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Microstructure and Properties of Zinc Oxide Nano-Crystalline Thin Films and Composites

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A thesis submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy in Engineering

Centre for Advanced Composite Materials (CACM)

Department of Mechanical Engineering

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Abstract

Zinc oxide (ZnO) is a II–VI compound semiconductor with a wide direct band-gap of 3.3 eV and a hexagonal structure. ZnO is often used in the paint, paper, rubber, food and drug industries. It is also a promising material in nanotechnology applications, for example in nano-electronics and nano-robotic technology. With its wide band-gap, high exciton binding energy and high breakdown strength, ZnO can be utilized for electronic and photonic devices, as well as for high-frequency applications. To produce such optoelectronic devices, control of electronic properties, such as the nature of conduction and carrier density, is required. However, such control has proved difficult for ZnO. Much research has been done to pursue p type ZnO using different processing techniques, however, there are few reports addressing the relationships of microstructure on optical and electrical properties, ion implantation doping of ZnO and nano-ZnO polymer composites.

The objectives of this project are to study the processing, composition, microstructure, electronic, optical, UV and electromagnetic shielding properties of ZnO thin films and composites; to explore ion implantation as a method to dope Al, Ag, Sb, Sn and TiN into ZnO thin films or single crystals; to develop conducting, transparent oxide films and/or p-type semiconductor for potential device applications; and to study the relationships of doping, microstructure and electro-optical properties of ZnO thin films and nano-ZnO polymer composites.
The experimental work included annealing, characterizing and implantation of magnetron sputtering ZnO thin films and ZnO single crystals. Ion implantation was employed to dope ZnO thin films or single crystals with Ti, N, Sb, Al, Sn and Ag. The diffusion behaviour of implanted and annealed ZnO and the ellipsometry of implanted ZnO thin films were investigated. The relationship of microstructure and properties of as-deposited, annealed and implanted ZnO was studied. The results show that compared to direct current (d.c.) sputtering, the films produced using radio frequency (r.f.) have significantly lower resistivity, porosity and stress. The residual stress can change the band gap of ZnO thin films. Conductivity experiments suggest that the conduction mechanism of sputtered ZnO thin films involves charge transport in the conduction band and electronic hopping between the nearest neighbour donor levels. Furthermore, the optical transmission of ZnO thin films is high in the visible, with excellent UV absorption properties. It is also found that annealing alters the grain size and composition, and reduces the stress of ZnO thin films. Moreover, ion implantation causes partial amorphousness of ZnO films in the implantation zone and introduces stress and interstitial dopants. Transport of Ions in Matter (TRIM) modelling and Secondary Ion Mass Spectrometer (SIMS) analysis confirm that lighter elements implant deeper than heavy elements. The implanted ZnO shows some p type tendency and evidence of photoluminescence. Lastly, the nano-ZnO and polymer composites show excellent mechanical, good UV barrier properties.
Dedication

To

all those who contribute greatly to my life.

• If I have seen further it is by standing on the shoulders of giants.

  Isaac Newton

• Imagination is more important than knowledge.

• Try not to become a man of success, but rather try to become a man of value.

  Albert Einstein
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<td>Donor-acceptor peak</td>
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<tr>
<td>DMTA</td>
<td>Dynamic Mechanical Thermal Analysis</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>FB</td>
<td>Forouhi and Bloomer Interband Model</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half-Maximum</td>
</tr>
<tr>
<td>LOA</td>
<td>Lorentz Oscillator Approximation</td>
</tr>
<tr>
<td>MEVVA</td>
<td>Metal vapor vacuum arc</td>
</tr>
<tr>
<td>NRA</td>
<td>Nuclear reaction analysis</td>
</tr>
<tr>
<td>PEN</td>
<td>Polyethylene Naphthalate</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinyl alcohol</td>
</tr>
</tbody>
</table>
### List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>Polyethylene oxide</td>
</tr>
<tr>
<td>PIXE</td>
<td>Particle-induced X-ray emission</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford Backscattering Spectrometry</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>SRIM</td>
<td>Stopping and Range of Ions in Matter</td>
</tr>
<tr>
<td>TRIM</td>
<td>Transport of Ions in Matter</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffractometry</td>
</tr>
</tbody>
</table>

### General Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>Energy</td>
</tr>
<tr>
<td>E’</td>
<td>Storage modulus</td>
</tr>
<tr>
<td>E”</td>
<td>Loss modulus</td>
</tr>
<tr>
<td>I</td>
<td>Current (A)</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann constant ((1.38 \times 10^{-23} \text{ J K}^{-1}))</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>R</td>
<td>Resistance ($\Omega$)</td>
</tr>
<tr>
<td>n</td>
<td>Refractive index</td>
</tr>
<tr>
<td>RUMP</td>
<td>Rutherford backscattering spectroscopy analysis package</td>
</tr>
<tr>
<td>T</td>
<td>Transmittance or Temperature (K)</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>V</td>
<td>Voltage (V)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Conductivity ($\Omega^{-1}$cm$^{-1}$)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Resistivity ($\Omega$.cm)</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Mobility ($\text{cm}^2$/V s) = ($1/(\text{qnsRS})$)</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>Phase shift introduced by the reflection</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Ellipsometric angles</td>
</tr>
<tr>
<td>$\tan \psi$</td>
<td>Ratio of the resulting amplitudes of two mutually perpendicular components of the reflected beam</td>
</tr>
<tr>
<td>$\tan \delta$</td>
<td>Damping or loss factor</td>
</tr>
</tbody>
</table>
Chapter 1

1 Introduction

1.1 Background

Wide-band gap semiconductors, such as 6H-SiC (3.0 eV, at 2 K) and GaN (3.5 eV), have come to the forefront in the past decade because of an increasing need for short-wavelength photonic devices, high-power, high-frequency electronic devices, and because of breakthroughs in growth techniques for these materials [1]. While many research efforts have focused on SiC, ZnSe and GaN, other wide band gap materials such as ZnO are now emerging as potential materials for the above applications. Recent improvements in the control of background conductivity of ZnO and demonstrations of p-type doping have intensified interest in this material for applications in UV light emitters, varistors, transparent high-power electronics, surface acoustic wave devices, piezoelectric transducers, and chemical and gas sensing [2-5]. Transparent, conducting oxides have important uses for a variety of applications, including flat panel displays, touch screens, IR reflectors, solar cells and optical sensors [6].

The main advantages of ZnO are a wide band gap, large refractive indices over the infra-red and visible ranges, its large exciton binding energy (60 meV) compared to GaN (25 meV), and the existence of well-developed bulk and epitaxial growth processes. For electronic applications, the attractiveness of ZnO lies in its high breakdown strength and high saturation velocity. Optical UV lasing, has already been demonstrated, although efficient electrical lasing must await the further development of
reliable, p-type material. ZnO is also much more resistant to radiation damage than are other common semiconductor materials, such as Si, GaAs, CdS, and even GaN [1]. Nanocrystal semiconductor materials have attracted much attention due to their unique physical, chemical and optical properties [7].

On other hand, it is difficult to control stoichiometry of ZnO which is frequently Zn rich because this is energetically favourable. The development of p-type ZnO is difficult [8]. This is partially due to compensation by donors with low formation enthalpies. Most of the basic aspects of how to reliably produce p-type ZnO are still not well understood [9]. There are still fundamental challenges in reliable routes to p-type ZnO. Therefore, ZnO is a well known wide-band-gap semiconductor material and of great interest for scientific research, as well as for applications in gas sensors, varistors, electro and photoluminescent devices [10-12].
1.2 Objectives and Methodology

1.2.1 Objectives

The objectives of this project are to study the processing, composition, microstructure, electronic, optical, UV and electromagnetic shielding properties of ZnO thin films; to explore ion implantation as a method to dope Al, Sb, Sn and TiN etc. into ZnO thin films; to develop conducting, transparent oxide films and/or p-type semiconductor for potential device applications, and to study the relationships of doping, microstructure and electro-optical properties of ZnO thin films. For comparison to the sputtered ZnO thin films, the properties of single crystal ZnO similarly modified, and of nano-ZnO polymer composite thin films are also studied.

The work has involved a series of issues in an attempt to advance the understanding of ZnO, particularly those of sputtered thin films. The following specific research directions were followed:

1. Determine optical, electrical, electronic properties and microstructure of nano ZnO (or doped) thin films prepared by magnetron sputtering;

2. Implantation of magnetron sputtered ZnO thin films on glass or Si substrates and ZnO single crystals with novel elements and compounds to achieve p-type ZnO, with improved photoluminescence;

3. Examine the UV and electromagnetic shielding properties of magnetron deposited ZnO thin films;
4. Study films of nano-ZnO dispersed in a polymer matrix.

1.2.2 Methodology

ZnO thin films are deposited by magnetron sputtering and modified in various ways such as ion implantation and annealing. The experimental work also includes characterizing the relationship between microstructure and composition of various films and the resulting electronic, electrical and optical properties. The methodology is listed below:

1. Magnetron Sputtering.

The ZnO thin films were prepared by r.f magnetron sputtering to examine the effects of deposition parameters on microstructure and properties, especially conductivity. Si or polymer substrates were also used as deposition substrates.

2. Doping ZnO thin films and single crystals with Ag, Al, Sn, Sb and TiN by ion implantation.

Ion implantation is used for introducing conduction carriers into IV and III–V group semiconductors. The doping profile follows a Gaussian distribution; the depth of the doping is determined by the accelerated energy. A primary advantage of ion implantation is the ability to selectively modify the electronic properties of a surface
without affecting bulk properties, largely because the process is carried out at low temperatures. The process is also controllable and reproducible, and can be tailored to modify different surfaces in desired ways.

Ag, Al, Sn, Sb and TiN by ion implantation were used with variations in dopants and ion doses. Emphasis was on improving conductivity, photoluminescence and/or developing p-type conductivity. Dopant Sb and N were chosen because they are promising p-type dopants with 5 valence electrons. TiN appears to present a novel and effective method of N introduction.

The implanted ZnO was annealed in vacuum to investigate the mitigation of some of the damage to the crystal structure induced by implantation. The effects of annealing on conductivity, especially with respect to stress relief were investigated. Mobility and carrier concentration, Current-Voltage curve and Photoluminescence were measured to determine if the implanted elements induce p-type behaviour.


Spectroscopic ellipsometry was used to determine refractive index (optical property), layer thickness, porosity, band gap and interface structure of implanted ZnO films in order to better understand the film structure and properties. The effects of parameters such as band gap and porosity can be modelled using an optical theory to refine understanding of film structure. Ion Beam Analysis determined the composition of implanted samples.
Dynamic SIMS provided depth profiling of the implanted ZnO thin films and single crystals enabling the difference in distribution, especially in Ti and N before and after annealing to be determined.

4. Annealing of ZnO thin films.

The samples of magnetron sputtered ZnO thin films were annealed at different temperatures and atmospheres in order to modify their structure and electrical properties.

5. Microstructure study of implanted magnetron sputtered ZnO thin films on Si substrates using SEM, AFM and XRD etc.

SEM and AFM were used to examine surface morphology, especially the influence of annealing. This can have significant effects on the sputtered films, especially in terms of light emission. XPS was used to examine effects on surface chemistry. X-Ray Diffraction (XRD) was used to identify the crystal phases and lattice parameters. Grain size, preferred orientation and defect structure were also studied with emphasis on differences before and after implantation and annealing.

6. Electrical, Electronic and optical properties of implanted magnetron sputtered ZnO thin films.
Electrical resistivity was measured by the traditional 4-point method. Mobility and carrier concentration were determined by Hall Effect measurements using the Van der Paw method. Optical transmittance was performed by UV-VIS spectrometer. The photoluminescence of ZnO thin films and crystals was also studied.

7. Electromagnetic shielding properties of ZnO thin films and nanocomposites on polymer substrates.

a). ZnO thin films were sputtered onto PEN and glass substrates and the samples tested for shielding effectiveness, particularly in the UV region.

b). Nanocomposite ZnO/polymer film samples were prepared on polymer or glass substrates by spinning or dipping, allowing shielding properties in various regions of the electromagnetic spectrum to be measured.

1.3 Outline of Thesis

Thin films of ZnO have been grown by magnetron sputtering on glass and Si substrates. The research in this thesis has focused on characterisation of as deposited and implanted ZnO. The principle goal of this work has been to study the relationship of microstructure and properties (electrical, electronical and optical) of ZnO. Chapters 1 and 2 cover an introduction and literature review of previous work on ZnO and background knowledge. Chapters 3 and 4 discuss characterisation and annealing of
ZnO thin films deposited by magnetron sputtering. Chapters 5 to 8 detail implantation and characterisation of magnetron deposited, nano-crystalline ZnO thin films and single crystals. The microstructure and electrical, electronic and optical properties of implanted ZnO thin films have been examined. Chapter 9 discusses p type ZnO and the electromagnetic shielding properties of ZnO thin films. Chapter 10 reports studies of nano-ZnO and polymer composites. Chapter 11 draws conclusions from the results and 12 makes recommendations for future studies (see Figure 1-1).
Chapter 8 Transmission and Ellipsometry Study of Implanted Polycrystalline ZnO Thin Films

Chapter 9 p Type ZnO and Electromagnetic Shielding Study of ZnO Thin Films

Chapter 10 Nano-ZnO and Polymer Composites

Chapter 11 Concluding Remarks

Chapter 12 Recommendations For Further Research

Appendix List of Publications; Figures

Figure 1-1 Flow chart of thesis.
1.4 References


2 Literature Review-ZnO

2.1 Introduction

Zinc oxide is a chemical compound with formula ZnO. It occurs in nature as the mineral zincite [1]. Zinc oxide is an important material for a variety of practical applications; therefore it has been under intensive investigation since the 1950s [2]. It is used as a pigment in paints, a filler for rubber goods, in coatings for paper, safe food additives and drugs [3]. Zinc peroxide, ZnO$_2$·1/2H$_2$O, is used in antiseptic ointments. Zinc oxide is also a semiconductor with a direct band gap of ~3.3 eV (387 nm, deep violet/borderline UV, Figure 2-5) which make it a possible candidate as a white light source when combined with certain types of phosphors (current light sources consume more than 20% of world electricity) [4]. Such solid state light sources offer huge advantages in energy efficiency. Because of the wide band gap, zinc oxide absorbs ultraviolet light; thus it can be used in ointments, creams and lotions to protect against sunburn. However in terms of future use, the major interests lie in semiconductor applications, due to the increasing need for near-ultra-violet optoelectronic devices. ZnO is a candidate for solid state blue to UV optoelectronics, including lasers. Its light sensitivity makes it a potential detector for radiation in the UV spectrum. Crystalline zinc oxide also exhibits the piezoelectric effect.
2.2 ZnO Definitions and Sources

Zinc oxide (ZnO), an amorphous white or yellowish powder, has the molecular weight of 81.37, average atomic weight of 40.69 amu and enthalpy of formation (298.15K) of -350.5 kJ/mol.

Two main processes are employed for producing powdered zinc oxide. In the direct, or American, method of manufacture, zinc ores (or residues) are heated in air with coke or anthracite, and the resulting zinc vapour is subjected to controlled oxidation. In the indirect, or French, process, the zinc vapour to be oxidized is obtained by boiling zinc [5].

2.3 Structural, Electrical and Optical Properties of ZnO

ZnO normally forms in the hexagonal (Wurtzite) crystal structure (6mm point group symmetry) with a=3.25 Å and c=5.12 Å. The Zn atoms are tetrahedrally coordinated to four O atoms [6, 7] (Figure 2-1). The oxygen anions occupy the octahedral sites.
Figure 2-1 Wurtze (hexagonal) structure of ZnO [6, 7].

The basic parameters of ZnO materials are presented in Table 2-1. As seen in Figure 2-1, the structure is non-centrosymmetric, which gives rise to polarization and piezoelectric properties.
Table 2-1 Properties of Wurtize ZnO [8]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters at 300K</td>
<td>$a_0 = 0.32495 \text{ nm, } c_0 = 0.52069 \text{ nm}$</td>
</tr>
<tr>
<td>Density</td>
<td>5.6803 g/cm$^3$</td>
</tr>
<tr>
<td>Melting point</td>
<td>1975°C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>100 mW/cm.K at 300K</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>8.656</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.008</td>
</tr>
<tr>
<td>Energy gap</td>
<td>3.4 eV, direct</td>
</tr>
<tr>
<td>Intrinsic carrier concentration</td>
<td>$&lt; 10^6 \text{ cm}^3 \text{ (max n-type}&gt; 10^{20}\text{cm}^3 \text{ electrons; max p type}&lt; 10^{17}$ cm$^3 \text{ holes})$</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>Electron effective mass</td>
<td>0.24</td>
</tr>
<tr>
<td>Electron Hall mobility at 330K</td>
<td>200 cm$^2$/Vs</td>
</tr>
<tr>
<td>Hole effective mass</td>
<td>0.59</td>
</tr>
<tr>
<td>Hole Hall mobility at 300K</td>
<td>5-50 cm$^2$/Vs</td>
</tr>
</tbody>
</table>
In the development of a crystalline morphology, the driving forces minimize the surface energy. Therefore, in near equilibrium conditions, a film grows with the crystallographic plane of the lowest free energy (i.e. the plane with the closest packing of atoms) parallel to the surface if no epitaxy exists between the film and substrate. ZnO tends to grow c-axis oriented normal to the substrate with minimization of surface energy.

ZnO is a II-VI semiconductor which tends to intrinsically form as an n-type semiconductor material, in which the electrical conductivity is due to excess zinc, presumably interstitially within the lattice and in oxygen vacancies [9, 10]. Extrinsic defects such as hydrogen are more likely to be incorporated as shallow donors [10]. However Studenkin et. al. [2] reported that the effect of H incorporation increases the number of zinc rich defects and therefore n type conductivity.

The defect chemistry for individually ionized Zn in vapour deposition can be written as follows [11]:

\[ \text{Zn(g)} \rightarrow \text{Zn}_{i} \]  \hspace{1cm} (1)

\[ \text{Zn}_{i} \rightarrow \text{Zn}_{i}^{+} + e^{-} \]  \hspace{1cm} (2)

\[ \text{Zn(g)} + \frac{1}{2} \text{O}_{2(g)} \rightarrow \text{ZnO (s)} \]  \hspace{1cm} (3)

Therefore the overall concentration of interstitial ions is determined by the vapour pressure (usually high for Zn) as indicated in equation (1). The extent of interstitial ionization is also a dependent of temperature. The mass-action equation for (2) is:
\[
K = [\text{Zn}^+] \frac{[e^-]}{P_{\text{Zn}(g)}} = \frac{[e^-]^2}{P_{\text{Zn}(g)}} \quad (4)
\]

\[
[e^-] = K^{1/2} P_{\text{Zn}(g)}^{1/2} = K^{1/2} K_{\text{O}_2}^{1/2} P_{\text{O}_2}^{-1/2} \quad (5)
\]

where \( K_{\text{O}_2} \) is the equilibrium constant for the reaction (3). It can be seen from equation (5) that the charge carrier concentration is a dependent of the partial pressure of oxygen.

A general expression for electrical conductivity \( \sigma \) and the concentration of conduction electrons \( n \) and holes \( p \) in an intrinsic semiconductor are expressed as

\[
\sigma = n e \mu \quad (6)
\]

\[
n_i = p_i = A T^{3/2} \exp \left(-\frac{E_g}{2 k_B T}\right) \quad (7)
\]

where \( n_i \) or \( p_i \) is the number of conduction electrons or holes in unit volume, \( e \) is electronic charge, and \( \mu \) is the mobility of current carriers, \( A \) is a constant, \( E_g \) is the energy gap, and \( k_B \) is the Boltzmann constant.

