultraviolet Laser Emission from Self-Assembled ZnO Microcrystallite Thin Films,” *Applied Physics Letters*, 72, 25, (1998), 3270-3272.
- [5] D. Raoufi, H.R. Fallah, A. Kiasatpour, A.S.H. Rozatian, *Applied Surface Science*, 254, (2008), 2168.
- [6] S.T. Tan, B.J. Chen, X.W. Sun, W.J. Fan, H.S. Kwok, X.H. Zhang, et al., *Journal of Applied Physics*, 98, (2005), 505–515.
- [7] Z.R. Tian, J.A. Voigt, J. Liu, B. McKenzie, M.J. Mcdermott, M.A. Rodriguez, H. Konishi, H. Xu, *Natural Matters*, 2, (2003), 821–826.
- [8] J.H. Park, S.J. Jang, S.S. Kim, B.T. Lee, *Applied Physics Letters* 89 (2006), 251-263.
- [10] A.R. Peaker, V.P. Markevich, I.D. Hawkins, B. Hamilton, K. Bonde Nielsen and K. Gościński, *Physica B: Condensed Matter*, 407, (2012), 3026-3030.

- [11] W. Mtangi, F.D. Auret, M. Diale, W.E. Meyer, A. Chawanda, H. De Meyer, P. Janse van Rensburg and J.M. Nel, *Journal of Applied Physics*, 111, (2012) 84 - 503.
- [12] P. Pushpharajah, S. Radhakrishna and A. K. Arof, "Transparent Conducting Lithium Doped Nickel Oxide Thin Films by Spray Pyrolysis Technique," *Journal of Material Science*, 32, (1997), 3001 -3006.
- [13] J.D. Ye, S. L. Gu, S. M. Zhu, T. Chen, L. Q. Hu, F. Qin, R. Zhang, Y. Shi and Y. D. Zheng, "The growth and Annealing of Single Crystalline ZnO Films by Low-Pressure MOCVD," *Journal of Crystal Growth*, 243, (2002), 151-160.
- [14] J. B. Lee, S.H. Kwak and H. J. Kim, "Effects of Surface Roughness of Substrates on the c-Axis Preferred Orientation of ZnO Films Deposited by r.f. Magnetron Sputtering," *Thin Solid Films*, 423, (2003), 262-266.
- [15] L. Znaidi, G. J. A. A. S. Illia, S. Benyahia, C. Sanchez and A. V. Kanaev, "Oriented ZnO Thin Films Synthesis by Sol-gel Process for Laser Application," *Thin Solid Films*, 428, (2003), 257-262.
- [16] H. Bahadur, A. K. Srivastava, D. Haranath, H. Chander, A. Basu, S. B. Samanta, K. N. Sood, R. Kishore, R.K. Sharma, Rashmi, V. Bhatt, P. Pal and S. Chandra, "Nanostructured ZnO Films by Sol-Gel Process," *Indian Journal of Pure and Applied Physics*, 45, (2007), 395-399.
- [17] H. X. Li, J. Y. Wang, H. Liu, H. J. Zhang and X. Li, "Zinc Oxide Films Prepared by Sol-Gel Method," *Journal of Crystal Growth*, 275, (2005), 943-946.

- [18] D. Banerjee, J.Y. Lao, D.Z. Wang, J.Y.Huang, Z.F.Ren, D.Steeves, B. Kimball, M. Sennett, Large-Quantity Free-Standing ZnO Nanowires. *Applied Physics Letters* 83, (2003), 2061–2063.
- [19] Y.B. Hahn, Zinc oxide nanostructures and their applications. *Korean Journal of Chemical Engineering*, 28, (2011), 1797–1813.
- [20] T.Frade, H. Melo, M.E.Jorge, A. Gomes, One-dimensional ZnO Nanostructured Films: Effect of Oxide Nanoparticles. *Materials Letters*, 82, (2012), 13–15.
- [21] R.Wahab, S.G.Ansari, Y.S.Kim, H.K.Seo, H.S. Shin, Room Temperature Synthesis of Needle-Shaped ZnO Nanorods via Sonochemical Method. *Applied Surface Science*, 253, (2007), 7622–7626.
- [22] X.Kong, Y.Ding, R.Yang, Z.L. Wang, Single-crystal Nanorings formed by Epitaxial Self-coiling of Polar-Nanobelts. *Science* 303, (2004), 1348–1351.
- [23] Z.W.Pan, Z.R.Dai, Z.L. Wang. Nanobelts of Semiconducting Oxides. *Science*, 291, (2001), 1947–1949.
- [24] J.J.Wu, S.C.Liu, C.T.Wu, K.H.Chen, L.C. Chenm, Heterostructures of ZnO–Zn Coaxial Nanocables and ZnO Nanotubes. *Applied Physics Letters*, 81, (2002), 1312– 1314.
- [25] W.J.Chen, W.L.Liu, S.H.Hsieh, T.K. Tsai, Preparation of Nanosized ZnO using α Brass. *Applied Surface Science*, 253, (2007), 6749–6753.

- [26] J.Liu, X.Huang, J.Duan, H.Ai, P. Tu, A Low-Temperature Synthesis of Multiwhisker-based Zinc Oxide Micron Crystals. *Materials Letters*, 59, (2005), 3710–3714.
- [27] Y.Huang, J.He, Y.Zhang, Y.Dai, Y.Gu, S.Wang, C. Zhou, Morphology, Structures and Properties of ZnO Nanobelts Fabricated by Zn-powder Evaporation Without Catalyst at Lower Temperature. *Journal of Material Science*, 41, (2006), 3057–3062.
- [28] B.Nikoobakht, X.Wang, A.Herzing, J. Shi, Scalable Synthesis and Device Integration of Self-Registered One-Dimensional Zinc Oxide Nanostructures and Related Materials. *Chemical Social Review*, 42, (2013), 342–365.
- [29] L.C.Tien, S.J.Pearnton, D.P.Norton, F. Ren, Synthesis and Microstructure of Vertically Aligned ZnO Nanowires Grown by High-Pressure-Assisted Pulsed-Laser Deposition. *Journal of Material Science*, 43, (2008), 6925–6932.
- [30] J.Cui, Zinc Oxide Nanowires. *Materials Characterisation*, 64, (2012), 43–52.
- [31] T.Xu, P.Ji, M. He, J. Li, Growth and Structure of Pure ZnO Micro/Nanocombs. *Journal of Nanomaterials*, (2012), 797-935.
- [32] W.S.Chiua, P.S.Khiew, M.Clokea, D.Isaa, T.K.Tana, S.Radimanb, R.Abd-Shukorb, M.A.Abud–Hamid, N.M. Huangc, H.N.Limd, Photocatalytic study of Two-Dimensional ZnO Nanopellets in the Decomposition of Methylene Blue. *Chemical Engineering Journal*, 158, (2010), 345–352.

- [33] M.Jose-Yacaman, C.Gutierrez-Wing, M.Miki, D.Q.Yang, K.N.Piyakis, E. Sacher, Surface Diffusion and Coalescence of Mobile Metal Nanoparticles. *Journal of Physical Chemistry B*. 109, (2005), 9703–9711.
- [34] V.Polshettiwar, B.Baruwati, R.S. Varma, Self-Assembly of Metal Oxides into Three-Dimensional Nanostructures: Synthesis and Application in Catalysis. *ACS Nano*, 3, (2009), 728–736.
- [35] Q.Xie, Z.Dai, J.Liang, L.Xu, W.Yu, Y. Qian, Synthesis of ZnO Three-Dimensional Architectures and their Optical Properties. *Solid State Communique*, 136, (2005), 304–307.
- [36] J. Liu, X. Huang, Y. Li, K.M. Sulieman, F. Sun, X. He, Selective Growth and Properties of Zinc Oxide Nanostructures. *Science. Materials*, 55, (2006), 795–798.
- [37] M. Bitenc, Z.C. Orel, Synthesis and Characterization of Crystalline Hexagonal Bipods of Zinc Oxide. *Materials Research Bulletin*. 44, (2009), 381–387.
- [38] International Organization for Standardization (ISO). *Rubber Compounding Ingredients—Zinc Oxide—Test Methods*; ISO 9298:1995. ISO: Geneva, Switzerland, 2010.
- [39] L.Pyskło, W.Parasiewicz, P.Pawłowski, K. Niciński, Zinc Oxide in Rubber Compounds; *Instytut Przemysłu Gumowego*: Piastow, Poland, 2007.
- [40] S.Mahmud, M.J.Abdullah, G.A.Putrus, J.Chong, A.K. Mohamad. Nanostructure of ZnO Fabricated via French Process and its Correlation to Electrical Properties of