Generally speaking there would appear to be five possible conduction mechanisms including: ionic conduction; space-charge-flow; tunnelling and internal field emission; Schottky emission and impurity conduction [12]. There are few reports about the electrical conduction mechanism in ZnO. Hartmann et. al. [12] have showed that copper implantation of ZnO thin films deposited by sputtering decreases the resistivity, while oxygen annealing increases the resistivity of the ZnO thin film due to electron trapping.
by the Cu 3d states of Cu$^{2+}$. It has been recognized that the presence of Al or Co has the effect of enhancing the electrical conductivity of ZnO thin films, whereas monovalent ions (Li, Na) usually hinder it [13]. The electron Hall mobility in ZnO single crystals is in the order of 200 cm$^2$/V.s at room temperature. Electron doping, in nominally undoped ZnO, has been attributed to Zn interstitials, oxygen vacancies or hydrogen.

The optical properties of ZnO, such as photoluminescence, photoconductivity and absorption, reflect the intrinsic direct band gap, a strongly-bound exciton state, and gap states due to point defects [14]. A strong room temperature near band-edge UV photoluminescent peak at ~3.2 eV is attributed to an exciton state, as the excitation binding energy is of the order of 60 meV [8].
2.4 Applications of ZnO

Zinc oxide (ZnO) is attracting attention for its application to UV light-emitters, varistors, transparent high power electronics, surface acoustic wave devices, piezoelectric transducers and as a window material for display and solar cells (Figure 2-2). A common application is in gas sensors. Recent improvements in the quality and control of conductivity in bulk and epitaxial ZnO have increased interest in the use of this material for short wavelength light emitters and transparent electronics [15-18]. It has been utilized in recent research to build blue LEDs (Light Emitting Diodes) and transparent TFTs (Thin Film Transistors). GaN-based lasers and LEDs have already achieved wide commercial realization. In fact, ZnO has several fundamental advantages over GaN: (1) its free exciton is bound with 60 meV, much higher than that of GaN (21–25 meV); (2) it has a native substrate; (3) wet chemical processing is possible; and (4) it is more resistant to radiation damage (although both are much better than Si or GaAs) [19].

As a wide band gap semiconductor, ZnO is a candidate for solid state blue to UV optoelectronics, including lasers. This has important applications in high density data storage systems, solid-state lighting (where white light is obtained from phosphors excited by blue or UV light-emitting diodes), secure communications and bio-detection [20].

Transparent conducting zinc oxide films have been extensively studied in recent years, because of their low material cost, relatively low deposition temperature and stability in hydrogen plasmas compared to Sn-doped In$_2$O$_3$ (ITO) and SnO$_2$ films. These advantages are of considerable interest for solar energy conversion applications.
Compared to undoped ZnO, Al-doped ZnO films have lower resistivity and better stability, however as yet, the resistivity is not competitive with ITO. Transparency to visible light provides opportunities to develop transparent electronics, UV optoelectronics and integrated sensors, all from the same material system [8]. Transparent conducting films deposited on polymer substrates have many merits, such as being lightweight and small volume, compared to those deposited on glass substrates making the devices portable. They can be used in plastic liquid crystal displays, transparent electromagnetic shielding materials, flexible electro-optical devices, touch sensitive overlay and unbreakable heat-reflecting mirrors [21].

Figure 2-2 Applications of ZnO.
In medical applications, zinc oxide works to prevent sunburn but is also used to treat nappy rash, skin irritations, cold sores, cuts and burns.

2.5 Crystalline Structure of ZnO Thin Films

A major factor affecting the physical properties of ZnO thin films is microstructure. This is strongly dependent on the deposition conditions, for example, deposition rate, the substrate temperature, the substrate roughness, as well as substrate type. The microstructure of thin films is the result of nucleation and grain growth processes. Preceding the nucleation stage, atoms or molecules impinge on the substrate creating aggregates of atoms. If the stable nuclei form islands or clusters, the next stage after saturation involves coalescence. When two clusters which are of different sizes and crystalline orientation coalesce, the resultant crystallite assumes the orientation of the largest one. ZnO film growth can be varied from randomly oriented to highly c-axis oriented, depending on growth conditions [22]. C-axis orientation is generally observed in the coarse columnar structure seen after extended growth (see Chapters 3 and 4).

2.5.1 Structure Zone Model
Structure zone models have been extensively used to classify the morphology of thin films deposited by physical vapour deposition techniques. The Movchan-Demchishin model [23] describes the morphology of deposited films in terms of reduced temperatures $T/T_m$ where $T$ is the deposited temperature and $T_m$ the melting temperature of the deposited material (Figure 2-3).

Zone 1 ($T/T_m < 0.3$) consists of tapered crystals with domed tops which are separated by voided boundaries (voids). The internal structure of the crystals is poorly defined, with a high dislocation density. The crystal diameter increases with $T/T_m$, and that dependence indicates a very low activation energy and implies very little surface diffusion.

Zone 2 ($0.3 < T/T_m < 0.5$) consists of columnar grains separated by distinct, dense, intercrystalline boundaries; the surface has a smooth, mat appearance. Dislocations are primarily in boundary regions. Grain sizes increase with $T/T_m$, and may extend through the coating thickness at high $T/T_m$. The grain width dependence on $T/T_m$ yields an activation energy about equal to that for surface diffusion.

Zone 3 ($0.5 < T/T_m < 1$) consists of equiaxed grains. A process of recrystallization and grain growth occurs [24].
Magnetron sputtering offers the important advantage of high energy input into the growing film. The basic feature of Magnetron sputtering is the confining of the plasma in the front of the cathode. ZnO films deposited by magnetron sputtering possess different degrees of crystallinity and are all c-axis oriented normal to the substrate. As expected our grown films are columnar with densely packed grains (Zone 2 or transitional zone between zone 1 and 2). After annealing of ZnO thin films, a process of coalescence and major grain growth result in a porous and cracked structure (Zone 3) [24].

2.5.2 X-Ray Diffraction Analysis

Nanocrystalline ZnO thin films have been widely characterised using X-ray diffraction. X-ray diffraction is a useful tool to identify the crystal structure of materials. X-rays primarily interact with electrons in atoms [25]. Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. Let us consider an incident x-ray beam interacting with the atoms arranged in a periodic manner as shown in Figure 2-4.
For a given set of lattice planes with an inter-plane distance of $d$, the conditions for diffraction to occur can be simply written as $2dsin\theta = n\lambda$ which is known as Bragg's law. In the equation, $\lambda$ is the wavelength of the x-ray, $\theta$ the scattering angle, and $n$ an integer representing the order of the diffraction peak. Bragg's Law applies to scattering centres consisting of any periodic distribution of electron density, such as colloids, polymers, proteins and virus particles.

A general exact treatment of the relationship gives

$$D = \frac{0.9\lambda}{(\beta \cos \theta)}$$  \hspace{1cm} (8)$$

where:

$D$ is the average crystallite size

$\lambda$ is the wavelength of the X-rays
$\theta$ is the Bragg angle for the peak at $2\theta$

$\beta$ is FWHM (full width at half maximum) for a Gaussian shaped peak [26].

There are several special considerations for using XRD to characterise thin film samples such as the magnetron sputtered ZnO films in this work. First, reflection geometry is used for these measurements as the substrates are generally too thick for transmission. Secondly, high angular resolution is required because the peaks from semiconductor materials are sharp due to very low defect densities in the material. Consequently, monochromators are used to provide a highly collimated x-ray beam for these measurements.

Basic XRD measurements made on the thin film samples include:

- precise lattice constants measurements derived from $2\theta - \theta$ scans, which provide information about lattice mismatch between the film and the substrate and therefore is indicative of strain and stress. Residual stresses change the spacing $d$ of lattice planes of a crystalline material. Therefore residual stress can be measured by XRD.

- rocking curve measurements made by doing a $\theta$ scan at a fixed $2\theta$ angle, the width of which is inversely proportional to the dislocation density in the film and is therefore used as a gauge of the quality of the film.

- glancing incidence x-ray reflectivity measurements, which can determine the thickness, roughness, and density of the film. This technique does not require a crystalline film and works even with amorphous materials.
texture measurements which are used to determine the orientation distribution of crystalline grains in a polycrystalline sample. A texture measurement is also referred to as a pole figure as it is often plotted in polar coordinates consisting of the tilt and rotation angles with respect to a given crystallographic orientation. The detector is fixed at a specified 2θ position.

2.6 Current Developments in ZnO

2.6.1 Advanced Processing Methods

There are many deposition techniques for ZnO thin films. Thin film deposition technologies can be either purely physical, such as evaporative methods, or purely chemical, such as gas and liquid phase chemical processes. A considerable number of processes that are based on glow discharges and reactive sputtering combine both physical and chemical reactions and can be categorized as physic-chemical methods. Thin films of ZnO can be grown by

- sol gel processing,
- molecular beam epitaxy,
- chemical vapour deposition,
- magnetron sputtering,
• pulsed laser deposition, and spray pyrolysis on several different substrates [27, 28].

The main advantage of sputtering techniques is the deposition of dense and crystallographically oriented films. Other advantages include controllable deposition rates and lower substrate temperature. Sputter deposition has disadvantages also. For instance, films do not conform to substrate geometries, defects are prevalent and high vacuum equipment is necessary. Using techniques such as pulsed laser deposition (PLD), molecular beam epitaxy (MBE), or even reactive sputtering, ZnO of reasonable quality can be deposited at lower growth temperatures than GaN. This leads to the possibility of transparent junctions on cheap substrates such as glass, with the potential to realise low-cost UV lasers or light-emitting diodes for high-density data storage systems, solid-state lighting (where white light is obtained from phosphors excited by blue or UV light-emitting diodes), secure communications, UV detectors [29] and biodetection [8].

2.6.2 n and p Type ZnO

For ZnO, n-type conductivity is common in the as grown material, or relatively easy to realise via excess Zn, or with Al, Ga, or In doping. Reports indicate that the resistivity of ZnO or Al doped ZnO thin films prepared by magnetron sputtering is in the range of $10^{-4}$ to $10^{5} \ \Omega \cdot \text{cm}$ [30, 31]. A common opinion is that Zn–rich defects such as zinc interstitials ($\text{Zn}_i$) and oxygen vacancies (VO) are the main source of conductivity in as
grown material. Thus the conductivity of films can be determined by the degree of nonstoichiometry of ZnO. It has been reported that many factors affect the electrical properties of ZnO thin films, such as film thickness, grain and agglomerate size, grain boundary and impurity distribution, all of which are determined by the synthesis conditions. However, the effect of microstructure on the electrical properties of ZnO thin films and related correlations has not been widely discussed in the literature.

Without question, the most significant barrier to the widespread exploitation of ZnO-related materials in electronic and photonic applications is the difficulty in carrier doping, particularly as it relates to achieving p-type material.

With respect to p-type doping, ZnO displays significant resistance to the formation of shallow acceptor levels. The shallow level is shown in Figure 2-5, the band model of ZnO [32, 33]. The model consists of conduction band and valance band. The energy difference between them is the energy gap of ZnO, \(~3.37\) eV. The Fermi energy is the maximum energy level occupied by an electron at 0K.

![Figure 2-5 The band model of ZnO](image)
Table 2-2 reviews some of the approaches to p-type ZnO growth. Difficulty in achieving bipolar (n- and p-types) doping in a wide band gap material is common. These difficulties are (i) the limited range of suitable shallow acceptors such as N [34] may be less soluble than the lowest achievable concentration of donors, (ii) the impurities that yield shallow acceptors on one site may act as donors when on another site or when at interstitials, and (iii) acceptors may have a natural tendency to pair with native defects or background impurities to form electrically inactive complexes [35, 36]. While most efforts to achieve p-type doping of ZnO have focused on nitrogen doping, a few studies have considered other group V elements for substitutional doping on the O site. Given the mismatch in ionic radii for P (2.12 Å), As (2.22 Å), N (1.32 Å) and Sb (2.45 Å) as compared to O (1.24 Å) [7], solubility of these elements in ZnO should be limited. The first p type ZnO was reported in 1992, with many follow ups from 1997 onward [37]. There are some preliminary reports of P [38], As [39], N [40, 41] (from NH₃, N₂ and N₂O etc.) doping and N-Al[42], N-Ga [42, 43] and N-In [44] co-doping p-type ZnO. As seen in Table 2-3, many different growth techniques including Chemical Vapour Deposition (CVD) [45], PLD [40], MBE [41], sputtering [39] and Metalorganic Chemical Vapour Deposition (MOCVD) [46, 47] etc. have been used for the successful growth of p-type ZnO. Many of them suffer from problems of instability and reproducibility. Dr. Look commented that “the future of ZnO light emitters depends on either producing low resistivity p-type ZnO, or in mating n-type ZnO with a p-type hole injector.” [37]
Table 2-2 Review of p type ZnO growth [37]

<table>
<thead>
<tr>
<th>Name</th>
<th>Growth method</th>
<th>Substrate</th>
<th>Dopants</th>
<th>Carrier conc. cm$^{-3}$</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eagle-Picher</td>
<td>MBE</td>
<td>Li-doped Zn-ZnO (0001)</td>
<td>Zn, Oxygen Plasma Doped with N</td>
<td>9X10$^{16}$</td>
<td>“p-type yield not high” “nitrogen doping results in rough surface”</td>
</tr>
</tbody>
</table>
| Y. R. Ryu                   | Hybrid Beam Deposition (plasma-assisted PLD) | O-ZnO, or Si-SiC | As      | 4X10$^{17}$             | Not successful with sapphire
Need substrate surface treatment
Take care of background impurities
Avoid hydrogen contamination during or after deposition (not stable in air). |
| Ye Zhizhen                  | MOCVD               | Sapphire  | Nitrogen | 10$^{14}$-10$^{19}$     | They raise a N-H co-doping mechanism, believe hydrogen passivated the V$_0$ (A. Hoffmann observed an increase of N is associated with an increase of H) |
| D. P. Norton, Univ of Florida | MBE                 | P         | Nitrogen | 10$^{15}$-10$^{18}$     | Observed mix Hall Signs                                                |
| D. C. Look                  | MBE                 | Nitrogen  |         |                         | Low p-type yield
Under light illumination (even room light), samples always are n-type, small Hall voltage and noise due to scattering of carriers. |
| J. F. Rommeluerue, France   | MOVPE               | Sapphire  | Nitrogen |                         | Annealing in NO, N$_2$, O$_2$ leads to some type conversion.       |
| X. Li (NREL)                | MOCVD               | Glass     | NO      | 10$^{15}$-10$^{18}$     | “p-type film unstable, become highly resistive after a month, surface cracked”
no p-type when using O$_2$+NO
“annealing in air makes p-type go away” “do not have Ohmic contact”
“Hall Effect measurement noisy” “use Seebeck Measurement instead”
Bob Davis’ Comment: Seebeck Measurement which is essentially a thermal transfer mechanism, thus the substrate buffer layer could significantly interfere with the experiment. |
Table 2-3 Data on p type samples reported in the literature [37].

<table>
<thead>
<tr>
<th>1st author</th>
<th>technique</th>
<th>dopant</th>
<th>source</th>
<th>substrate</th>
<th>resis. (Ω·cm)</th>
<th>year publ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minegishi</td>
<td>CVD</td>
<td>N</td>
<td>NH₃</td>
<td>Al₂O₃</td>
<td>34</td>
<td>1997</td>
</tr>
<tr>
<td>Joseph</td>
<td>PLD</td>
<td>N</td>
<td>N₂O</td>
<td>Glass</td>
<td>4</td>
<td>1999</td>
</tr>
<tr>
<td>Ryu</td>
<td>PLD</td>
<td>As</td>
<td>GaAs</td>
<td>Glass</td>
<td>?</td>
<td>2000</td>
</tr>
<tr>
<td>Joseph</td>
<td>PLD</td>
<td>N, Ga</td>
<td>N₂O, Ga</td>
<td>Glass</td>
<td>0.5</td>
<td>2001</td>
</tr>
<tr>
<td>Guo</td>
<td>PLD</td>
<td>N</td>
<td>N₂O</td>
<td>Glass</td>
<td>2</td>
<td>2001, 2002</td>
</tr>
<tr>
<td>Butkluzi</td>
<td>Quasi-epi</td>
<td>none</td>
<td>none</td>
<td>ZnO</td>
<td>900</td>
<td>2001</td>
</tr>
<tr>
<td>Ashrafi</td>
<td>MOMBE</td>
<td>N</td>
<td>MMHy</td>
<td>Al₂O₃</td>
<td>?</td>
<td>2002</td>
</tr>
<tr>
<td>Xiong</td>
<td>DC Mag. Sputt.</td>
<td>none</td>
<td>none</td>
<td>Si</td>
<td>3</td>
<td>2002</td>
</tr>
<tr>
<td>Look</td>
<td>MBE</td>
<td>N</td>
<td>N₂</td>
<td>ZnO</td>
<td>40</td>
<td>2002</td>
</tr>
<tr>
<td>X. Li</td>
<td>MOCVD</td>
<td>N</td>
<td>NO</td>
<td>Glass</td>
<td>20</td>
<td>2003</td>
</tr>
<tr>
<td>B. S. Li</td>
<td>CVD</td>
<td>N</td>
<td>Zn₁₁N₂</td>
<td>Fused silica</td>
<td>150</td>
<td>2003</td>
</tr>
<tr>
<td>Haang</td>
<td>DC Mag. Sputt.</td>
<td>N</td>
<td>NH₃</td>
<td>Si</td>
<td>1</td>
<td>2003</td>
</tr>
<tr>
<td>Ryu</td>
<td>Hybrid beam</td>
<td>As</td>
<td>As</td>
<td>ZnO, SiC</td>
<td>2</td>
<td>2003</td>
</tr>
<tr>
<td>Kim</td>
<td>RF Sputt.</td>
<td>P</td>
<td>P₂O₅</td>
<td>Al₂O₃</td>
<td>0.6</td>
<td>2003</td>
</tr>
<tr>
<td>Lu</td>
<td>DC Mag. Sputt.</td>
<td>N</td>
<td>NH₃</td>
<td>Al₂O₃</td>
<td>31</td>
<td>2003</td>
</tr>
<tr>
<td>J. Wang</td>
<td>MOCVD</td>
<td>N</td>
<td>NH₃</td>
<td>Al₂O₃</td>
<td>100</td>
<td>2003</td>
</tr>
</tbody>
</table>

2.6.3 ZnO and Nanotechnology

2.6.3.1 Introduction

Nanoscience and nanotechnology involve studying and working with matter on an ultra-small scale from subnanometer to several hundred nanometres [48]. These nanosize materials have properties that are often significantly different from their counterparts.
with “ordinary size”. Nanotechnology is the next phase of Moore’s Law. This law predicted in 1965 that the dimension of a device would halve approximately every 18 months. By combining silicon innovations with other novel non-Si nanotechnologies, it is expected that Moore's Law will extend well into the next decade [49].

ZnO is a promising material for the realization and future of nanotechnology. With its wide band-gap (3.37eV), high excitonic binding energy and high breakdown strength, ZnO can be utilized for electronic and photonic devices, as well as for high-frequency applications. The availability of a native substrate and the potential for room temperature operations opens the door to ZnO applications including chemical sensors and subscale electronic circuits. As a source of unique properties, Zinc Oxide (ZnO) has been widely studied as a novel material for its practical and potential applications such as micro, nano-electronics and micro, nano-robotic (machining) technology [50].

Several synthesis methods of ZnO nanoparticles or nanocrystalline films, such as sputtering, pulsed laser deposition, epitaxial techniques and chemical routes have been developed. Mechanical attrition appears also to be a suitable method for obtaining semiconductor nanocrystals [51].

2.6.3.2 Nanostructures

Recently, basic one-dimensional nanostructures and their assembly in two-dimensional and three-dimensional ordered architectures have been one of major challenges faced by the modern synthetic chemists and materials scientists [52].
Up to now, much effort has been devoted to the fabrication of well-defined ZnO 1D nanostructure such as nanowires (or nanorods) [53], nanobelts (nanoribbons) [54], nanorings [55], nanocolumns [56], nanonails [57] and well-aligned ZnO nanorods and nanotube arrays [58]. One-dimensional ZnO nanostructures such as nanowires and nanorods have been studied for optoelectronic nanodevice applications as a promising candidate for UV light-emitting diodes and laser diodes because of both their fundamental importance and the wide range of their potential applications in nanodevices. ZnO nano-wires have potential for applications in laser devices due to their desirable optical properties. Therefore a detailed understanding of ZnO wires and the influence of impurities on their properties is important. ZnO nanorods can be grown or deposited on various substrates including Si [59]. Many groups have recently demonstrated the catalyst-driven growth of ZnO nanorods using MBE or vapour transport [60, 61]. The large surface area of nanorods makes them attractive for gas and chemical sensing, and the ability to control their nucleation sites makes them good candidates for micro-lasers or memory arrays. Nanorods and nanowires will lead to the possibility of nano devices, such as nanolasers or memory arrays [62]. An SEM of a single rod is shown in Figure 2-6 (a).

In addition, ZnO nano-particles are equally interesting and can be grown and synthesized by different methods. These nano-particles are of great interest for many technological as well as medical applications. Exchange-spring magnets are nanocomposites that are composed of magnetically hard and soft phases that interact by magnetic exchange coupling. Such systems are promising for advanced permanent magnetic applications[63].

The two-dimensional system of thin coatings has been studied widely. Three-dimensional (3D) interconnected networks of ZnO nanowires and nanorods are
synthesized by a high temperature solid–vapour deposition process [64]. The nanorods and nanowires have diameters of 20–100 nm and they grow along the c-axis. The thickness of the multilayer nano-network could be as thick as 30 μm. The sharp nanowire tips, the high degree of networking, and the high surface area of these unique nanonetworks make them a potential candidate for field emission, ultra-sensitive gas sensing, catalysts and filtering. Large-scale synthesis of ZnO nanowires has been achieved on Au-coated silicon substrates by physical evaporation of the mixture of ZnO, graphite powders and polycrystalline ZnO nanowires have been fabricated within the nanochannels of porous alumina [65]. In this work nanocrystalline ZnO films on glass and Si have been prepared by magnetron sputtering.

More recently, complex and oriented ZnO 3D structures, e.g. flower- and urchin-like assemblies [58], dandelion-like structures [66], hollow microspheres [67], polyhedral cages and shells [68], complex architecture [69], and hierarchical nanostructure [70], comb-like nanowire arrays, nanoneedle arrays [71], nanohelics (Figure 2-6 b [72]), and nanobows [73] have been successfully synthesized. For example, single crystalline ZnO nanohelices have been prepared by thermal evaporation of ZnO powder. The piezoelectric and semiconducting properties of ZnO suggest that the nanohelix could be a fundamental unit for investigating electromechanically coupled nanodevices by using the superlattice piezoelectric domains. The nanohelix is likely to have important applications in sensors, transducers, resonators, and photonics. The structural configurations of ZnO nano-objects could form the basis for fabricating nanoscale sensors, transducers, and resonators [72]. In this study nano-ZnO and polymer composites have been made in a water solution as a novel method of producing these materials.
Figure 2-6 (a) TEM images of single-crystal ZnO nanorod (top) and showing cored (Zn$_{1-x}$Mg$_x$)O nanorods (bottom) [8]; (b) SEM images of the left- and right-handed ZnO nanohelices [72].
2.6.4 Implantation Doping

Ion implantation is an important and controllable technique of introducing dopants into a semiconductor and creating high resistance regions for inter-device isolation. Dopants may become embedded in the solid and occupy the interstitial positions, thereby changing the chemical composition of the solid. Implantation doping is in its infancy in ZnO and there has been no clear demonstration of activation of an implanted donor or acceptor. Damage due to ion implantation may occur as a result of ionization as well displacement collisions, associated diffusion processes and phase changes. The residual implantation damage remaining after annealing appears to have donor-like characteristics. To minimize this damage, it may be necessary to adopt techniques used for other compound semiconductors, such as elevated temperatures during the implantation step, to take advantage of so-called dynamic annealing in which vacancies and interstitials created by the nuclear stopping process are annihilated before they can form stable complexes [8].

Ion implantation is used for introducing conduction carriers into IV and III–V group semiconductors, including selective-area doping, electrical and optical isolation, dry etching, and ion slicing. A wide range of implant conditions (implanted species, ion mass, dose ($10^{12-18}$ atoms.cm$^{-2}$), and implant temperature) affects the formation of lattice interstitials, vacancies and planar defects in a crystal such as GaN and ZnO [74]. Ion implantation of potential p-type dopants and co-implantation studies are beginning to show promising results for producing p-type ZnO [75]. Miyakawa [76], Komatsu[36], Jeong [77] and Ip[78] have reported implantations of As, In, N, Ga and H in a ZnO crystal at room temperature. Hartmann and Puchert [27] reported Cu implantation of
ZnO thin films. Kucheyev et. al. [79] have recently reported a systematic study of implant isolation in n-type ZnO epilayers grown on sapphire.

Mn-implanted (5×10^{16} \text{ atoms cm}^{-2}) ZnO nanorod samples show magnetization vs. magnetic field (H) behaviour at 300 K after a 700 °C, 5 min anneal (Figure 2-7). Hysteretic behaviour is clearly present. Possible explanations include ferromagnetism, superparamagnetism or spin-glass effects. The magnetization of unimplanted, annealed nanorods was as much as 3 orders of magnitude lower than in the implanted, annealed samples, demonstrating that the transition metals are responsible for the observed magnetic properties[8]. There was no significant chemical effect noted for Cr, Fe or Ni implantation relative to O, indicating these elements do not introduce a large concentration of deep acceptors into ZnO.

![Figure 2-7 Magnetization vs. field at 300 K for Mn-implanted ZnO nanorods [8].](image)

In transparent oxides, although the implantation is mainly applied to the fabrication of optical devices such as wave guides and fluorescent materials, the history of application
to carrier control is rather new as an approach to the fabrication of p-type ZnO. In this study, the dopants, Al, Ag, Sn, Sb, and TiN, are selected for this investigation to determine if these species can improve the conductivity of ZnO thin films and impart p-type properties to ZnO.
Chapter 2

2.7 Composites and ZnO

A composite material consists of a combination of materials which differ in composition or form, remain bonded together, and retain their identities and properties. Composites include: (1) fibrous (composed of fibres, and usually in a matrix), (2) laminar (layers of materials), (3) particulate (composed of particles or flakes, usually in a matrix), and (4) hybrid (combinations of any of the above) [80]. Laminar and particulate composites have been used in our ZnO composites such as ZnO thin films deposited on PEN, nano-ZnO particles and polyvinyl alcohol blends and Al, Ag, Sn, Sb and TiN implanted ZnO thin films. Their structure and properties such as electrical, optical and mechanical properties will be addressed in Chapter 10.

The ancient concept of composite materials was to combine different materials to produce a new material with performance unattainable by the individual constituents, e.g. adding straw to mud for building stronger mud walls. More recent examples are carbon black in rubber and fibreglass in resin etc. Epoxy resin composites are filled with nano-particulates using a KH-560 silane coupling agent to enhance the interfacial bonding between the inorganic reinforcing agent and the polymer matrix [81]. The incorporation of modifying Zn ions into "polydiene latex-silica" systems increases their mechanical characteristics due to an increase of the interaction between the organic and inorganic networks [82]. In nature, examples are abound: cellulose fibres in lignin matrix (wood), collagen fibres in an apatite matrix (bone) etc. Today, given the most efficient design, of for example an aerospace structure, a boat or a motor, we can make a composite material that meets or exceeds the performance requirements because of its
unique combination of properties. Most of the savings are in weight and cost. These are measured in terms of ratios such as stiffness/weight, strength/weight, etc.[83, 84]

### 2.7.1 Components of Composite Materials

There are several types of composites depending on the nature of the reinforcement. The bulk phase of the material is called matrix which holds and protects the reinforcing phase.

- **Matrix**

  Polymers, Metals and Ceramics etc. Poly (ethylene-naphthalate) (PEN) and polyvinyl alcohol (PVA) have been used in this study.

- **Reinforcement**

  1. Fibres as the reinforcement (Fibrous Composites) [85]

  2. Particles as the reinforcement (Particulate composites) such as nano-ZnO particles:

  3. Flat flakes as the reinforcement (Flake composites)

  4. Fillers as the reinforcement (Filler composites)
• Interface

The interface is a bonding surface or zone where a discontinuity occurs. The matrix material must "wet" the fibre/particles. Well "wetted" fibres/particles increase the interface surface area. Surfactants are used to improve the wetting properties, for example polyethylene oxide has been used to improve nano-ZnO particles wetting properties with PVA. To obtain desirable properties in a composite, the applied load should be effectively transferred from the matrix to the fibres/particles via the interface. Bonding with the matrix can be either weak Van der Walls forces or strong covalent bonds. Interfacial strength is measured by simple tests that induce adhesive failure between the fibres/particles and the matrix.

2.7.2 Properties of Composites

The matrix has the important function of transferring the applied load to the fibres. It is of great importance to be able to predict the properties of a composite, given the component properties and their geometric arrangement.

1) Surface Properties:

Corrosion resistance; Weather resistance; Tailored surface finish.

2) Thermal Properties:
Low thermal conductivity; Fire resistance; Low coefficient of thermal expansion.

3) Electrical Property:

Conductivity, High dielectric strength; Non-magnetic; Electromagnetic shielding property.

4) Stress-strain relationships

Stress can be induced in implanted and sputtered ZnO thin films and reduced by annealing. Nano-ZnO can be used to reinforce the mechanical properties of polymer composites.

The residual stress of ZnO polycrystalline thin films can be measured by XRD, by calculating the elastic strains from the measured changes in inter-planar spacing [86]. The relationship between stress and strain can be described by Hooke's law. For isotropic material, the 3-D Hooke's law [87] in matrix form is:

\[
\begin{bmatrix}
\varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\
\varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\
\varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz}
\end{bmatrix} =
\begin{bmatrix}
\frac{1}{E} & -\nu & -\nu \\
-\nu & \frac{1}{E} & -\nu \\
-\nu & -\nu & \frac{1}{E}
\end{bmatrix}
\begin{bmatrix}
\sigma_{xx} \\
\sigma_{yy} \\
\sigma_{zz}
\end{bmatrix}
\]

\[
\begin{bmatrix}
\sigma_{xx} \\
\sigma_{yy} \\
\sigma_{zz}
\end{bmatrix} =
\begin{bmatrix}
\frac{1}{E} & -\nu & -\nu \\
-\nu & \frac{1}{E} & -\nu \\
-\nu & -\nu & \frac{1}{E}
\end{bmatrix}
\begin{bmatrix}
\varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\
\varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\
\varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz}
\end{bmatrix}
\]

Where:

\[G = \frac{E}{2(1+\nu)}\]
E is Young’s modulus, G is the shear modulus, \( \sigma \) is the stress, \( \nu \) is the Poisson’s ratio. 

\( \varepsilon \) is the strain.

5) Rule of Mixture

It is of interest to consider the mixing effects of composite properties, for example nano-ZnO particles with PVA. The Rule of Mixture is a rough tool that considers the composite properties as volume weighted averages of the component properties. It is important to realise that this rule works accurately only in certain simple situations, such as determining composite density and elastic modulus for example in this case with nano-ZnO polymer films. For most other properties, this provides only a rough estimate for initial design purposes. Below are some equations derived for unidirectional continuous fibre composites. The principle used is that in longitudinal direction, both fibres and matrix have the same strain (isostrain) and in transverse direction, both fibres and matrix have the same stress (isostress).

The subscripts f, m, v and c refer to fibre, matrix, voids and composite respectively.

The subscripts l and t refer to longitudinal and transverse respectively.

E is the Young’s Modulus, and \( d \) is density.

Lowercase \( \nu \) refers to volume, whereas uppercase V refers to volume fraction (volume of a component divided by total volume).
a. Density

\[ d_c = \frac{m_c}{V_c} = \frac{(m_f + m_m)}{(V_f + V_m + V_c)} = \frac{(d_f V_f + d_m V_m)}{(V_f + V_m + V_c)} = d_f V_f + d_m V_m \]  

(10)

b. Young’s Modulus

Longitudinal

\[ E_l = E_f V_f + E_m V_m \]  

(11)

Transverse

\[ \frac{1}{E_t} = \frac{V_m}{E_m} + \frac{V_f}{E_f} \]  

(12)

These equations are used to predict the properties of polymer composites.
2.7.3 Biomedical Issues

ZnO composites could have potential for biomedical use as discussed in section 2.4. Two important issues are discussed here:

1) A composite is made of two or more materials, and each individual component can elicit a different biological response. This complicates testing for biocompatibility since every additional material increases the requirements for approval;

2) Composite material processing for non-medical applications tends to involve strong solvents and reagents, particularly in thermosetting matrices like epoxy and phenolics, where considerable solvent residues are present. Modifying these processes for medical-grade implantable products is challenging.

2.8 ZnO and Polymer Composites

The introduction of nano-ZnO into polymers could improve the mechanical, electrical and optical properties of the polymers due to a strong interfacial interaction between the organic polymer and the inorganic nanoparticles, nanoparticle's small size, large specific area, and quantum effect, respectively. Consequently, these nanocomposites could be widely applied in coatings, rubbers, plastics, sealants, fibres and other applications [88, 89].
Poly (ethylene-naphthalate) (PEN) is a transparent aromatic polyester which was developed many years ago, but it has been largely replaced by poly (ethylene-terephthalate) (PET) whose production cost is lower. However, in the past few years, there has been a renewal of interest in PEN because of its better thermal and mechanical properties. PEN is a biaxially oriented film with high stiffness and mechanical strength, low thermal shrinkage and high chemical resistance. PEN offers good resistance to temperature up to 160 °C and to traction (120 MPa). It is considered as a material with a future in various branches of industry as electricity, electronics and also in food-packaging. This makes it an interesting target for composite preparation with incorporation of ZnO.

There have been some reports of ZnO thin films deposited on polymer substrates. Guedri Knani et. al. have reported the photo-protection of PEN by ZnO coating [90]. Highly transparent (T > 80%) and conductive (~ 10\(^{-3}\) Ω.cm) zinc oxide thin films were deposited by atomic layer-controlled growth on flexible polyethylene terephthalate (PET) at temperatures of 100–210°C using diethylzinc (DEtZn) and water [91]. Zhang et. al. have reported that highly transparent conducting Al-doped ZnO films with good adherence and low resistivity have been prepared on polyisocyanate (PI) and polypropylene adipate (PPA) substrates by r.f. magnetron sputtering [21]. Fortunato et. al. have reported that Ga doped ZnO thin films on PEN substrates and Al doped ZnO thin films on poly(ethylene-terephthalate) (PET) substrates by r.f. magnetron sputtering [92, 93]. The lowest resistivity obtained of Ga doped ZnO thin films was 5×10\(^{-4}\) Ω .cm\(^{-1}\) and an average optical transmittance in the visible part of the spectra of 80%. Kuoni et. al. have reported using polyimide membrane with ZnO piezoelectric thin film pressure transducers as a differential pressure liquid flow sensor. The pressure sensor membrane
is a thin polyimide sheet bonded to a silicon wafer and the sensing material is a sputtered ZnO piezoelectric thin film [94].

Umeda et. al. have reported that in the layered photovoltaic cells with the structure of indium-tin-oxide (ITO)/ZnO /fullerene/conducting polymer/Au, a monochromatic energy conversion efficiency of 5.2% under 0.6 mW/cm² illumination at 500 nm and an external quantum efficiency reaching 74% at the peak wavelength have been realised, which can be explained by the interpenetrated fullerene/conducting polymer interface and the short distance between the electron-generation region and electrode, enhancing electron collection of the electrode [95].

Shirakawa et. al. have investigated photovoltaic properties of a photovoltaic cell with the structure indium–tin oxide (ITO)/ZnO/C60/poly (3-hexylthiophene) (PAT6)/Au. This photovoltaic cell has demonstrated a high efficiency for solar cells based on organic polymers, i.e. a monochromatic external quantum efficiency of over 70% at the peak wavelength and a power conversion efficiency of 1.0% under AM1.5 spectral illumination of 100 mW cm⁻² [96].

Jiu et. al. have reported the formation of organic/inorganic supramolecular structures containing semiconductor ZnO whose shape are controlled by organic thiophene acids containing different number of thiophene units [97]. These materials are most promising to fabricate a controllable molecular array and shape for efficient intermolecular energy and electron transfer between an organic moiety and inorganic unit and to construct devices to combine the superior electronic, magnetic, and optical properties.

Abdullah et. al. [98] have succeeded in producing ZnO/polymer composites with stable luminescence peaks down to 465 nm (blue region) by in-situ growth of ZnO nanoparticles in a poly(ethylene glycol) (PEG) matrix. Ali et. al. [99] have reported that
a thin ZnO nanocomposite poly(styrene–acrylic acid) diblock copolymer film containing self-assembled ZnO nanoclusters on Si and SiO$_2$ surfaces. The approach holds promise for the large area application of patternable nanocomposite films and stand-alone nanostructures on Si wafers. Zheng et. al. [100] have examined the influence of ZnO nanoparticles on the crystalline structures of nylon-6. The inducing effect increases with a decreasing ZnO particle size. The total crystallinity of composites containing ZnO is a little smaller than that of nylon-6 under the same crystallization conditions. Xiong [89] has investigated poly(styrene butylacrylate) latex/ZnO nanocomposites. The tensile strength, UV and NIR (near infrared) shielding properties of the nanocomposite polymers increased, and the Tg first increased then decreased, with increasing nano-ZnO content. Hong et. al. have reported that ZnO/ low density polyethylene nanocomposites had exhibited a slower decrease in resistivity with filler concentration compared to the conventional composite [101].
2.9 Summary

Major advances have been made by many groups around the world recently in demonstrating p-type ZnO, implant isolation processes and in realizing room temperature ferromagnetism in ZnO. Remarkable progress has been made in achieving high quality, single crystal substrates. Many innovative technologies have been developed relating to the fabrication of thin-film organic devices with high performance and long operational lifetime. However for ZnO based materials, there are still many areas of limited understanding requiring further exploration including:

(1) higher p-type doping levels in epitaxial films, this will require even better control of the background n-type conductivity in the material that arises from native defects and impurities such as hydrogen.

(2) realization of high quality p–n junctions by epitaxial growth, with good breakdown characteristics, these are the building blocks for devices such as UV LEDs or lasers.

(3) p-type Ohmic contacts with lower specific contact resistance, a desirable goal is to achieve a contact resistance of $10^{-5} \ \Omega \text{cm}^2$ or less for ZnO-based light emitters so that self-heating in the contact region does not degrade their reliability.

(4) development of implant doping processes, to realise both n and p-type layers, this will require a better understanding of the defects created by the implant step and their thermal stability and also a better understanding of the stability of the ZnO surface during activation annealing.
Although many innovative technologies have been developed relating to the fabrication of thin-film organic devices with high performance and long operational life, very few of these technologies have left the laboratory and found their way into an economically viable manufacturing environment.

The work reported in this thesis has involved a series of issues in an attempt to advance the understanding of ZnO, particularly those of sputtered thin films.