Semiconducting Varistors. *Synthetic Reaction of Inorganic Materials and Organic Nano Material Chemistry*, 36, (2003), 155–159.

- [41] T.Tsuzuki, P.G. McCormick, Mechanochemical Synthesis of Nanoparticles. *Journal of Material Science*, 39, (2004), 5143–5146.
- [42] T.H. Mahato, G.K.Prasad, B.S.J.Acharya, A.R.Srivastava, R. Vijayaraghavan, Nanocrystalline Zinc Oxide for the Decontamination of Sarin. *Journal of Hazardous Materials*. 165, (2009), 928–932.
- [43] D. Raoufi, T, Raoufi. The Effect of Heat Treatment on the Physical Properties of Sol-gel Derived ZnO Thin Films, *Applied Surface Science*, 255, (2009), 5812 - 5817.
- [44] L. Znaidi, Sol-gel-Deposited ZnO Thin Tilms: *A review of Material Science Engineering*, 174, (2010), 18–30.
- [45] A.B.Djurišić, X.Y. Chen, Y.H. Lung, Recent Progress in Hydrothermal Synthesis of Zinc Oxide Nanomaterials. *Recent Patterns of Nanotechnology*, 6, (2012), 124–134.
- [46] T.Tsuzuki, H.Dawkins, J.Dunlop, G.Trotter, M.Nearn, P.G. McCormick, Nanotechnology and cosmetic chemist. *Cosmetic Aeorosol ToiletriesAuster's*, 15, (2002), 10–24.
- [47] A. Kołodziejczak-Radzimska, E. Markiewicz, T. Jesionowski, Structural Characterization of ZnO Particles Obtained by the Emulsion Precipitation Method. *Journal of Nanomaterials*, (2012), 656-753.

- [48] X. Li, G. He, G. Xiao, H. Liu, Wang, M. Synthesis and Morphology Control of ZnO Nanostructures in Micro Emulsions. *Journal of Colloid Interface Science*, 333, (2009), 465–473.
- [49] A. Kołodziejczak-Radzimska, T Jesionowski, A. Krysztalkiewicz, Obtaining Zinc Oxide from Aqueous Solutions of KOH and $\text{Zn}(\text{CH}_3\text{COO})_2$. *Physicochemical Problems of Mineral Process*, 44, (2010), 93–102.
- [50] M.Smirnov, C.Baban, G.I.Rusu, Structural and Optical Characteristics of Spin-Coated ZnO thin films, *Applied Surface Science*, 256, (2010), 2405
- [51] S. Ilican, Y. Caglar, M. Caglar, F. Yakuphanoglu, J. Cui, Phys. E: Structural Characterization of ZnO Particles. *Low-dimension Systems Nanostructures*, 41, (2008), 96.
- [52] E.M. Wong, P.C. Searson, *Applied Physics Letters*, 74, (1999), 2939
- [53] B.L. Allen, P.D. Kichambare, A. Star, *Advanced Materials*, 19, (2007), 1439.
- [54] A.L. Briseno, S.C.B. Mannsfeld, X. Lu, Y. Xiong, S.A. Jenekhe, Z. Bao, Y. Xia, *Nano Material Letters*, 7, (2007), 668.
- [55] Y. Jian-Feng, L. You-Ming, L. Hong-Wei, L. Yi-Chun, L. Bing-Hui, F. Xi-Wu, Z. Jun-Ming, *Journal of Crystal Growth*, 280, (2005), 206.
- [56] M.K. Li, D.Z. Wang, S. Ding, Y.W. Ding, J. Liu, Z.B. Liu, *Applied Surface Science*, 253, (2007), 4161.