- processing (changes in deposition conditions; annealing; implantation), composition, microstructure, electronic, optical and electromagnetic shielding properties of ZnO thin films deposited by magnetron sputtering;
- ion implantation as a method to dope Al, Ag, Sb, Sn and TiN into ZnO thin films or single crystals; to develop conducting, transparent oxide films and/or p-type semiconductor for potential device applications;
- the relationships of doping, microstructure and properties of ZnO thin films and composites, for example, effects of d-spacing, X-ray density, residual stress, doping and temperature on resistivity of magnetron sputtered ZnO thin films.

It is likely that many of these areas will see significant progress in the near future as the promise of ZnO for low cost transparent electronics and UV light emission becomes more widely known and utilized [8]. The interaction of inorganic materials such as ZnO with polymer substrates especially in device structures is particularly important. It can be expected that organic electronic devices will one day revolutionize the technological world.
2.10 References


31. Fang, Guojia J., Li, Dejie, and Yao, Bao-Lun, *Influence of post-deposition annealing on the properties of transparent conductive nanocrystalline ZAO thin


52. Xie, Qin, Dai, Zhou, Liang, Jianbo, Xu, Liqiang, Yu, Weichao, and Qian, Yitai, *Synthesis of ZnO three-dimensional architectures and their optical properties*, in *Solid State Communications*. 57


Chapter 3

3 Microstructure, Electrical and Optical Properties of Sputter Deposited Nanocrystalline ZnO Thin Films

3.1 Introduction

Magnetron sputtering is a popular technique to prepare thin films. Zinc oxide thin films were prepared by d.c. (direct current) and r.f. (radio frequency) magnetron sputtering on glass substrates.

The reported resistivities of ZnO or Al doped ZnO thin films prepared by magnetron sputtering are in the range of $10^{-4}$ to $10^5 \Omega \cdot \text{cm}$ [1, 2]. Generally, Zn– rich defects such as zinc interstitials ($Zn_i$) and oxygen vacancies ($V_O$) are believed to be the main source of conductivity in as grown ZnO samples [3, 4]. The effects of several parameters like film thickness, grain and agglomerate size, grain boundaries and impurities on the electrical properties of ZnO thin films have been reported [5-8]. However, there are fewer reports addressing the relationships of microstructure on the optical and electrical properties of ZnO thin films.

This chapter reports a detailed study on electrical, optical and microstructural parameters of d.c. and r.f. sputtered undoped and Al doped ZnO thin films. It has been found that ZnO films produced by d.c. sputtering have a high resistance, while the films
produced using r.f. sputtering are significantly more conductive. While the conductive films have a compact nodular surface morphology, the resistive films have a relatively porous surface with columnar structures in cross section. Compared to the d.c. sputtered films, r.f. sputtered films have a microstructure with smaller d-spacing, lower internal stress, larger band gap energy and higher density. The dependence of conductivity on the deposition technique and the resulting d-spacing, stress, density, band gap, film thickness and Al doping are discussed. Correlations between the electrical conductivity, microstructural parameters and optical properties of the films have been made. However the relationship between the band gap and the conductivity of ZnO thin films is complex.

### 3.2 Experimental

A series of ZnO films were deposited by d.c. and r.f. magnetron sputtering using direct and reactive sputtering modes. Argon or argon-oxygen mixtures were used as the plasma-forming gas. Working pressure in the chamber was varied from 2 to 20 mTorr keeping the cathode-to-substrate distance 13 cm and deposition time 1-4 hrs. The sputtering targets were ZnO (99.9%) or Zn (99.99%), with an Al thin strip attached on the surface of the target for Al doping. Microscopic glass slides were used as substrates, which were in rotation during deposition.

The principle of sputter deposition of ZnO thin films is shown in Figure 3-1. To initiate the process, a large negative potential is applied between target and the ground so that
electrons are emitted from the target surface. The ejected electrons accelerate through
the potential. They collide with gas atoms and ionize them. Positive ions are accelerated
to the cathode. When they hit the target, different types of particles are emitted. There
are of course neutral atoms that will eventually get to the substrate and build the film,
but also negative ions, photons and secondary electrons. If the secondary electron yield
is high enough, a plasma will be created [9].

ZnO thin films were deposited under various deposition conditions as listed in Table 3-
1. The electrical resistivity of the films was measured by standard two-probe and four-
probe (Figure 3-2) techniques. Scanning electron microscopy (SEM, Philips XL-30S
with Energy-dispersiveX-ray (EDX) using analytical ZnO pellets as standard materials)
and X-ray diffractometry (XRD, Bruker D8, Cu Kα) were used to characterise the
microstructure of the films. SEM was used for thickness measurement of the films. Hall
coefficients of the samples were measured at room temperature by an automated d.c.
Hall measurement system using the technique devised by Van Der Pauw in the
laboratory of National University of Singapore. A HP 8254 spectrophotometer was used
for recording the optical transmission spectra of the samples in the 190 – 800 nm
spectral range.
Figure 3-1 Magnetron sputtering and its deposition principles.
\[ \rho = \frac{(V/I)}{(W^*t)/L} \ (\Omega \cdot \text{cm}) \]

Figure 3-2 Four-probe technique for measuring conductivity.

Table 3-1 Processing parameters and properties of some typical ZnO thin films deposited by magnetron sputtering.

<table>
<thead>
<tr>
<th>No.</th>
<th>Pm/Torr</th>
<th>Power</th>
<th>Bias</th>
<th>Time</th>
<th>Target</th>
<th>Thickness</th>
<th>Resistivity</th>
<th>Band gap, eV</th>
<th>X-ray density, g/cm³</th>
<th>d-spacing, Å</th>
<th>Stress, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-16</td>
<td>10.0/Ar</td>
<td>0.25A/DC</td>
<td>-50.0</td>
<td>4.0hrs</td>
<td>ZnO</td>
<td>1240</td>
<td>1.0 x 10⁶</td>
<td>3.09</td>
<td>5.650</td>
<td>0.2614</td>
<td>-1.0758</td>
</tr>
<tr>
<td>Z-17</td>
<td>20.0/Ar</td>
<td>0.25A/DC</td>
<td>-50.0</td>
<td>4.0hrs</td>
<td>ZnO</td>
<td>954</td>
<td>9.7 x 10⁶</td>
<td>3.12</td>
<td>5.650</td>
<td>0.2614</td>
<td>-1.0570</td>
</tr>
<tr>
<td>Z-25</td>
<td>20.0/Ar</td>
<td>0.25A/DC</td>
<td>-150.0</td>
<td>4.0hrs</td>
<td>ZnO</td>
<td>1598</td>
<td>5.0 x 10⁶</td>
<td>3.09</td>
<td>5.649</td>
<td>0.2614</td>
<td>-1.1066</td>
</tr>
<tr>
<td>Z-22</td>
<td>20.0/Ar</td>
<td>125W/RF</td>
<td>0</td>
<td>4.0hrs</td>
<td>ZnO</td>
<td>675</td>
<td>0.160</td>
<td>3.20</td>
<td>5.661</td>
<td>0.2699</td>
<td>-0.5786</td>
</tr>
<tr>
<td>Z-19</td>
<td>20.0/Ar</td>
<td>125W/RF</td>
<td>-50.0</td>
<td>4.0hrs</td>
<td>ZnO</td>
<td>576</td>
<td>1.060</td>
<td>3.19</td>
<td>5.664</td>
<td>0.2608</td>
<td>-0.4446</td>
</tr>
<tr>
<td>Z-20</td>
<td>10.0/Ar</td>
<td>125W/RF</td>
<td>-50.0</td>
<td>4.0hrs</td>
<td>ZnO</td>
<td>681</td>
<td>0.031</td>
<td>3.17</td>
<td>5.666</td>
<td>0.2607</td>
<td>-0.3672</td>
</tr>
<tr>
<td>Z-21</td>
<td>20.0/Ar</td>
<td>250W/RF</td>
<td>-50.0</td>
<td>40min</td>
<td>ZnO</td>
<td>417</td>
<td>0.010</td>
<td>3.20</td>
<td>5.668</td>
<td>0.2606</td>
<td>-0.2372</td>
</tr>
<tr>
<td>Z-23</td>
<td>10.0/Ar</td>
<td>250W/RF</td>
<td>-50.0</td>
<td>1.0hr</td>
<td>ZnO</td>
<td>464</td>
<td>0.009</td>
<td>3.16</td>
<td>5.664</td>
<td>0.2607</td>
<td>-0.4128</td>
</tr>
<tr>
<td>Z-36</td>
<td>2.0/Ar:O₂=6:4</td>
<td>0.25A/DC</td>
<td>-50.0</td>
<td>2.0hrs</td>
<td>Zn+Al</td>
<td>437</td>
<td>2.7 x 10⁶</td>
<td>3.08</td>
<td>5.601</td>
<td>0.2637</td>
<td>-3.3554</td>
</tr>
<tr>
<td>Z-37</td>
<td>2.0/Ar:O₂=6:4</td>
<td>0.25A/DC</td>
<td>-100.0</td>
<td>2.0hrs</td>
<td>Zn+Al</td>
<td>437</td>
<td>2.1 x 10⁶</td>
<td>3.11</td>
<td>5.602</td>
<td>0.2636</td>
<td>-3.2830</td>
</tr>
<tr>
<td>Z-38</td>
<td>2.0/Ar:O₂=6:4</td>
<td>0.25A/DC</td>
<td>0</td>
<td>2.0hrs</td>
<td>Zn+Al</td>
<td>456</td>
<td>1.03 x 10⁶</td>
<td>3.14</td>
<td>5.612</td>
<td>0.2632</td>
<td>-2.8572</td>
</tr>
<tr>
<td>Z-43</td>
<td>10.0/Ar:O₂=9:1</td>
<td>250W/RF</td>
<td>-50.0</td>
<td>2.0hrs</td>
<td>Zn+Al</td>
<td>267</td>
<td>1.19</td>
<td>3.23</td>
<td>5.666</td>
<td>0.2606</td>
<td>-0.3216</td>
</tr>
<tr>
<td>Z-44</td>
<td>10.0/Ar:O₂=9:1</td>
<td>250W/RF</td>
<td>0</td>
<td>2.0hrs</td>
<td>Zn+Al</td>
<td>337</td>
<td>0.137</td>
<td>3.29</td>
<td>5.669</td>
<td>0.2605</td>
<td>-0.2094</td>
</tr>
<tr>
<td>Z-45</td>
<td>10.0/Ar:O₂=9:1</td>
<td>250W/RF</td>
<td>-100.0</td>
<td>2.0hrs</td>
<td>Zn+Al</td>
<td>315</td>
<td>3.69</td>
<td>3.24</td>
<td>5.671</td>
<td>0.2604</td>
<td>-0.1201</td>
</tr>
<tr>
<td>Z-46</td>
<td>10.0/Ar:O₂=9:1</td>
<td>250W/RF</td>
<td>-50.0</td>
<td>2.0hrs</td>
<td>Zn</td>
<td>300</td>
<td>763</td>
<td>3.22</td>
<td>5.659</td>
<td>0.2610</td>
<td>-0.6679</td>
</tr>
</tbody>
</table>
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3.3 Results

The XRD patterns of the ZnO films are shown in Figure 3-3. The patterns revealed only strong (002) and weak (004) peaks, indicating a strong preferred orientation perpendicular to the substrate. As the surface energy density of the (002) orientation is the lowest in a ZnO crystal, (002) orientation is favored in the film [10]. In most of the samples, d002 values (Table 3-1) are higher than the standard d002 value for unstressed powder (0.26033 nm, ASTM [11]) suggesting an elongation of unit cells along the c axis, and existence of compressive stresses along the plane of the films.

From diffraction simulations using ‘Rietan 2000’ (Authors: F. Izumi and T. Ikeda), if strong preferred orientation to the C-axis is introduced into the calculation, only (00n) diffraction can be observed (Figure A-2).

![XRD patterns of d.c. sputtered and r.f. sputtered ZnO thin films.](image)

To derive the stress $\sigma_{\text{film}}$ parallel to the film surface, the following formula can be used for a hexagonal lattice [12]:
\[
\sigma_{\text{film}} = \left[2C_{13}^2 - C_{33} (C_{11} + C_{12})\right] \frac{(C_{\text{film}} - C_{\text{bulk}})}{(2C_{13}C_{\text{bulk}})} \quad (1)
\]

Where \(C_{ij}\) are the elastic constants, \(C_{\text{film}}\) and \(C_{\text{bulk}}\) are lattice constants of the film and bulk, respectively. \(C_{ij}\) data for single crystal ZnO have been used as \(C_{11} = 208.8\) GPa, \(C_{33} = 213.8\) GPa, \(C_{12} = 119.7\) GPa and \(C_{13} = 104.2\) GPa. This yields the following numerical relation for the stress derived from XRD results:

\[
\sigma_{\text{film}} = -232.8 \frac{(C_{\text{film}} - C_{\text{bulk}})}{C_{\text{bulk}}} \quad (2)
\]

The calculated d-spacing and stress for the films are listed in Table 3-1. The negative estimated stress for the films indicates that the lattice constant \(c\) is elongated, as compared to the unstressed powder sample.

In order to estimate the density in a unit cell of ZnO thin film by X-ray analysis, I use the relationship:

\[
\text{X-ray density} = \frac{M}{(NV)} \quad (3)
\]

where \(M\) is the total mass in a unit cell of ZnO; \(N\), the Avogadro number, and \(V\) is the volume of the unit cell. Considering the bulk lattice parameter “a” value [11], my
calculated densities for the films were in the range of 5.602-5.671 g/cm³, which are lower than the value for unstressed ZnO powder (5.674 g/cm³). The error in the estimation of x-ray density was ± 0.002 g/cm³. Such a lower density of unit cells in our films is due to stress induced elongation.

Typical surface and cross-sectional SEM micrographs of the ZnO films are shown in figure 3-4. From the micrographs we can observe the formation of nanometer size grains in the films with varying grain size for the films grown under different conditions. In general, the d.c. sputtered films grow along the c axis with a good columnar structure; whereas, the r.f sputtered films grow along the c axis with shorter columnar structures and with slightly arbitrary orientation (Figure 3-4b). The r.f. sputtered films reveal lower surface porosity than their d.c. counterparts (Figure 3-4a).

Almost all films prepared by d.c. sputtering from the ZnO target (Table 3-1) have resistivity higher than $10^5 \, \Omega \cdot \text{cm}$, whereas all the films prepared by r.f. sputtering have lower resistivity ($9.0 \times 10^{-3} - 7.63 \times 10^2 \, \Omega \cdot \text{cm}$). In the case of reactive sputtering, while the doping of Al did not cause any substantial change in conductivity of the films prepared by the d.c. process, the resistivity of the films decreased with Al doping (0.86-1.65%) for the r.f. sputtered films. A similar decrease of resistivity in ZnO films is observed by Majumdar et. al. [13] for <4% Al doping in their chemical solution deposited films.
Figure 3-4 SEM micrographs of ZnO thin films: (a) top view, and (b) cross section. Samples Z-16 and Z-17 were prepared by d.c. sputtering; Z-21 and Z-44 were prepared by r.f. sputtering.

It is well known that the composition of thin films strongly affect their electrical conductivity [2, 4]. I performed energy dispersive spectroscopy (EDS) analysis of the samples but could not notice any gross variation in their compositions. Though the oxygen content in the samples varied from 46.8 at. % to 49.8 ± 2 at. %, their resistivity varied from $9.0 \times 10^{-3}$ to $2.7 \times 10^{6}$ Ω⋅cm, implying that not only the composition, but also other factors such as the microstructure have significant influence on the conductivity of the films.
Figure 3-5 d-spacing and resistivity relationship for ZnO thin films produced by direct (top) and reactive sputtering (bottom).

From the Table 3-1, I can see that all ZnO films with good conductivity (samples with resistivity less than 10 Ω⋅cm) have relatively small d-spacing (<0.261 nm), while the poorly conductive ZnO films (samples with resistivity >500 Ω⋅cm) have a larger d-spacing (>0.261 nm). Plots of log ρ vs. d-spacing for the films prepared with the ZnO
target and through Zn reactive sputtering are shown in Figure 3-5. Both the plots follow more or less a linear relationship. From the slopes of the linear fits, the relationship between the resistivity and lattice spacing for the two cases could be extracted. For the highly resistive films (>10^4 Ω·cm), the linear fits are not as good as for low resistivity films. Hence, the lattice spacing alone can not account for conductivity differences.

The results also show that the most conductive ZnO films have higher density (>5.66 g/cm³), while the poorer conducting films have lower density (<5.66 g/cm³). The log ρ vs. x-ray density plots for the ZnO films are shown in Figure 3-6. While the highly conductive films have absolute stress values less than 0.70 GPa, the poorly-conductive films (resistivity higher than 10^3 Ω·cm) have stress values higher than 0.72 GPa (Table 3-1).

As the conductivity of the films depends on their thicknesses, films with several different deposition times were prepared to obtain films with thicknesses varying from 150 to 675 nm. The log ρ of the films decreased almost linearly with the increase of film thickness.
thickness (Figure 3-7) as observed by other workers [14]. However, similar behaviour is not observed for the films prepared with different processing parameters.

Figure 3-7 Variation of resistivity with film thickness for Z-22 series ZnO thin films.

All the doped and undoped films, prepared either by d.c. or r.f. sputtering show n-type conductivity which might be due to the Zn excess (as determined from the EDS measurements). From Table 3-2, I can see that the highly conductive film (sample Z-21, \( \rho = 0.0097 \ \Omega \cdot \text{cm} \)) has a mobility of 13.7 cm\(^2\)/V·s and a carrier concentration of 2.0\times10^{19}/\text{cm}^3, whereas, a higher resistivity film (sample Z-45, \( \rho = 42.0 \ \Omega \cdot \text{cm} \)) has a mobility of 0.33 cm\(^2\)/V·s and a carrier concentration of 4.5\times10^{17}/\text{cm}^3. Therefore, as expected, the carrier concentration and the carrier mobility of the samples decreased with their conductivity.
Table 3-2 Resistivity, mobility and carrier concentration data of selected ZnO films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>P (mTorr)</th>
<th>Power</th>
<th>Bias (V d.c.)</th>
<th>Target</th>
<th>Resistivity (Ω cm)</th>
<th>Mobility (cm²/V s)</th>
<th>Carrier conc. (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-21</td>
<td>20.0/Ar</td>
<td>250W/RF</td>
<td>-50.0</td>
<td>ZnO</td>
<td>0.0097</td>
<td>13.7</td>
<td>2.00x10¹⁹</td>
</tr>
<tr>
<td>Z-44</td>
<td>10.0/Ar:O₂:9:1</td>
<td>250W/RF</td>
<td>0</td>
<td>Zn+Al Reactive</td>
<td>0.137</td>
<td>0.287</td>
<td>6.00x10¹⁸</td>
</tr>
<tr>
<td>Z-45</td>
<td>10.0/Ar:O₂:9:1</td>
<td>250W/RF</td>
<td>-100.0</td>
<td>Zn+Al Reactive</td>
<td>3.69</td>
<td>0.330</td>
<td>4.50x10¹⁷</td>
</tr>
</tbody>
</table>

To study the conduction mechanism in my undoped ZnO films, conductivity measurements were performed at different temperatures for the films prepared by d.c. and r.f sputtering of ZnO targets. In Figure 3-8 the plots of resistivity vs. temperature for the ZnO films prepared by r.f sputtering (Figure 3-8a) and d.c. sputtering (Figure 3-8b) are shown. The calculated conductivity was found to follow the Arrhenius equation:

\[
\sigma = \sigma_0 \exp \left(\frac{-E_a}{kT}\right)
\]  \hspace{1cm} (4)

where, \(\sigma_0\) is a constant, \(E_a\) is the activation energy of the electron transport in the conduction band, \(k\) is the Boltzmann constant and \(T\) is the absolute temperature. Figure 3-8 shows two linear regions for both r.f. and d.c. sputtered ZnO films, revealing two activation energies, one for higher and one for the lower temperature ranges. The activation energies (\(E_{a1}\) and \(E_{a2}\)) calculated for the respective temperature ranges are shown in figure 3-8. The evaluated activation energies are in agreement with the values reported for sol–gel derived ZnO films [15].
Figure 3-8 Variation of resistivity with 1/kT for (a) r.f. sputtered and (b) d.c. sputtered ZnO thin films.