- [57] N. Parkansky, G. Shalev, B. Alterkop, S. Goldsmith, R.L. Boxman, Z. Barkay, L. Glikman, H. Wulff, M. Quaas, *Surface Coating Technology*, 201, (2006), 2844.
- [58] Y.S. Kim, W.P. Tai, S.J. Shu, *Thin Solid Films*, 491, (2005), 153.
- [59] S. Mridha, D. Basak, *Materials Research Bulletin*, 42, (2007), 875.
- [60] Z.W. Li, W. Gao, *Thin Solid Films*, 515, (2007), 3323.
- [61] Powder Diffraction File 36-1451 for Hexagonal Zinc Oxide (1997 JCPDS-International Center for Diffraction data).
- [62] M. Law, D.J. Sirbuly, J.C. Johnson, J. Goldberger, R.J. Saykally, P. Yang, *Science*, 305,(2004), 1269.
- [63] J.I. Pankove, *Optical Processes in Semiconductors*, Prentice-Hall Inc., Englewood Cliffs, NJ, 1971.
- [64] M. Guo, C.Y. Yang, M. Zhang, Y. Zhang, T. Ma, Xi Dong Wang, *Electrochim Acta*, 53, (2008), 4633.
- [65] Z. Yang, Z. Z. Ye, Z. Xu and B. H. Zhao, “Effect of the Morphology on the Optical Properties of ZnO Nanostructured,” *Physica E. Low-Dimensional Systems and Nanostructures*, 42, (2009), 116-119
- [66] T. Ivanova, A. Harizanova, T. Koutzarova and B. Vertruyen, “Study of ZnO Sol-Gel Films: Effect of Annealing,” *Materials Letters*, 64, (2010), 1147-1149.
- [67] Y. J. Kwon, K. H. Kim, C. S. Lim and K. B. Shim, “Characterisation of ZnO Nanopowders Synthesized by the Polymerized Complex Method via an

- Organochemical Route,” *Journal of Ceramic Processing Research*, 3, (2002), 146-149.
- [68] J. Jose, M. Abdul Khadar, *Material Science Engineering A-Structure*, 304-306, (2001), 810.
- [69] J. Lee, J.H. Hwang, J.J. Mashek, T.O. Mason, A.E. Miller, R.W. Siegel, *Journal of Materials Research*, 10,(1995), 2295.
- [70] C. Kilic, A. Zunger, *Physics Review Letters*, 88, (2002), 095501.
- [71] A. Kołodziejczak-Radzimska, T. Jesionowski, Zinc Oxide—From Synthesis to Application, *Materials*, 7, (2014), 2833-2881
- [72] A. Das, D.Y. Wang, A. Leuteritz, K. Subramaniam, H. C. Greenwell, U. Wagenknecht, G. Heinrich, Preparation of Zinc Oxide Free, Transparent Rubber Nanocomposites using a Layered Double Hydroxide Filler. *Journal of Material Chemistry*, 21, (2011), 7194–7200.
- [73] H. Liu, D. Yang, H. Yang, H. Zhang, W. Zhang, Y. Fang, Z. Liu, L. Tian, B. Lin, J.Y an, Comparative Study of Respiratory Tract Immune Toxicity Induced by Three Sterilization Nanoparticles: Silver, Zinc Oxide and Titanium Oxide. *Journal Hazardous Materials*, 248, (2013), 478–486.
- [74] M. Mirhosseini, F. Firouzabadi, Antibacterial Activity of Zinc Oxide Nanoparticle Suspensions on Food-Borne Pathogens. *International Journal on Dairy Technology*, 65, (2012), 1–5.