The band gap energy of the films has been measured from the optical transmission spectra using the photon energy at half maximum absorption [16]. From the calculated values presented in Table 3-1, all the films produced by d.c. sputtering show band gaps smaller than 3.15 eV; however, the band gaps of the films produced by r.f. sputtering are higher. As the residual stress can change the lattice spacing [17] and band gap (Figure 3-9), we expect higher lattice constant c for the films grown by d.c. sputtering. The
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The elongated c-axis might decrease the overlap between the atom wave-functions, decreasing the separation between the conduction and valence bands [18] and therefore causing a decrease in band gap.

![Diagram showing the variation of band gap with stress](image)

Figure 3-9 Variation of band gap of ZnO thin films with stress (as measured by XRD).

### 3.4 Discussion

My results indicate that r.f. sputtered films have better conductivity than those produced by d.c. sputtering. In r.f. sputtering, breakdown ionization occurs by heating electrons in the gas plasma with a fluctuating field, an effect which is not present with a constant d.c. field. The main difference between d.c. and r.f. excitation is a much higher ion to neutral ratio (by a factor of 4-10) for the r.f. discharge, which is caused by a higher plasma density in front of the substrate and a lower deposition rate for the same discharge power. Thus, the ion bombardment can be achieved at a lower pressure with r.f. sputtering compared to d.c. sputtering. r.f. deposition leads to a more homogeneous...
distribution of grains. The lower resistivity of the r.f. sputtered films is attributed to their higher carrier concentration and higher carrier mobility. It is also suggested that the lower internal stresses in the r.f. sputtered films, caused by the better crystalline quality, lead to their higher carrier mobility [12]. In my samples, although the average crystallite size of the r.f. sputtered films is smaller than those of the d.c. sputtered films, the lower resistivity of the r.f. sputtered films is likely due to lower internal stress. This lower stress in the r.f. deposited films might be due to strain relaxation through breaking the columnar structures into smaller grains (figure 3-4).

Defects such as zinc interstitials (Zn\textsubscript{i}) and oxygen vacancies (V\textsubscript{O}) are commonly accepted as the main sources of conductivity in as grown films [3, 4]. The conductivity of these films comes from the stoichiometric deviations (oxygen vacancies and excess metal ions). The incorporation of point and textured defects, however, might be one of the reasons for lower conductivity [18]. It is also thought that porosity contributes to their poor conductivity.

The resistivity of the r.f. sputtered ZnO films decreased on incorporation of Al probably due to the contribution of extra free carriers from Al\textsuperscript{3+} ions substituting Zn\textsuperscript{2+} ions. However, as an Al atom is smaller than a Zn atom, part of the incorporated Al may occupy interstitial positions in the ZnO lattice[19].

The conductivity (\(\sigma\)) is a combination of mobility \(\mu\) and carrier concentrations \(n\) and can be written as:

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

(5)
The total mobility, $\mu$, is represented as [20]:

\[
\frac{1}{\mu} = \frac{1}{\mu_L} + \frac{1}{\mu_i} + \frac{1}{\mu_g}
\]  

(6)

where $\mu_L$ is the mobility due to the lattice scattering, $\mu_i$ and $\mu_g$ represent the mobilities due to the impurity scattering and grain boundary scattering, respectively.

Several reports [7, 8, 21] suggest that the Hall mobility ($\mu_H$) of ZnO is influenced by ionized impurity scattering and grain boundary scattering. $\mu_H$ is expressed as:

\[
\frac{1}{\mu_H} = \frac{1}{\mu_i} + \frac{1}{\mu_g}
\]  

(7)

Where $\mu_i$ and $\mu_g$ are the mobilities due to the impurity scattering and grain boundary scattering, respectively. It is believed that the grain boundary scattering of charge carriers is predominant in the electrical conductivity of ZnO films [7, 8, 21]. Mobility is determined by both ionized impurity scattering and grain boundary scattering.

The effects of grain boundaries on the electrical properties are prominent when the grain size is small. XRD analysis and SEM observations revealed the average crystallite size in the r.f. sputtered and d.c. sputtered samples to be of the order of 35 nm and 82 nm respectively. To interpret the conductivity behaviour of ZnO thin films, I can assume...
that the resistivity of these films comes from grain boundary resistivity $\rho_G$, lattice resistivity $\rho_L$, impurity resistivity $\rho_I$ and porosity resistivity $\rho_d$, i.e.:

$$\rho = \rho_G + \rho_L + \rho_I + \rho_d \quad (8)$$

or

$$\frac{1}{\sigma} = \frac{1}{\sigma_G} + \frac{1}{\sigma_L} + \frac{1}{\sigma_I} + \frac{1}{\sigma_d} \quad (9)$$

where $\sigma$ is the respective conductivity. Equation (9) assumes that the resistance from grain boundaries, lattice, impurities and pores are additive.

The grain boundary conduction plays an important role in the conductivity of thin films because of the very small grain sizes. The grain boundary barrier depends on the microvoids, inter-grain distance, grain size, impurity concentration, crystallinity, and non coordinated atoms at the grain boundaries [6, 22]. In the r.f. sputtered undoped ZnO films, we obtained activation energy values (0.028 and 0.0058 eV for $E_{a1}$; 0.008 and 0.0026 eV for $E_{a2}$) considerably smaller than the values (0.378 and 0.300 eV for $E_{a1}$; 0.047 and 0.043 eV for $E_{a2}$) for d.c. sputtered films. While the activation energy at higher temperatures is derived from charge transport in the conduction band, the lower energy activation energy is derived from electronic hoping between the nearest neighbors (donors) [15]. We can see both the transition temperature and activation energy are different for the ZnO films prepared by r.f. and d.c. sputtering (Figure 3-8). I believe the changes are due to the difference in grain size in the films. A smaller grain
size in the r.f. sputtered films induces a lower temperature transition in conduction mechanism (i.e. from hopping conduction to band type conduction).

The effects of film thickness on the electrical conductivity are complex. The results obtained from limited samples show that the conductivity of the films increased with increasing thickness. The increased thickness or crystal size weakens the inter-crystallite boundary scattering and increases the carrier lifetime, consequently, increasing the mobility of carriers[6]. However, the porosity of the films may also play an important role in their conductivity.

ZnO is an ionic crystal, with binding determined mostly by the Madelung energy due to the long range Coulomb interaction. Smaller inter-atomic spacing will stretch the electronic spectrum due to the increased overlap between atomic wavefunctions, which we believe is responsible for the higher band gap in r.f. sputtered films.

An increase in band gap by Al doping is observed in the r.f. sputtered ZnO films while their electrical conductivity increased (Table 3-1). The shift of the absorption edge to higher energy in the Al doped films can be attributed to the increase in carrier concentration of the Fermi level and blocking of energy transitions, causing a Burstein Moss effect [10, 23, 24].
3.5 Summary

Zinc oxide thin films were prepared by d.c. and r.f. magnetron sputtering on glass substrates. The electrical conductivity of the films has been studied in relation to the microstructure and optical properties. Most of the ZnO films produced by d.c. sputtering have a high resistance, while the films produced by r.f. sputtering are significantly more conductive. The band gap energies of the ZnO films prepared by d.c. sputtering are smaller than the films prepared by r.f. sputtering. While the highly conductive films have a nodular and compact surface texture, the poorly conducting films grow with columnar grains and porous surface texture. Compared to d.c., r.f. deposition leads to the formation of ZnO films with more homogeneous microstructure, smaller d-spacing, higher calculated X-ray density and lower internal stress. The electrical conductivity of ZnO films follows a linear relationship with their d-spacing, stress, density and thickness. Incorporation of Al in low concentration (<2%) mainly causes substitution for Zn in the ZnO lattice thereby reducing its resistivity. The conduction mechanism in sputtered n-type ZnO films is controlled through the charge transport in the conduction band and electronic hoping between the nearest neighbor donor levels. The electrical conductivity of sputtered ZnO thin films is affected by many factors including film processing, composition and microstructure. A good understanding of these parameters is necessary to improve the electrical conductivity of ZnO films for industrial applications.
3.6 References


4 Microstructure, Electrical and Optical Properties of Annealed Sputter Deposited Nanocrystalline ZnO Thin Films

4.1 Introduction

Post deposition annealing is an important processing technique for thin films because of the effects of annealing on the structural, morphological and properties of thin films [1-3]. Puchert and Gupta et. al. [3, 4] reported that annealing in air resulted in lower stress and increased average crystallite size in all ZnO films on a silica substrate. S.Y. Chu [5] reported that post deposition annealing in vacuum of ZnO thin films on a silicon substrate improved the film structure and electrical characteristics, resulting in a dense structure, smooth surface, stress relief and increasing resistivity. J.H. Lee [6] reported that the electrical resistivity of ZnO thin films prepared by a sol gel method was reduced by annealing in nitrogen with 5% hydrogen. The morphology was also modified by thermal treatment in a reducing atmosphere.

The micro structural model of the thin film annealing can be described by the structural zone model (Figure 4-6 b) [7]. Zone 1 is recognized by the columnar crystallites, and associated coating-flux shadowing where porous structure appears. Zone 2 where films contain an unvoided columnar structure with smoother surface morphology is
characterised by evolutionary growth due to adatom diffusion as the substrate temperature increases. The densification occurs by the movement of the grain surface to the void centers. Zone 3 is characterised by bulk diffusion processes such as recrystallization and grain growth (grain coarsening) with microcracks and roughness on the surface after further increasing substrate temperature [7].

In this chapter I present a study of the effects of annealing at different temperatures and in the different atmospheres on the microstructure, optical and electrical properties of ZnO thin films prepared on a glass substrate by d.c. and r.f. magnetron sputtering.

### 4.2 Experimental

ZnO films were deposited by either d.c. or r.f. magnetron sputtering methods. Both methods used direct and reactive sputtering modes (Table 4-1). Argon or argon-oxygen mixtures were used for the plasma-forming gas. Total pressure in the chamber was varied from 2 to 20 mTorr. The cathode to substrate distance was 13 cm. Sputtering targets used in the experiment were ZnO (99.9%) or Zn (99.99%), with an Al thin strip attached to the surface of the target in the samples with Al doping. Glass microscope slides were used as the substrates and were rotated during deposition. After deposition, annealing of the ZnO thin films was carried out in the temperature range of 200-550 °C and in an atmosphere of air or nitrogen for one hour.
Table 4-1 The processing parameters of ZnO thin films deposited by magnetron sputtering.

<table>
<thead>
<tr>
<th>No.</th>
<th>P/Torr</th>
<th>Power</th>
<th>Bias/ VDC</th>
<th>Deposition Time</th>
<th>Target</th>
<th>Thickness /nm</th>
<th>Grain Sizes /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-22 (1)</td>
<td>20.0/Ar</td>
<td>125W/RF</td>
<td>0</td>
<td>4.0 hrs</td>
<td>ZnO</td>
<td>~675</td>
<td>35</td>
</tr>
<tr>
<td>Z-36 (1)</td>
<td>2.0/Ar:O₂=6:4</td>
<td>0.25A/DC</td>
<td>-50.0</td>
<td>2.0 hrs</td>
<td>Zn+Al Reactive</td>
<td>~437</td>
<td>45</td>
</tr>
<tr>
<td>Z-44 (1)</td>
<td>10.0/Ar:O₂=9:1</td>
<td>250W/RF</td>
<td>0</td>
<td>2.0 hrs</td>
<td>Zn+Al Reactive</td>
<td>~337</td>
<td>40</td>
</tr>
<tr>
<td>Z-17 (2)</td>
<td>20.0/Ar</td>
<td>0.25A/DC</td>
<td>-50.0</td>
<td>4.0 hrs</td>
<td>ZnO</td>
<td>~752</td>
<td>74</td>
</tr>
<tr>
<td>Z-21(2)</td>
<td>20.0/Ar</td>
<td>250W/RF</td>
<td>-50.0</td>
<td>40 min</td>
<td>ZnO</td>
<td>~286</td>
<td>38</td>
</tr>
<tr>
<td>Z-23 (2)</td>
<td>10.0/Ar</td>
<td>250W/RF</td>
<td>-50.0</td>
<td>1.0 hr</td>
<td>ZnO</td>
<td>~215</td>
<td>50</td>
</tr>
<tr>
<td>Z-33 (2)</td>
<td>5.0/Ar:O₂=6:4</td>
<td>0.25A/DC</td>
<td>-50.0</td>
<td>2.0 hrs</td>
<td>Zn Reactive</td>
<td>~338</td>
<td>64</td>
</tr>
<tr>
<td>Z-40 (2)</td>
<td>5.0/Ar:O₂=6:4</td>
<td>0.25A/DC</td>
<td>-50.0</td>
<td>2.0 hrs</td>
<td>Zn+Al Reactive</td>
<td>~292</td>
<td>55</td>
</tr>
<tr>
<td>Z-44 (2)</td>
<td>10.0/Ar:O₂=9:1</td>
<td>250W/RF</td>
<td>0</td>
<td>2.0 hrs</td>
<td>Zn+Al Reactive</td>
<td>~200</td>
<td>44</td>
</tr>
</tbody>
</table>

Note: The (1) and (2) specimens were deposited using different brands of glass microscope slides.

The electrical resistivity of the films was measured by a standard two or four-probe technique [8]. Scanning electron microscopy (SEM, Philips XL-30S) and X-ray diffractometry (XRD, Bruker D8) were used to characterise the microstructure and to measure the thickness and composition of the films. The optical transmission spectra were measured in the wavelength range of 190 – 800 nm using a HP 8254 spectrophotometer.

### 4.3 Results and Discussion

In this work, labeled ZnO thin films Z22(1), Z36(1) and Al doped Z44(1) as identified in Table 4-1, were annealed in nitrogen at 250°C and 350°C for 1 h. Samples Z17(2), Z21(2), Z23(2), Z33(2), Al doped Z40(2) and Z44(2) were annealed in air or nitrogen at
550°C for 1h. These samples were characterised before and after annealing (see Tables 4-2 and 4-3).

Table 4-2 The parameters of several ZnO thin films annealed in nitrogen at different temperatures.

<table>
<thead>
<tr>
<th>Films</th>
<th>Before annealing</th>
<th>After 200°C under nitrogen</th>
<th>After 350°C under nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O at%</td>
<td>Ω.cm</td>
<td>d nm</td>
</tr>
<tr>
<td>Z22(1)</td>
<td>43.6</td>
<td>0.160</td>
<td>0.2609</td>
</tr>
<tr>
<td>Z36(1)</td>
<td>43.7</td>
<td>V.H</td>
<td>0.2640</td>
</tr>
<tr>
<td>Z44(1)</td>
<td>44.8</td>
<td>0.137</td>
<td>0.2608</td>
</tr>
</tbody>
</table>

Table 4-3 The parameters of a second group of ZnO thin films annealed in different atmospheres.

<table>
<thead>
<tr>
<th>Film</th>
<th>Before annealing</th>
<th>After annealing at 550°C under nitrogen</th>
<th>After annealing at 550°C under air</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O at%</td>
<td>Ω.cm</td>
<td>d nm</td>
</tr>
<tr>
<td>Z21(2)</td>
<td>44.5</td>
<td>0.47</td>
<td>0.2608</td>
</tr>
<tr>
<td>Z23(2)</td>
<td>42.3</td>
<td>12</td>
<td>0.2612</td>
</tr>
<tr>
<td>Z33(2)</td>
<td>42.6</td>
<td>N.C</td>
<td>0.2616</td>
</tr>
<tr>
<td>Z40(2)</td>
<td>43.3</td>
<td>3.7E+4</td>
<td>0.2620</td>
</tr>
<tr>
<td>Z44(2)</td>
<td>43.6</td>
<td>3.9</td>
<td>0.2604</td>
</tr>
</tbody>
</table>

Note: N.C/V.H means not conductive/very high.
4.3.1 X-Ray Diffraction

The XRD patterns of the annealed ZnO films are shown in Figures 4-1 and 4-2. The patterns show only a (002) peak, evidence of the strong preferred c-axis orientation perpendicular to the substrate. As evidenced in Figure 4-1, the XRD patterns after annealing at 200°C were similar to those at room temperature, but at 350°C they became significantly different, with a stronger 002 reflection and narrower FWHM. This is indicative of increased crystallinity.

The in situ XRD patterns of sample Z22(6) annealed in nitrogen at 25°C, 110°C, 300°C and 550°C are shown in Figure 4-3. At 25°C and 110°C, the XRD patterns are similar. At 300°C and 550°C the crystal structure has changed significantly.

Figure 4-1 XRD patterns of ZnO thin films annealing at different temperatures under N₂.
In different atmospheres, for example, air or nitrogen at 550°C, they have a measurable peak shift (Table 4-3). After annealing under a nitrogen atmosphere they show stronger (002) orientation than that in air (Figure 4-2).

**Figure 4-2** XRD traces over the 002 peak from ZnO thin films after annealing at 550°C in different atmospheres.
The annealing can reduce the disorder and film stress, and the relaxed crystallites will show reduced d-spacing (Table 4-2).

FWHM data are shown in Tables 4-2 and 4-3. FWHM is related to the crystal size [3]. A smaller FWHM implies a larger crystal size, which may reduce the grain boundary density.

Figure 4-3 In situ XRD patterns of Z22(6) at 25°C, 110°C, 300°C, 500°C in N₂ atmosphere.
4.3.2 SEM

The columnar grain structure has been partially or fully transformed by diffusion after annealing at 550°C (Figure 4-4 a). Under air annealing at 550°C, the columnar structure coalesced. Under N₂ annealing at 550°C, the columnar structure recrystallized into a compact nodular grain structure.
23(2) As deposited

23 (2) Annealing in air

23 (2) Annealing in N₂
40(2) As deposited

40(2) Annealing in air

40(2) Annealing in N₂
17 (2) As deposited

17(2) Annealing in air

17(2) Annealing in N₂
23(2) As deposited

23(2) Annealing in air

23(2) Annealing in N₂
Figure 4-4 (a) Cross section, (b) Surface SEM images of annealed ZnO thin films (23(2), 40(2) and 17(2)) under different atmospheres at 550°C.
On the surface (see Figure 4-4 b) the grains of annealed ZnO thin films often appear aggregated to form larger grains, which in some cases produced a porous grain structure. Under N\textsubscript{2} annealing the grains often aggregate with less porosity, while under air annealing the films had a more porous structure, showing a number of voids. Under annealing at 550°C, film cracking on the surface was not observed.

Film compositions analyzed by EDX (Al-K and Cu-L calibrations) are shown in Tables 4-2 and 3. There are small increases in the oxygen content of the film after annealing in N\textsubscript{2}. This may be attributed to the surface smoothness of ZnO films after annealing and minor oxygen in the system, but could also reflect some loss of Zn. However, there are larger increases in the oxygen content after annealing in air. The oxygen content affects the conductivity of thin films [9] because it is related to oxygen defects which act as electron donors, but this must be considered in parallel with other structural factors such as grain size and crystallinity [10].

4.3.3 Electrical Resistivity

The resistivity measurements are shown in Tables 4-2 and 3.

Annealing in nitrogen often decrease their resistivity compared to annealing in air at 550°C perhaps because it may help grains to be recrystallized into a dense structure in the film (Table 4-3). After annealing, samples which initially had low resistivity often
displayed higher resistivity, for example Z22 (1) and Z21 (2). On the other hand, poorly conducting samples often became better conductors, for examples Z36 (1) and Z40 (2). After annealing at 550°C in N₂, the resistivity of sample Z23(2) decreased sharply from 12 Ω.cm to 0.00044 Ω.cm. SEM evidence suggested the film recrystallized with a dense grain structure after annealing (see Figure 4-4). The sharp decrease in resistivity is attributed to the densification of the film and decreased impact of grain boundaries on resistivity.

### 4.3.4 Optical Transmission

Transmission spectra of some of the ZnO thin films annealed at different temperatures and in various atmospheres are shown in Figure 4-5.
All the films, for example, 22(1) and 23(2) (Figure 4-5), exhibit a high transmittance (> 75%) and show a sharp absorption edge, sometimes with a blue shift. Annealing at lower temperature does not change the transmission (%T) much (Figure 4-5). Annealing
under N₂ at 550°C can significantly improve optical transparency of these ZnO thin films, which implies better quality (i.e. fewer defects) in the films.

### 4.3.5 Discussion

Annealing of these films is known to reduce the film stress, and cause diffusion, grain coarsening and recrystallization. Small crystallites can coalesce together to make larger crystallites, resulting in microcracks and increased surface roughness [4]. The influence of postdeposition annealing on the microstructural properties is quite similar to the structure zone model due to a change in substrate temperature. On the same basis a simple model is constructed as shown in Figure 4-6 a, showing the influence of postdeposition annealing on microstructure of the sputtered ZnO film. Here I propose three zones to describe the microstructures that can develop in the film due to postdeposition annealing treatment in air ambient. Zone I is the same as expected from the structure zone model. For \( T_A/T_m > 0.25 \) and \( T_A/T_m < 0.35 \), where \( T_A, T_m \) are annealing temperature and melting temperature respectively, Zone II, columnar unvoided structure forms. Here the stress in the film is completely eliminated and the increase in grain size is small as compared to the as-grown film. For \( T_A/T_m > 0.35 \), zone III occurs where a process of coalescence and major grain growths results in a porous and cracked structure.
Because annealing reduces the disorder and stress of the film, it often decreases the d-spacing. A higher temperature oxidation of metallic Zn and oxygen incorporation can increase the d-spacing. Therefore annealing, particularly in air, could result in over
stoichiometric oxygen content and an increased d-spacing. After annealing, the intensity of the (002) reflection increased, and this strongly preferred orientation may reduce the contact area between grains. This would decrease the conductivity. FWHM is generally changed by coalescence and recrystallization. Recrystallization may help (002) orientation and peak growth, making the FWHM smaller. Coalescence may mix up different phases and destroy (002) orientation, making the FWHM larger [7].

When annealing at temperatures below 200°C little modification of the crystal structure is observed; however above 300°C, the crystal structure changes significantly. Annealing often improves the conductivity of initially higher resistivity samples, and decreases the conductivity of samples with initially high conductivity. These changes with annealing are associated with modification to the microstructure and porosity of the ZnO thin films.

Annealing under different atmospheres affects crystal structure and surface roughness. Annealing under N₂ also often improves the film transparency and conductivity. Annealing in air, especially at higher temperatures, increases the oxygen content and the porosity of the thin films, leading to an increase in resistivity.

4.4 Summary

There are two competing processes in annealing: coalescence and recrystallization. Annealing at lower temperatures (less than 200°C) does not have much effect on the crystal structure. But annealing at higher temperatures (more than 300°C) and in
different atmospheres has a large effect on these ZnO thin films. It affects crystal structure, surface roughness and conductivity. Conductivity often becomes worse for dense samples with good initial conductivity, but becomes better for samples of previously poor conductivity. Annealing under N\textsubscript{2} often improves film transparency and conductivity. The resistivity of some as-grown films was observed to decrease from $10^3 \ \Omega \text{cm}$ to $10^{-4} \ \Omega \text{cm}$ after annealing in nitrogen. It is believed that annealing alters the distribution of oxygen defects, and causes grain coarsening and recrystallization.
4.5 References


5 Ion Implantation of ZnO

5.1 Introduction

Ion implantation is a doping process which is non-equilibrium in nature. It is possibly the most versatile technique for surface doping of semiconductors. The process consists essentially of the introduction of atoms in the surface layer of a solid substrate by bombardment of the solid with ions in the keV and MeV ranges [1]. Dopants may become embedded in the solid and occupy the interstitial positions, thereby changing the chemical composition of the solid. One of the more important physical effects that alteration of the chemical composition of a solid can lead to is modification of the electrical conductivity of a semiconductor. Damage due to ion implantation may occur as a result of ionization as well displacement collisions, associated diffusion processes and phase changes. By 1956 the potential of ion implantation for introducing dopants had been realised. The relatively slow employment of ion implantation accelerated from about 1966 [2]. There has been a resurgence of interest in the use of ion beam processing to alter the physical, chemical, electrical, optical and mechanical properties of insulators [3]. Today almost all semiconductor devices are fabricated using one or more ion implantation steps. Ion implantation is widely used for introducing conduction carriers into semiconductors, to realise selective-area doping, electrical and optical isolation, dry etching, and ion slicing [4]. Ion implantation of potential p-type dopants
and co-implantation studies are beginning to show promising results for producing p-type ZnO [5].

A metal vapour vacuum arc generates an ion population suitable for implantation. The process involves a plasma discharge that occurs between conducting electrodes in vacuum. The fundamental phenomenon which drives the vacuum arc is that the solid cathode material is vaporized, ionized, and injected into the interelectrode arc region. Ions can subsequently be attracted from the arc region and used in implantation.

5.2 Experiment

In this study ion-implantation was carried out by using a metal vapour vacuum arc (MEVVA) ion source located at the Australian Nuclear Science and Technology Organization (ANSTO). The MEVVA system is shown in Figure 5-1. A schematic of the MEVVA ion implanter is shown in Figure 5-2. The ion source is a high current device which can readily produce ion beam currents of several hundred milliamperes on target. Extraction potentials in the range 0-50 kV are available. Ion beams of most metallic elements, either individually or in combination, and some non-metals can be generated with a MEVVA source. Targets of up to 75 mm diameter can be implanted on the existing system.

Using Ag, Al, Sn, TiN and Sb (>99.9% purity) rods as targets, the implantation of metal ions into ZnO films were performed after 2000 conditioning shots at the chamber base
pressure of $2 \times 10^{-6}$ mbar and extraction potential of 40 kV. Using a 40 mA beam current, a metal ion dose of about $1.0 \times 10^{16}$ cm$^{-2}$ was implanted.

Figure 5-1 MEVVA system
Figure 5-2 Schematic of MEVVA Ion Implanter.

N.B. The Extractor Power Supply is not located within the enclosure.
5.3 Modelling of Ion Implantation-SRIM

The SRIM (The Stopping and Range of Ions in Matter, Author: James F. Ziegler) program originated in 1983 as a DOS based program. SRIM is a collection of software packages which calculate many features of the transport of ions in matter (TRIM). SRIM is a group of programs which calculate the stopping and range of ions (up to 2 GeV/amu) into matter using a quantum mechanical treatment of ion-atom collisions (assuming a moving atom as an "ion", and all target atoms as "atoms"). During the collisions, the ion and atom have a collision including exchange and correlation interactions between the overlapping electron shells. The ion has long range interactions creating electron excitations and plasmas (ripples of waves) within the target. These are described by including a description of the target's collective electronic structure and interatomic bond structure when the calculation is setup. The charge state of the ion within the target is described using the concept of effective charge [6].

Typical applications of SRIM include:

**Ion Stopping and Range in Targets:** Most aspects of the energy loss of ions in matter are calculated in **SRIM**. SRIM includes quick calculations which produce tables of stopping powers, range and irregular distributions for any ion at any energy in any elemental target. More elaborate calculations include targets with complex multi-layer configurations.

**Ion Implantation:** Ion beams are used to modify samples by injecting atoms to change the target chemical and electronic properties. The ion beam also causes damage to solid targets by atom displacement.
**Sputtering:** The ion beam may knock out target atoms, a process called *ion sputtering.* The calculation of sputtering, by any ion at any energy, is included in the *SRIM* package.

The range of ions may depend on ion energy, ion species, angle of ion incidence, ion dose and the density of target. The TRIM modelling results of ions implantation are shown in Figure 5-3 (XY Longitudinal, Layer 1).

(a) Ag

(b) Al
(c) Sn

(d) Sb

(e) N
Figure 5-3 Ions range plots by TRIM modeling for 40 kV implants of ZnO thin films.

In Figure 5-3, lighter elements Al and N penetrate deeper and broader than heavy elements Ag, Sn and Sb, which indicate the mass dependence of depth profiles. This is consistent with other reports [7]. Table 5-1 lists the maximum ions ranges of implanted elements obtained by TRIM modeling.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Ag</th>
<th>Al</th>
<th>Sn</th>
<th>Sb</th>
<th>N</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic weight (amu)</td>
<td>108</td>
<td>27</td>
<td>119</td>
<td>122</td>
<td>14</td>
<td>48</td>
</tr>
<tr>
<td>Ion ranges (Max, nm)</td>
<td>58</td>
<td>130</td>
<td>44</td>
<td>45</td>
<td>178</td>
<td>78</td>
</tr>
</tbody>
</table>
5.4 Rutherford Backscattering Spectrometry (RBS)

RBS primarily provides information on the profile of concentration versus depth particularly for heavy elements in a light material, e.g. titanium in alumina. Typically, a beam of 2-3 MeV He\(^+\) ions is directed perpendicularly on the sample’s surface. As the energetic ion penetrates the material, it loses energy mainly in collisions with electrons and only occasionally with nuclei. When the positively charged He\(^+\) ion comes close to the nucleus of an atom, it will be repelled by positively charged nucleus. The repulsion force increases with the mass of the target atom. For very heavy atoms such as lead or gold, the He\(^+\) ion can be repelled backwards with nearly the same energy as it had before the collision. By measuring the energy spectrum of the recoiled ions, information on the composition of the elements, and their depth within the sample can be obtained. In RBS, only backscattered ions are detected, and backscattering can only occur if the target atom’s mass is heavier than that of the incident ion. Conventional RBS is done with \(^4\)He ions. There are however several advantages using heavier ions such as \(^{12}\)C, \(^{16}\)O, \(^{28}\)Si or \(^{35}\)Cl, where for example, better mass resolution is required for heavy elements or to eliminate large amounts of backscattering from oxygen when studying ceramic oxides.

Typically, MeV (million electron volt) particles hit the surface of a solid state material. Different ion-matter interactions occur. The incident particles can be (i) scattered in a backward direction (RBS), (ii) scattered in the forward direction (elastic recoil detection, ERD), (iii) penetrate into the nuclei and cause nuclear reaction (nuclear reaction analysis, NRA, particle induced \(\gamma\)-ray emission, PIGE) and (iv) even excite the
electron shell (particle induced X-ray emission, PIXE). RBS, ERD and PIXE have been used in this work to analyze the dose and composition. These analysis techniques have in common that they are non-destructive, highly sensitive, all elements of the periodic table can be studied, only a small amount of materials is required and, in some cases, even depth profiles can be measured.

5.4.1 Dose Analysis

A blank Si wafer has been implanted at the same time as the ZnO thin films to determine the implanted doses. The standard and implanted Si samples were mounted on the sample rack. RBS analysis produces a spectrum of the number of backscattered particles as a function of energy. The spectrum obtained is dependent upon known experimental parameters such as beam energy, collected charge, incident angle, backscatter angle, solid angle of the detector, etc. The measurement configuration and beam energy (\(^4\)He ions at energy 2MeV) are fixed so the height (ie. Intensity) of the spectrum is mostly determined by the collected charge, which was set at 20 microcoulombs. The implanted dose takes account of all these parameters which are used as input into the RUMP program (Rutherford Backscattering Spectroscopy analysis package) [8].

The RBS spectra are shown in Figure 5-4. The implanted doses are determined and listed in Table 5-2. The doses are around \(10^{16}/\text{cm}^2\).
(c) Sn

(d) Sb
Figure 5-4 RBS spectra of implanted Si using above elements as a calibration of dose for ZnO implantations.

Table 5-2 Implanted doses determined by RBS (Dose from implanter ~1.0 x10\(^{16}\)/cm\(^2\)).

<table>
<thead>
<tr>
<th>Implanted elements</th>
<th>Ag</th>
<th>Al</th>
<th>Sn</th>
<th>Sb</th>
<th>Ti (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doses (/cm(^2))</td>
<td>5.6x10(^{15})</td>
<td>2.0x10(^{16})</td>
<td>1.0x10(^{16})</td>
<td>1.4x10(^{16})</td>
<td>7.4x10(^{15})</td>
</tr>
</tbody>
</table>
5.4.2 RBS Analysis Results of the Composition of ZnO Thin Films

Based on the above method, RBS has been used (Helped by GNS, New Zealand) to get Zn and O composition and PIXE for Ti and NRA for N. Table 1 summarises the results. Statistical and common errors are estimated at 5-10% for all the samples. The composition of most ZnO thin films is about 51 at% Zn and 49 at% O. On the surface of sputtered ZnO thin films there is also some absorbed O determined by XPS measurements. It is also found that Ti and N were not implanted at the exact ratio 1:1 of the target.

Table 5-3 The composition of ZnO thin films analyzed by RBS

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Film thickness (nm**)±10</th>
<th>Zn±2 at (%)</th>
<th>O±2 (at.%)</th>
<th>Ti (x10¹⁵ at.cm⁻²)</th>
<th>N (x10¹⁵ at.cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22(6)</td>
<td>578</td>
<td>51</td>
<td>49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22(6)a*</td>
<td>698</td>
<td>51</td>
<td>49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>385</td>
<td>51</td>
<td>49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>1398</td>
<td>48</td>
<td>52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>05a2</td>
<td>374</td>
<td>51</td>
<td>49</td>
<td>2.3</td>
<td>5±3</td>
</tr>
</tbody>
</table>

** Based on ZnO density of 5.6. a* means annealing at 300°C under vacuum.
5.5 Summary

Zinc oxide thin films were implanted with selected elements to improve their conductivity and attempt to achieve p type ZnO. The implantation profiles have been modelled by TRIM calculations. The implanted doses and the composition of implanted ZnO thin films can be determined by RBS. TRIM calculations confirm that lighter elements implant deeper than the heavy elements.

5.6 References


6 Implanted ZnO Thin Films: Microstructure, Electrical and Electronic Properties

6.1 Introduction

Ion implantation is an important and controllable technique for introducing conduction carriers into IV and III–V group semiconductors, including selective-area doping, electrical and optical isolation, dry etching, and ion slicing. A wide range of implant conditions (such as ion mass, dose ($10^{12-18}$ atoms.cm$^{-2}$), and implant temperature) affects the formation of lattice interstitials, vacancies and planar defects in a crystal such as GaN [1, 2]. Alivov et. al. [3] have attempted to convert n-type ZnO to p-type by N$^+$ ion implantation of Ga-doped films, and observed an increase in the resistivity from about $10^{-3}$ to $10^5$ ohm.cm. Miyakawa and co-workers have reported hole doping by N$^+$ implantation into n-type Ga-doped ZnO (ZnO:Ga) thin films in an attempt to realise p-type ZnO films [2]. However, conductive type conversion (n$\rightarrow$p) was not observed irrespective of implantation conditions. Hartmann reported that the resistivity of ZnO films was increased by the implantation of copper [4]. The electrical properties of ZnO are related closely to the composition and the microstructure, which affect its energy gap, carrier concentration and porosity[5, 6]. There are very few reported studies on the microstructure and properties of implanted ZnO thin films. We have therefore studied
implantation effects using different dopants on microstructure, electrical and electronic properties of ZnO thin films.

6.2 Experiment

The ZnO thin films were deposited by r.f. magnetron sputtering (Table 6-1). Working pressure in the chamber was 2 Pa. The sputtering target was ZnO (99.9%). Glass microscope slides were used as substrates and were rotated during deposition.

<table>
<thead>
<tr>
<th>No.</th>
<th>$P_{\text{total}}$/mTorr</th>
<th>Power to Target</th>
<th>Bias/VD C</th>
<th>Deposition Time</th>
<th>Thickness /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>20.0/Ar</td>
<td>250W/RF</td>
<td>-50.0</td>
<td>40min</td>
<td>~294</td>
</tr>
<tr>
<td>22</td>
<td>20.0/Ar</td>
<td>125W/RF</td>
<td>0</td>
<td>4.0hrs</td>
<td>~422</td>
</tr>
</tbody>
</table>

Low energy ion-implantation was carried out using a metal vapour vacuum arc (MEVVA) ion source. The base pressure of the implanter was $2 \times 10^{-4}$ Pa. The extraction potential was 40 kV and the ion beam current 40mA. The implantation dose was $\sim 1.0 \times 10^{16}$ atoms$\cdot$cm$^{-2}$. Al, Ag, Sn, Sb and TiN cathodes were used. After implantation some of the implanted ZnO thin films were annealed under vacuum ($\sim 10^{-5}$ mbar) at 300°C for one hour.
Chapter 6

The electrical resistivity of the films was measured by standard four-probe techniques. Scanning electron microscopy (SEM, Philips XL-30S with analytical system), X-ray diffractometry (XRD, Bruker D8) and atomic force microscopy (AFM, Digital Instruments NanoScope IIIa) were used to characterise the microstructure of the films. Hall coefficients of the samples were measured (helped by Dr. Robert Kinsey, University of Canterbury) at room temperature by an automated d.c. Hall measurement system using the Van Der Pauw technique. The depth profiles were measured using Dynamic Secondary Ion Mass Spectrometry (SIMS).

6.3 Results and discussion

6.3.1 Microstructure Study of Implanted ZnO Thin Films

Depth profiles of Ag, Al and Sn implanted in ZnO are shown in Figure 6-1. They depended on the implant species. At the low implantation extraction potential 40 kV, Al, Ag and Sn concentration depth profiles have peaks at a depth of 25, 17 and 10 nm respectively. The heavier dopants penetrate a shorter distance into the films, consistent with predictions and other reports [1] (See Chapter 5).
Figure 6-1 The depth profiles of Al, Ag and Sn implanted ZnO thin films.

Figure 6-2 shows the XRD patterns of Ag and Sn implanted ZnO thin films. XRD measurements indicated that the films were still crystalline with a preferred (002) orientation. However, the as-implanted samples have smaller 002 peak area, 002 peak or
d-spacing shifts and a larger (+29% Sb to 54% Al) FWHM compared to an unimplanted ZnO thin film (Table 6-2). These results indicated the crystalline structure was partly amorphous, especially by a lighter element, and grain sizes of the implanted ZnO thin films become smaller according to the Scherrer formula [7].

Figure 6-2 XRD patterns of unimplanted and implanted ZnO thin films.
Table 6-2 XRD data of implanted samples.

<table>
<thead>
<tr>
<th>Implanted Elements</th>
<th>Al</th>
<th>Sn</th>
<th>Sb</th>
<th>Unimplanted</th>
</tr>
</thead>
<tbody>
<tr>
<td>D (nm)</td>
<td>0.26107</td>
<td>0.26094</td>
<td>0.26104</td>
<td>0.26076</td>
</tr>
<tr>
<td>FWHM</td>
<td>0.411</td>
<td>0.407</td>
<td>0.378</td>
<td>0.267</td>
</tr>
<tr>
<td>Change of FWHM after implantation</td>
<td>+0.144</td>
<td>+0.14</td>
<td>+0.111</td>
<td>–</td>
</tr>
</tbody>
</table>

AFM surface images of the implanted samples before and after implantation are shown in Figure 6-3. In the Ag implanted samples, the presence of a modified grain structure at the surface was observed. EDS mapping (Figure 6-4) shows uniform distribution of Ti and N along the implanted thin film surface of ZnO.