- [75] P. Mason, Physiological and Medicinal Zinc. *Pharmacology Journal*, 276, (2006), 271–274.
- [76] A. Yadav, V. Prasad, A.A. Kathe, S. Raj, D. Yadav, C. Sundaramoorthy, N. Vigneshwaran, Functional Finishing in Cotton Fabrics using Zinc Oxide Nanoparticles. *Bulletin of Material Science*, 29, (2006), 641–645.
- [77] Mao, Z.; Shi, Q.; Zhang, L.; Cao, H. The Formation and UV-Blocking Property of Needle-Shaped ZnO Nanorod on Cotton Fabric. *Thin Solid Films* 517, (2009), 2681–2686.
- [78] A. Becheri, D. Maximilian, P. Lo Nostro, P. Baglioni, Synthesis and Characterization of Zinc Oxide Nanoparticles: Application to Textiles as UV-Absorbers. *Journal on Nanoparticles Research*, 10, (2008), 679–689.
- [79] R.Wang, J.H.Xin, X.M.Tao, W.A. Daoud, ZnO Nanorods Grown on Cotton Fabrics at Low Temperature. *Chemistry Physics Letters*, 398, (2004), 250–255.
- [80] S. Roy, S. Basu, Improved Zinc Oxide Films for Gas Sensor Applications. *Bulletin on Material Science*, 25, (2002), 513–515.
- [82] D.S.Bhachu, G.Ankar, I.P. Parkin, Aerosol Assisted Chemical Vapor Deposition of Transparent Conductive Zinc Oxide Films. *Chemical Materials*, 24, (2012), 4704–4710.
- [83] M. Bizarro, High photocatalytic activity of ZnO and ZnO:Al Nanostructured Films Deposited by Spray Pyrolysis. *Applied Catalytic B Environment*, 97, (2010), 198–203.

- [84] M.Y.Guo, M.K.Fung, F.Fang, X.Y.Chen, A.M.C.Ng, A.B.Djurišić, W.K. Chan, ZnO and TiO₂ 1-Dimensional Nanostructures for Photocatalytic Applications. *Journal Alloyed Compounds*, 509, (2011), 1328–1332.
- [85] Q.Li, C.Wang, M. Ju, W.Chen, E. Wang, Polyoxometalate-Assisted Electrochemical Deposition of Hollow ZnO Nanospheres and their Photocatalytic Properties. *Microporous Mesoporous Material*, 138, (2011), 132–139.
- [86] S.S.Ma, R.Li, C.P.Lu, W.Xu, X.L. Gou, Facile synthesis of ZnO Nanorod Arrays and Hierarchical Nanostructures for Photocatalysis and Gas Sensor Applications. *Journal on Hazardous Material*, 192, (2010), 730–740.
- [87] C.Xu, L.X.Cao, G.Su, W.Liu, X.F.Qu, Y.Q. Yu, Preparation, Characterization and Photocatalytic Activity of Co-doped ZnO Powders. *Journal on Alloyed Compounds*, 497, (2010), 373–376.
- [88] S.Pyne, G.P.Sahoo, D.K.Bhui, H.Bar, P.Sarkar, S.Samanta, A.Maity, A. Misra, Enhanced Photocatalytic Activity of Metal Coated ZnO Nanowires. *Spectrochim. Acta Part A Molecular & Biomolecular Spectroscopy*, 93, (2012), 100–105.
- [89] C. Wöll, The Chemistry and Physics of Zinc Oxide Surfaces. *Programme on Surface Science*, 82, (2007), 55–120.
- [90] C. Klingshirn, ZnO: From Basics towards Applications. *Physics Status Solidi*, 244, (2007), 3027–3073.