Figure 6-3 AFM images of unimplanted and Ag implanted ZnO thin films.
Figure 6-4 EDS mapping of TiN implanted ZnO thin films (an area of 10µm x 10µm).

Typical surface and cross-sectional SEM micrographs of the implanted ZnO films are shown in Figure 6-5. From the micrographs we can observe a coarsening of the film surface after implantation. The columnar structure has been dislocated, and grain size becomes smaller, in agreement with the XRD patterns after implantation. A more porous columnar structure of the as implanted ZnO thin films was also observed. The blistering is also observed in the glass substrate possibly due to the substrate porosity (Figure 6-5b). These suggest that implantation leads to defects, smaller grain size and partial amorphism of ZnO thin films.
(a)
Figure 6-5 Scanning micrographs of unimplanted and implanted ZnO thin films: (a) top view, and (b) cross section.
6.3.2 Resistivity of Implanted ZnO Thin Films

The resistivity of the implanted ZnO films is shown in Table 6-3. The conductivity of poorly conductive samples is generally improved as a consequence of implantation, for example samples in the 22 group. However, implantation often decreases the conductivity of samples initially with high conductivity, for example the sample 21 group. The group 21 Al and group 22 TiN doped ZnO thin films (Table 6-3) shows better conductivity compared to the other dopant in the same group. The Ag implanted ZnO thin film (0.048 Ω.cm) has greater resistivity than an Al implanted one (0.012 Ω.cm). The heavier Ag may cause more damage to the crystalline structure than the lighter Al (Figure 6-5) [4]. The shorter range of the heavier Ag (Figure 6-1) will also concentrate the damage in a shallower zone. Kucheyev et. al. [1] reported that ion mass affects not only the level of implantation-produced lattice disorder but also the main features of the damage build-up behaviour in GaN.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Implant (ohm.cm)</th>
<th>Before</th>
<th>After implantation</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>Ag 0.01</td>
<td>0.048</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>0.01</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td></td>
<td>0.027</td>
</tr>
<tr>
<td>22</td>
<td>Sb 92.8</td>
<td>1.07</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>TiN</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.3.3 Annealing and Hall Measurements

Hall measurements were performed on some of the vacuum annealed ZnO films (see 6.2). The results of these measurements are shown in Table 6-4.

### Table 6-4 Hall measurements of implanted and annealed ZnO thin films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Resistivity (Ω.cm)</th>
<th>Carrier Type</th>
<th>Mobility (cm² / V.s)</th>
<th>Carrier concentration (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb implanted</td>
<td>0.218 ± 0.001</td>
<td>n-type</td>
<td>10.4 ± 0.3</td>
<td>(2.7 ± 0.2) x 10¹⁸</td>
</tr>
<tr>
<td>TiN implanted</td>
<td>(73.9 ± 0.02) x 10⁻³</td>
<td>n-type</td>
<td>2.4 ± 0.3</td>
<td>(3.6 ± 0.5) x 10¹⁹</td>
</tr>
<tr>
<td>unimplanted</td>
<td>24.4 ± 0.04</td>
<td>n-type</td>
<td>33.8 ± 1.0</td>
<td>(5.6 ± 1.0) x 10¹⁵</td>
</tr>
</tbody>
</table>

After implantation and vacuum annealing, the resistivity of the TiN implanted (co-doping Ti and N) ZnO thin films is 0.0739 Ω.cm, however the resistivity of the annealed unimplanted sample is 24.4 Ω.cm. This may be related to the combination of electron-hole pairs introduced by this co-doping strategy. Although the mobility of implanted samples decreases to a certain extent after implantation (irradiation-induced degradation of the carrier mobility[3]), the carrier concentration of these implanted and annealed films has been significantly enhanced, because of implanted dopants introducing more carriers, the presence of more interstitials and the lower energy gap. For example, the carrier concentration of a TiN implanted and annealed ZnO thin film reaches 10¹⁹ cm⁻³. The group V elements Sb and N [8] are potential p-type dopants and TiN [9] appears to be promising in this regard. However, after annealing these films still showed n-type conductivity, suggesting that they may be not doped sufficiently to cause n- to p-type
transfer in the ZnO thin films. Therefore, heavy doping is demanded for the conversion of the conduction mechanism from n- to p-type without the generation of oxygen vacancies by ion bombardment [2]. Annealing also causes diffusion of dopants and may reduce the implanted defects in the ZnO thin films. The resistivity of an Al implanted ZnO thin film decreases from 0.012 $\Omega$.cm to 0.0065 $\Omega$.cm after vacuum annealing. The decrease in resistivity may be attributed to the enhancement of the oxygen deficiency or zinc excess in the films, which could be exaggerated during the vacuum annealing process, owing to the increased mobility and out-gassing of oxygen in the film [10]. The EDS analysis result shows that Zn content of Sb implanted ZnO thin films increases ~2 at.\% after annealing. Table 6-5 shows XRD results before and after annealing of implanted ZnO thin films. After annealing the d-spacing of the implanted ZnO thin films becomes smaller because annealing can reduce the stress [6]. At the same time the FWHM becomes smaller. The larger grain sizes of implanted ZnO thin films after vacuum annealing may also have improved the conductivity of the implanted films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Before annealing</th>
<th>After annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d-spacing (nm)</td>
<td>FWHM</td>
</tr>
<tr>
<td>1</td>
<td>0.26098</td>
<td>0.338</td>
</tr>
<tr>
<td>2</td>
<td>0.26107</td>
<td>0.411</td>
</tr>
<tr>
<td>3</td>
<td>0.26112</td>
<td>0.290</td>
</tr>
</tbody>
</table>

Table 6-5 XRD data of unannealed and annealed (vacuum, 300 °C) implanted ZnO thin films.
6.4 Summary

Ion implantation was employed to implant ZnO thin films with Al, Ag, Sb, Sn and TiN. XRD measurements indicated that the implanted ZnO films are partly amorphous and grain sizes of the implanted ZnO thin films become smaller compared to the unimplanted samples. The presence of a dislocated crystalline structure was observed after implantation, with a coarse surface structure. Improvement in conductivity is observed in the implantation of poorly conductive samples. However, deterioration in conductivity is seen as a consequence of implantation of samples that were initially highly conductive. Annealing in vacuum may enhance the Zn excess, reduce the stress and increase the grain sizes of implanted ZnO thin films. After annealing these implanted films still show n-type behaviour with a significant increase of carrier concentrations in line with their conductivity improvement. Implantation introduces defects and interstitial dopants, which change in the composition, carrier concentration and microstructure. These effects can collectively account for the observed changes in electrical and electronic properties.

6.5 References


7 SIMS Investigation into the Diffusion Behaviour of Implanted and Annealed ZnO

7.1 Introduction

SIMS (Secondary Ion Mass Spectrometry) is an ultra high vacuum surface analysis technique used to gather compositional information about the surface and near-surface layers of a wide variety of solid materials. Progressive removal ('sputtering') of the surface layers and analysis of ions through a mass spectrometer provide compositional data. SIMS is capable of detecting ppm to ppb quantities of elements ranging from hydrogen to uranium. Thus SIMS is an excellent technique to measure dopant profiles in implanted semiconductors and is widely used for this purpose. In this work it has been used to measure depth profiles of implants in ZnO thin films and single crystals.

Ion implantation of potential p-type dopants and co-implantation studies are beginning to show promising results for producing p-type ZnO [1]. Recently N as an acceptor and Al, Ga, and In as donors have been identified as key dopants for preparing p-type material [2-4]. Park et. al. [5] reported the diffusion behaviour of co-implanted nitrogen and indium in a ZnO single crystal annealed at 800°C under oxygen. Diffusion of N into the crystal was not detected, while In was observed to diffuse deeper into the single crystal with annealing. Depth profiles of implanted ZnO single crystals reveal anomalous behaviour due to the plateau region in profiles after annealing [6].
Gerasimenko et. al. [7] found that the redistribution of implanted impurities was dependent on temperature and the presence of impurities. Komatsu et. al. found that for Ga and N co-implanted ZnO single crystals the annealing induced N and Ga diffusion deeper into the ZnO crystal, especially in the case of Ga [8]. Friesel et. al. determined that the diffusion of tin in germanium followed the vacancy mechanism and depended on the temperature [9]. TiN and Sb are potential p-type dopants [10]. In this chapter, the diffusion behaviour of TiN and Sb implants in a ZnO single crystal and thin films is discussed.

**7.2 Experiment**

Ion-implantation was carried out on ZnO thin films deposited on Si substrates by r.f. magnetron sputtering, and ZnO single crystal with a (0001) surface (Universitywafer), using a metal vapour vacuum arc (MEVVA) ion source. TiN and Sb rods (>99.9% purity) were chosen as targets. The base pressure was $2 \times 10^{-7}$ Pa. After 2000 conditioning shots, TiN and Sb were implanted at the dose of about $1 \times 10^{16}$ ions/cm$^2$ at room temperature using an extraction power 40 kV. The ion beam current was 40mA.

The ion-implanted samples were then annealed at 800 C for 1 hour, under a nitrogen atmosphere for TiN implanted samples, and under vacuum for Sb implanted samples. Depth profiling of each sample before and after annealing was carried out using a dynamic SIMS (CAMECA ims-5f, Figure 7-1) with $^{133}$Cs$^+$ as the primary ion, with a net accelerating voltage of 2.2 kV, and a beam current of 15 nA. A 10 μm diameter area of the samples was analyzed from the centre of a 250 μm x 250 μm area rastered by the
primary ions. Secondary ions of interest were monitored as the MCs$^+$ [11] adducts with intensities normalized using the Cs$^+$ yield.

Figure 7-1 ANSTO’S Cameca ims 5f Dynamic SIMS.
ANSTO's Cameca ims 5f Dynamic SIMS is termed Dynamic because of its ability to continuously analyse whilst sputtering the surface. This method allows depth profiling of materials to a depth of 10 microns. SIMS is a destructive surface analytical technique (Figure 7-2).

![Figure 7-2 The principle of SIMS.](image)

A primary ion bombards the surface, causing ions, atoms and molecules to be ejected ('sputtered') from the surface. The energy of the primary ions is of the order of a few kV to 10s of kV, more than enough to eject atoms and molecules from the surface layers. The actual depth of interaction is usually a few nm. As the beam moves ('rasters') across the surface it sputters a crater deeper into the sample. Continuous detection of the sputtered ion population allows the SIMS to create a depth profile of the surface and
underlying layers to a depth determined by sputtering time, but typically less than 10 microns.

Primary ions are produced by a cesium (1) or oxygen (2) source and are accelerated along the primary column (3-4) and focused onto the sample surface (5). Sputtered secondary ions pass through a secondary column (6-8), where they are collected and separated by charge (9). The secondary ions are then collected and focussed through the mass spectrometer (13). The analysed ions are then directed into detectors, and a signal is measured. The electron multiplier (22) amplifies the incoming signal for each element to be large enough to be measured (Figure 7-3, 10, 14 slit; 11, 15 lens, 12 spectrometer, 19 screen, 17, 20 deflector).

Figure 7-3 Schematic of Cameca ims 5f SIMS.
7.3 Results

The results compare the behaviour of ZnO single crystals and thin film samples, and the behaviour of the different dopants. As expected, implant range was sensitive to the mass of dopant and the dopant distribution was broadened with annealing as implanted elements migrated deeper into the film. Figure 7-4 shows the depth profiles of N and Ti co-implanted in ZnO before and after annealing. The Zn intensity of the ZnO thin films remained constant before and after annealing, which means that the results are comparable. The depth profiles of Ti and N co-implanted into ZnO thin films showed that the lighter element N penetrated further compared to Ti. The depths of the N and Ti peak concentrations were around 20-30 nm at an accelerating voltage of 40 kV. The boundary between the ZnO film and Si substrate is easily identified before annealing. N piles up at the interface, however, comparison of the $^{133}$Cs$^{48}$Ti$^+$ and the $^{49}$Ti$^+$ signal suggests that the former at the interface may be associated with an interfering molecular ion. The depth profile of the sample after annealing for 1 hr in nitrogen shows that the N profile after annealing was similar to that of the implanted sample. However Ti shows high mobility in the ZnO thin film with annealing. After annealing there is inter-diffusion at the boundary between film and substrate. Si appears to migrate towards the surface of the ZnO thin film. Ti and N show some accelerated migration to the interface with the substrate.

There are different depth profiles for N and Ti in the Ti and N co-implanted ZnO single crystal profiles before and after annealing for 1 h at 800 °C, as shown Figure 7-5. Both Ti and N migrated further after annealing, but Ti was less mobile than N. The Ti and N
were observed to decouple. This is a somewhat different result from that in the ZnO thin film.

Figure 7-4 SIMS concentration depth profiles of N and Ti in the co-implanted ZnO thin films before and after annealing for 1 h at 800°C.
Figure 7-5 Concentration depth profiles of N and Ti in the co-implanted ZnO single crystal before and after annealing for 1 h at 800 °C.

For Sb implanted ZnO thin films, a Sb concentration peak was not observed (Figure 7-6). Annealing as expected induced the diffusion of the Sb dopant into the film and led to a very broad Sb plateau region up to a depth of 220nm.
Figure 7-6 Concentration depth profiles of Sb implanted ZnO thin films before and after annealing for 1 h at 800 °C.

In contrast, for the SIMS results for Sb implanted into a ZnO single crystal (Figure 7-7), Sb shows low mobility, however it may vaporize into the gas phase because of a high vapour pressure of Sb (100Pa at a temperature of 738°C [12]). After annealing, redistribution of the Sb into the crystal occurred. The Sb diffusion behaviour on annealing differs between a thin film and a single crystal.
Figure 7-7 The depth profiles of Sb implanted ZnO single crystal before and after annealing for 1 h at 800 °C.

From the SIMS results, annealing causes less diffusion of dopants in a ZnO single crystal than in the thin film because there are fewer defects and no grain boundaries in a ZnO single crystal. In both cases for ZnO thin films deposited on Si, annealing induced some Si diffusion onto the surface of the films.

Cross-sectional SEM observation (Figure 7-8) of unimplanted, TiN co-implanted ZnO thin films before and after annealing at 800°C for 1 h under nitrogen was carried out to further understand the micro structural effects caused by implantation and annealing. Before implantation the ZnO thin film deposited by magnetron sputtering on Si shows a fine columnar nanocrystalline structure. After implantation the crystalline structure appears to be disrupted to be more amorphous. Near the surface of the film, surface defects are observed. After annealing at 800°C, the structure recrystallized into a coarse columnar morphology with damage remaining near the surface.
Figure 7-8 SEM cross section micrographs of unimplanted (a), TiN implanted before (b) and after annealing (c) of ZnO thin films (041102).
Figure 7-9 shows that XRD patterns of unimplanted, TiN co-implanted ZnO thin films before and after annealing. After the implantation the c axis orientation and polycrystalline structure has been significantly reduced. After annealing the c axis orientation has been enhanced compared to the unimplanted ZnO thin films, since the minimization of the surface energy favours the texture along the c axis. These verify the observations in Figure 7-8.

![XRD patterns (002 orientation) of unimplanted (1), TiN implanted before (2) and after annealing (3) of ZnO thin films on Si.](image)

**7.4 Discussion**

The concentration depth profile of implanted titanium and nitrogen shows a Gaussian-type distribution in the implanted samples. The diffusion of N in the Ti and N co-implanted ZnO thin film was not significant after annealing. The ionic radius of nitrogen (III, 132nm) is the largest among those of Zn (II, 80nm), Ti (III, 81nm), and O (II, 120nm), and this may be one reason why nitrogen has difficulty diffusing in the ZnO
thin films. The N-implanted ZnO could also form zinc oxynitride compounds[13], which hinder the diffusion of N in the Ti, N co-implanted ZnO thin films under these experimental conditions. This means that the implanted N is very stable. Park et. al. [5] have reported that the N occupied an O site. Komatsu et. al. have demonstrated the enhancement of the N solubility limit by coexistence with Ga in ZnO single crystals [8]. In the Ti and N co-implanted ZnO single crystal, N shows some mobility. This is somewhat at variance with the observations of Park et.al. for In and N co-implanted into ZnO. Hence, it was proposed that the N occupied an O site in the N-doped ZnO thin film [5], but an interstitial site in the ZnO single crystal in the presence of Ti.

Furthermore, the implanted Ti diffused well in the ZnO thin film and the diffusion behaviour of Ti in the ZnO thin film was very different from that of Ti in a ZnO single crystal. As Ti diffusion progressed during annealing in the ZnO thin film, Ti distribution followed that of nitrogen.

The implanted Sb profiles in the ZnO single crystal don’t have a Gaussian shape under these implantation conditions. After annealing at 800 °C for 1h, diffusion and loss of Sb to the gas phase (this is quite different from Ti diffusion) was observed. A small peak in the concentration depth profile of Sb was formed in the 30-50nm region in Sb implanted and annealed ZnO single crystals. It is considered that the above distribution is related to Sb diffusion and the swelling surface layer (implanted surface area) [7] under annealing at 800°C in the ZnO single crystal. It is possible that the partially implanted Sb occupied an O site in the implanted modified region of the ZnO single crystals. However in the ZnO thin film recrystallization and residual defects in the film made Sb diffuse more easily, forming a very broad plateau in the depth profiles (Figure 7-6). The Ti and also N have a broad plateau in the depth profile of the Ti and N co-implanted ZnO thin films.
Therefore dopants diffuse more easily in the ZnO thin film compared with a single crystal. This is similar to the observation of Mg diffusion in InSb [7].

From the shape of the depth profiles, the diffusion plateau of Sb in the ZnO single crystal is somewhat similar to In implanted ZnO single crystals [14]. In this case channelling was observed in the ZnO thin films. The ZnO thin films have a c axis columnar crystalline structure. This may provide a necessary condition for the channelling of dopants.

From the SEM images as discussed above, after implantation the columnar crystalline structure of ZnO thin films appears to be disrupted to be amorphous in spite of using a relatively low implantation energy. After annealing the structure recrystallizes into a coarse columnar morphology. This is consistent with the XRD observations.

### 7.5 Summary

The diffusion behaviour of Sb, Ti and N co-implants in a ZnO thin film and single crystal during annealing at 800°C was investigated. From the SIMS results, different implanted dopants, a thin film and a single crystal show different depth profiles and diffusion behaviour. In an as-implanted sample, N, Ti and Sb concentration depth profiles exhibited maxima at depths of around 50 nm. Diffusion of N in the ZnO thin film was not significant, while Ti was observed to diffuse deeper into the sample during annealing. For Ti and N implanted into a single crystal, the implanted species are observed to decouple in terms of depth distribution during the implantation. Annealing induced diffusion causes more redistribution of the lighter N than Ti. Under annealing at
800 °C implanted Sb may be lost into the gas phase. Generally speaking dopants diffuse more easily in the thin film compared with the single crystal. The depth profiles under annealing also depended on dopants. Some accelerated migration of Si, Ti and N was observed in the implanted ZnO thin films on Si. After implantation the columnar crystalline structure of ZnO thin films appears to be disrupted to be amorphous. After annealing, the structure recrystallized into a coarse columnar morphology.

7.6 References


Chapter 8

8 Transmission and Ellipsometry Study of Implanted Polycrystalline ZnO Thin Films

8.1 Introduction

Zinc oxide (ZnO) is a direct band gap semiconductor with the Wurtzite structure, and hence exhibits uniaxially anisotropic optical properties. ZnO crystals are unintentionally n-type due to slight non-stoichiometry, and the band gap is rather large (3.4 eV). The latter feature makes this material attractive for ultraviolet optoelectronic devices. Furthermore, ZnO has excellent acousto-optic properties, and hence it is widely used in integrated acoustic-optical devices and surface acoustic wave devices [1].