- [91] X.Tang, E.S.G.Choo, L.Li, J.Ding, J. Xue, One-Pot Synthesis of Water-Stable ZnO Nanoparticles via a Polyol Hydrolysis Route and their Cell Labeling Applications. *Langmuir*, 25, (2009), 5271–5275.
- [92] P.J.P.Espitia, N.F.F.Soares, J.S.R.Coimbra, N.J.de Andrade, R.S.Cruz, E.A.A. Medeiros, Zinc Oxide Nanoparticles: Synthesis, Antimicrobial Activity and Food Packaging Applications. *Food Bioprocess Technology*, 5, (2012), 1447–1464.
- [93] A.Moezzi, A.M.McDonagh, M.B. Cortie, Zinc Oxide Particles: Synthesis, Properties and Applications. *Chemical Engineering Journal*, 185–186, (2012),1–22.
- [94] N.Padmavathy, R. Vijayaraghavan, Enhanced Bioactivity of ZnO Nanoparticles - An Antimicrobial Study. *Science Technological Advanced Materials*, 9, (2008)
- [95] https://www.researchgate.net/figure/293781541_fig3_Figure 4.2: Schematic Sketch of a Four Point Probe Measuring Resistivity (Vidhya and Velumin, 2009).
- [96] <http://hyperphysics.phy-astr.gsu.edu/hbase/magnetic/Hall.html>
- [97] S. Mondal, K.P. Kanta, P. Mitra, *Journal of Physical Sciences*, 12, (2008), 221-229.
- [98] Y. Kashiwaba, F. Katahira, K. Haga, T. Sekiguchi, H. Watanabe, *Journal of Crystal Growth*, 221, (2000), 431.
- [99] Y.R. Ryu, W.J. Kim, H.W. White, *Journal of Crystal Growth*, 219, (2000), 419.
- [100] S. Amirhaghi, V. Craciun, D. Craciun, J. Elders, I.W. Boyd, *Microelectronic Engineering*, 25, (1994), 321.

- [101] R. Ghosh, D. Basak, S. Fujihara, *Journal of Applied Physics*, 96, (2004), 2689.
- [102] Y. Zhang, B. Lin, Z. Fu, C. Liu, W. Han, *Optoelectronic Materials*, 28, (2006), 1192.
- [103] H.S. Lee, J.Y. Lee, T.W. Kim, D.W. Kim, W.J. Cho, *Journal of Material Science*, 39, (2004), 3525.
- [104] H.R. Fallah, M. Ghasemi, A. Hassanzadeh, H. Steki, *Physica B*, 373, (2006), 274.
- [105] A. Ashour, M.A. Kaid, N.Z. El-Sayed, A.A. Ibrahim, *Applied Surface Science*, 252, (2006), 7844.
- [106] J. Tauc, R. Grigorovichi, A. Vancu, *Physica Status Solidi*, 15, (1966), 627.
- [107] D. Bao, H. Gu, A. Kuang, *Thin Solid Films*, 312, (1998), 37.
- [108] N.D. Kumar, M.N. Kamalasanan, S. Chandra, *Applied Physics Letters*, 65, (1994), 1373.
- [109] R. Banerjee, S. Ray, N. Basu, A.K. Batabyal, A.K. Barua, *Journal of Applied Physics*. 62, (1987), 912.
- [110] C.J. Pan, C.W. Tu, J.J. Song, G. Cantwell, C.C. Lee, B.J. Pong, G.C. Chi, *Crystal Growth*, 282, (2005), 112.
- [111] K.B. Sundaram, A. Khan, *Thin Solid Films* 295 (1997) 87. [45] H.L. Hartnagel, A.L. Dawar, A.K. Jain, C. Jagadish, *Semiconducting Transparent Thin Films*, Institute of Physics Publishing, Bristol/PA, 1995.

- [112] S.Y. Tong, J.M. Wu, Y.T. Huang, M.D. Yang, M.J. Tung, *Journal of Applied Physics D: Applied Physics*, 43, (2010), 445 - 502.
- [113] T. Minami, T. Miyata, T. Yamamoto, *Journal of Vacuum Science & Technology A*, 17, (1999), 1822-1826.
- [114] R.J. Hong, X. Jiang, G. Heide, B. Szyszka, V. Sittinger, W. Werner, *Journal of Crystal Growth*, 249, (2003), 461-469.
- [115] J.I. Pankove, *Optical Progress in Semiconductors*, Dover, New York, (1975).
- [116] F.J. Manjon, B. Mari, J. Serrano, A.H. Romero, *Journal of Applied Physics*, 97, (2005), 503-516.
- [117] K.T. Igamberdiev, S.U. Yuldashev, T.W. Kang, V.O. Pelenovich, *Journal of the Korean Physical Society*, 55, (2009), 934-937.
- [118] F. Maldonado, A. Stashans, *Journal of Physics and Chemistry of Solids*, 71, (2010), 784-787.
- [119] C. Klingshirn, *Physics Status Solidi B*, 244, (2007), 3027
- [120] D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason and G. Cantwell, *Applied Physics Letter*, 81, (2002), 1830