Transmission measurements play a far more significant role in advancing the general knowledge of optical properties of materials. This is mainly because spectrophotometers suited to this work have been available for many years. In addition, there has been extensive theoretical work on the methods of extracting index of refraction data from reflection and transmission measurements. Recently Spectroscopic ellipsometry has become a useful, non-destructive technique for characterising the optical properties of thin films. The basic property measured is the change in polarisation state of a light beam after reflection at non-normal incidence on the surface. The technique is highly sensitive to surface irregularities and thus substrates such as silicon and glass are optimal, although in the case of transparent substrates, the back reflection must be
eliminated. The method is indirect in that the data must be interpreted in terms of a model and is thus best used in conjunction with other characterisation methods. Measurements are generally conducted at a number of angles, above and below the Brewster angle of the substrate. At this angle from the normal, reflected light will therefore be completely polarized (no reflection) [2], to improve the modelling statistics.

Postava et. al. [3] have reported a spectroscopic ellipsometry study of Al and Ga doping effects on the optical properties of ZnO. Garcia-Serrano et. al. [4] have determined optical constants of Si/ZnO polycrystalline nanocomposites by spectroscopic ellipsometry. There are only limited reports on the systematic study of the optical properties of metal doped ZnO, either in bulk or in thin film form [5]. In this work, optical properties of metal (Al, Ag, Sb and Sn) ion implanted ZnO films have been studied by UV-Vis spectroscopy and spectroscopic ellipsometric techniques.

8.2 Transmission Study

8.2.1 Experiment

ZnO thin films were deposited by r.f. magnetron sputtering on microscopic glass substrates at room temperature. The thickness of the ZnO films was measured in the cross section using SEM. The ion-implantation was carried out by using a metal vapor vacuum arc (MEVVA) ion source using Ag, Al, Sn and Sb (>99.9% purity) rods as
targets at the chamber base pressure of $2 \times 10^{-6}$ mbar, extraction potential of 40 kV and the dose of about $1.0 \times 10^{15}$ cm$^{-2}$ (See Chapter 6).

The optical transmittance measurements at normal incidence were carried out using a UV-vis-NIR spectrometer (HP 8453) in the range of 200-800 nm.

### 8.2.2 Results and Discussion

Figure 8-1 shows the optical transmittance spectra in the wavelength range 300–800 nm for different ZnO thin films. Following the metal ion implantation, the transmission spectra are modified significantly and sharp absorption edges are observed in the ultraviolet region. It can be noted that transmission for undoped ZnO films is very high (about 90%). The average optical transmittance values of the Al implanted ZnO thin films are still higher than 84% in the visible range. The transmittance of the implanted ZnO films decreased gradually for Al, Ag, Sn, and Sb doping, attaining a value of about 70% for Sb-doping. Such a decrease in optical transmittance has also been observed in Ag-doped ZnO sputtered films and is attributed to the metallic character grown in the film [5].
The absorption coefficient $\alpha$ is given by the following equation [6]

$$\alpha = \frac{\ln (1/T)}{d}$$  \hspace{1cm} (1)$$

where $T$ is the transmittance and $d$ is the film thickness. The relation between the coefficients of absorbance $\alpha$ and the incident photon energy $hv$ is given by

$$\alpha = A (hv - E_g)^{1/2}/hv$$  \hspace{1cm} (2)$$
where $E_g$ is the optical band gap energy, $A$ is a constant having value between $10^5$ and $10^6 \text{ cm}^{-1}\text{eV}^{-1}$ [6].

Using the above relationship, the plot of $(\alpha h \nu)^2$ as a function of the energy $(h \nu)$ of the incident radiation has been shown in Figure 8-2. The band edge can be evaluated from the intercept of the extrapolated linear part of the curve with the energy axis. The corresponding values of $E_g$ are shown in Table 8-1.

**Table 8-1 Energy gaps of both unimplanted and implanted ZnO thin films.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Energy Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>3.30</td>
</tr>
<tr>
<td>Al-ZnO</td>
<td>3.32</td>
</tr>
<tr>
<td>Ag - ZnO</td>
<td>3.23</td>
</tr>
<tr>
<td>Sn - ZnO</td>
<td>3.28</td>
</tr>
<tr>
<td>Sb- ZnO</td>
<td>3.15</td>
</tr>
</tbody>
</table>
Figure 8-2 Plots of $(\alpha h \nu)^2$ against $h \nu$ for different ZnO films.
The optical band gaps for the ZnO-M thin films are 3.32, 3.23, 3.28 and 3.15 eV for M=Al, Ag, Sn, and Sb, respectively compared with 3.30 eV for ZnO. There is an increasing red-shift in the band gap for the implantation of Sn, Ag and Sb ions respectively, and a blue shift [7] for the Al implanted ZnO thin films. Such a red-shift of the optical band gap in sputtering deposited Ag-doped ZnO films has been reported by Jeong et. al. [5].

8.3 Ellipsometry Study

8.3.1 Introduction

The Ellipsometry measurements provide the change in the polarization state that an incident light beam, with monochromic parallel light of a known polarization state, suffers when it is reflected by a surface. It is necessary to always use a sample model and dielectric functions of individual layers to fit the ellipsometry data. The resulting state of polarization is characterised by the two so called ellipsometric parameters, tan ψ and cosΔ; the first one describes the ratio of the resulting amplitudes of two mutually perpendicular components of the reflected beam, whereas Δ represents the phase shift introduced by the reflection between these components [4]. This change is expressed as the ratio ρ between the complex reflection coefficients for polarization parallel \( r_p \) and perpendicular \( r_s \) to the plane of incidence [8],
\[ \rho = \frac{r_p}{r_s} = \tan \Psi \exp(i\Delta) \] (3)

Figure 8-3 Reflection of plane polarized light on a sample surface.

As shown in Eq. (3), the spectroscopic measurements are measured in terms of the ellipsometric angles \( \Psi \) and \( \Delta \) as azimuthal angles of the analyzer and polarizer at which the light intensity at the detector has a minimum [1]. Thus the construction of a physical model for the coefficients \( r_p \) and \( r_s \) allows the determination of several parameters by fitting the calculated spectra using Eq. (3) with the experimental spectra. In particular, the optical constants, refractive index \( (n) \), extinction coefficient \( (k) \) and thicknesses of unknown layers can be obtained.
8.3.2 Experiment

Thin films of ZnO on glass substrates with the back surface scratched to eliminate back reflection, were measured on a GESP 5 spectroscopic ellipsometer (Sopra) which employs a rotating analyser helped by C. Depagne at ANSTO, Sydney or Jobin Yvon Uvisel DH10 system by Prof. Pal from Universidad Autónoma de Puebla, Mexico. Scans were conducted over the range 250 – 800 nm, at the reflectance angles $60^\circ$, $55^\circ$, and $50^\circ$ or $60^\circ$, $65^\circ$, $70^\circ$.

8.3.3 Forouhi and Bloomer Interband Model (FB)

8.3.3.1 Modelling of ZnO thin films

As a starting point, the nk-file of ZnO in the manufacturer (Sopra) software was used to model the layer on top of the glass substrate. The fit using the Sopra nk-file was not ideal, however the FB model [4] was used successfully for the modelling of undoped ZnO thin films. The FB model has parameterized the spectroscopic dielectric functions of amorphous semiconductors using a five parameter model. Table 8-2 summarises the constants used to build the FB Model of ZnO thin films.
Table 8-2 FB Model parameters for ZnO thin films

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>n (∞)</td>
<td>1.86</td>
</tr>
<tr>
<td>Eg [eV]</td>
<td>2.82</td>
</tr>
<tr>
<td>A</td>
<td>0.06</td>
</tr>
<tr>
<td>B [eV]</td>
<td>6.85</td>
</tr>
<tr>
<td>C [eV^2]</td>
<td>11.81</td>
</tr>
</tbody>
</table>

Where \( n_\infty \) is the refractive index when \( E \to \infty \), Eg is the optical energy band gap, A B and C are positive non zero constants characteristic of \( 4C-B^2>0 \). Using the FB model, the refractive index and extinction coefficient of ZnO thin films were calculated for different wavelengths.

![Figure 8-4 Refractive index and extinction coefficient of ZnO thin film using a FB model.](image)
Figure 8-5 $\tan(\Psi)$ and $\cos(\Delta)$ fits of the ZnO thin films.
The modelling of measurement results of ZnO thin films were shown in Figure 8-5. The fits are not particularly accurate partly because the model may not consider the crystalline phase and the rough surfaces of ZnO thin films. The measured thickness of this ZnO film on glass was 307.42nm (SEM results: 293 nm).

8.3.3.2 Modelling of implanted ZnO thin films.

For modelling the doped films, the following structure model was used:

| Ambient | Doped layer | ZnO | Glass |

The doped layer was chosen as a mixture of metallic Al and ZnO, with a low concentration of Al. The parameters (Table 8-3) were used for the FB model. The refractive index and the extinction coefficient of such a model are shown on Figure 8-6.

Table 8-3 FB parameters for the Al-doped ZnO film

<table>
<thead>
<tr>
<th>Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$n (\infty)$</td>
<td>1.65</td>
</tr>
<tr>
<td>$E_g$ [eV]</td>
<td>1.80</td>
</tr>
<tr>
<td>$A$</td>
<td>0.16</td>
</tr>
<tr>
<td>$B$ [eV]</td>
<td>7.30</td>
</tr>
<tr>
<td>$C$ [eV$^2$]</td>
<td>14.52</td>
</tr>
</tbody>
</table>
Figure 8-6 Refractive index and extinction coefficient of undoped and Al-doped ZnO thin films obtained by FB modelling.

Using this FB model we could determine the thickness of the Al doped ZnO thin film:

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient</td>
<td></td>
</tr>
<tr>
<td>Al-doped ZnO</td>
<td>62 nm</td>
</tr>
<tr>
<td>ZnO</td>
<td>230 nm</td>
</tr>
<tr>
<td>Glass</td>
<td></td>
</tr>
</tbody>
</table>

This suggests a concentration profile some distance from the Gaussian profile experimentally observed (Chapter 6).
Figure 8-7 tan(ψ) and cos(Δ) fit for the Al-doped ZnO thin films.
The fits of the measurements (Figure 8-7) are not good for cos (Delta) fit 50. This indicates that the model used is not very accurate for the reasons subsequently discussed.

To conclude, the modelling of the implanted ZnO thin films was not accurate. The reason is that this model may not accommodate the crystalline phase, surface roughness of the implanted ZnO thin films.

### 8.3.4 Lorentz Oscillator Approximation (LOA)

The dielectric functions are stimulated using LOA model which is frequently used for materials constituting of a mixture of crystalline and amorphous phases [4]. The films are considered as an air/roughness/ZnO-M, ZnO/glass system, comprised of a mixture of 50%-50% volume fractions for air and ZnO [9] (see Figure 8-8). The effective dielectric function of the ZnO films was represented by a generalized form of the Lorentz harmonic oscillator expression and Kramers-Kroning analysis [10]. The fitting was performed simultaneously using the measurements at the three angles of incidence. The best-fitted calculated spectra (Figure 8-9) were obtained. All the features in the ellipsometric spectra of the films could be fitted quite well. The optimum values of film thickness and roughness producing best fit for the experimental spectra are listed in Table 8-4.

Figure 8-9 (a) shows the experimental and best-fit ellipsometric spectra for the measurements taken at the three angles of incidence on the undoped ZnO samples. In Figure 8-9 (b), the ellipsometric spectra of metal-doped ZnO samples obtained for a 65°
angle of incidence are presented. There are noticeable differences between the data of the metal-doped (Figure 8-9 (b)) and undoped samples (Figure 8-9 (a)) for $\phi=65^\circ$. The differences are greatest for the samples implanted with Ag, Sb, and Sn metal ions, which show more broad and lesser intense features in the 2-3 eV range. The optical band gaps for the ZnO-M layers are 3.13, 3.43, 3.01, and 3.31 eV for $M=$Ag, Al, Sb, and Sn, respectively. Clearly, there is an increasing red-shift in the band gap for the implantation of Sn, Ag and Sb ions respectively, and a blue-shift for the Al ions. The optical constants, refractive index ($n$) and extinction coefficient ($k$), for the undoped and doped ZnO films obtained from the analyses are in agreement with data previously reported for single crystals and thin films [11].

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{layered_models.png}
\caption{Figure 8-8 Layered models used to analyze the ellipsometric spectra: (a) for undoped ZnO sample; (b) for metal-doped ZnO samples.}
\end{figure}
(a)
Figure 8-9 Ellipsometric spectra of unimplanted ZnO (a) and metal-implanted ZnO samples for 65° incidence angle (b) (Courtesy of Prof. Pal, Universidad Autónoma de Puebla).
Table 8-4 Surface roughness (r), thickness of the metal-doped (t1) and un-doped (t2) ZnO layers and effective band gap values for the samples obtained from best-fitted ellipsometric spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>r (nm)</th>
<th>t1 (nm)</th>
<th>t2 (nm)</th>
<th>Eg (eV) (the band gap from optical spectra)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>15.5</td>
<td>--------</td>
<td>277</td>
<td>3.32 (3.30)</td>
</tr>
<tr>
<td>ZnO-Ag</td>
<td>7.9</td>
<td>51</td>
<td>197</td>
<td>3.13 (3.23)</td>
</tr>
<tr>
<td>ZnO-Al</td>
<td>14.1</td>
<td>136</td>
<td>131</td>
<td>3.43 (3.32)</td>
</tr>
<tr>
<td>ZnO-Sb</td>
<td>9.8</td>
<td>41</td>
<td>203</td>
<td>3.01 (3.15)</td>
</tr>
<tr>
<td>ZnO-Sn</td>
<td>18</td>
<td>45</td>
<td>240</td>
<td>3.31 (3.28)</td>
</tr>
</tbody>
</table>

8.4 Discussion

Implanted ions may enter and become embedded in the thin film, therefore introducing dopants into the thin film which produce localized energy levels. By displacing atoms from the normal positions (creating defects), the energetic ion can also alter the structure and physical properties. Therefore implantation can affect the band gap of ZnO thin films. A shift in the band gap for the implanted ZnO thin films has been observed. An increase in band gap by Al doping can be attributed to the increase in carrier concentration of the Fermi level due to Burstein-Moss effect and blocking of energy transitions. A red shift (decrease) in the band gap is caused by the exchange energy due to electron–electron and electron–impurity interactions [4].
The FB model fits are not particularly accurate partly because the model may not consider the crystalline phase and the rough surfaces of ZnO thin films, but for the unimplanted and implanted ZnO thin films the LOA model works extremely well.

### 8.5 Summary

Optical properties of nanocrystalline ZnO thin films doped with Al, Ag, Sb, and Sn by ion-implantation have been determined by optical transmission and spectroscopic ellipsometry. Transmission for undoped and Al doped ZnO films is very high (about 90%). The transmittance of the implanted ZnO films decreased gradually for the Al, Ag, Sn, and Sb doping, reaching a value of about 70% for Sb-doping. There is a shift in the band gap for the implanted ZnO thin films. Considering a simple air/roughness/ZnO-M (layer 1)/ZnO (layer 2)/glass model for the doped films and utilizing a generalized form of the Lorentz harmonic oscillator expression for effective dielectric function of ZnO, all the features in the ellipsometric spectra of the films could be described well. Implantation of the metal ions into ZnO thin films strongly affects their band gap, refractive index in the visible region and extinction coefficients.
8.6 References


9  p-Type ZnO and Electromagnetic Shielding

Study of ZnO Thin Films

9.1 Introduction

Recent interest in ZnO lies in the availability of epitaxial films on high-quality substrates and the p-type conduction and ferromagnetic behaviour when doped with transitions metals. While high quality n-type ZnO has been available for many years, the development of good p-type material is a much more recent phenomenon. The most successful acceptor dopants have been the group V elements, N, P and As; N substitutes on the O site. Many p-type ZnO materials suffer from the problem of long yield [1, 2] and instability [3]. In addition, the verification of p-type conduction by Hall effect measurement is difficult due to the low mobility of samples [4]. On the other hand, observations of donor-acceptor pair (DAP) luminescence, and sometimes acceptor bound exciton[5] or free electron-acceptor transitions[6], have been reported. Optical fingerprints of p-type ZnO often include a photoluminescence line at 3.31 eV, and strong donor-bound exciton lines at 3.357 and 3.367 eV, both of which are well known from previous studies of n-type ZnO [7]. However, most of the basic aspects of p-type ZnO are still not well understood.

Kobayashi et. al. [8] predicted that N is a good candidate as a shallow p-type dopant in ZnO although N is not very soluble in ZnO, suggesting that N doping might need to be
achieved by ion implantation. Lin et. al. [9] have obtained p-type ZnO by nitrogen-ion implantation of ZnO films grown on Si substrates with SiN buffer layers using r.f. magnetron sputtering. Georgobiani et. al. [10] obtained p-type ZnO by ion implantation of nitrogen with post-implantation annealing in oxygen radicals.

In this study, an attempt has been made to obtain p-type ZnO using implantation. ZnO thin films and ZnO single crystals have been implanted with different elements. Post-annealing has been carried out to remove the defects introduced by implantation. These implanted ZnO samples were investigated using photoluminescence (PL) and measurement of the I-V characteristics.

There is an increasing interest in electromagnetic interference (EMI) shielding with the increasing levels of electromagnetic pollution and the wide use of commercial communication products [11]. In general, the metals are used as the electromagnetic wave shielding materials. However metals also shield visible light. Transparent conductive oxides are a promising alternative shielding material, for example, Indium Tin Oxide and Zinc Oxide. ZnO thin films have attracted increasing interest because of advantages such as low cost, resource availability, nontoxicity, and relatively high chemical and thermal stability. Electromagnetic wave shielding of ZnO thin films was studied in the radio frequency range from 8.2 ~12 GHz.
9.2 Current-Voltage (I-V) Study

9.2.1 Experiment

The ion-implantation was carried out on ZnO thin films on Si substrates, deposited by r.f. magnetron sputtering and ZnO single crystals with a (0001) surface supplied by Eagle-Picher Inc. and University Wafer. The ion-implantation was carried out using a metal vapour vacuum arc (MEVVA) ion source, a high current device which can readily produce ion beam currents of several hundred mA on the target. A TiN and an Sb rod (>99.9% purity) were chosen as targets. The base pressure was 2x10^{-6} mbar. After 2000 conditioning shots. TiN and Sb were implanted at a dose of about 1\times10^{16} ions/cm^2 at room temperature using an extraction power 40 kV. The ion beam current was 40mA. The ion-implanted samples were then annealed at 800 C for 1 hour, under a nitrogen atmosphere for TiN implanted samples, and under vacuum for Sb implanted samples.

To form Ohmic contacts, Ti electrodes and then Ag electrodes were deposited on the ZnO side (Figure 9-1). The Al electrode was contacted on the back side to n type Si (100). The I-V characteristics were measured with the help of Dr. Robert Kinsey, University of Canterbury using a HP4155A Semiconductor Parameter Analyzer.
F- contacts 1 and 2

T-contacts 1 and 3 or 2 and 4.

**Figure 9-1 Schematic of contact layout.**

### 9.2.2 Results and Discussions

Figure 9-2 plots the I-V characteristic curves of TiN implanted ZnO thin films on n type Si. These show p-n junction behaviour. The threshold voltage of this junction is about 1 V. This is consistent with the previous reported value for ZnO [12]. After annealing at 800 °C the rectifying ability of the p-n junction becomes weaker. The turn on voltage is about 0.2 V. Figure 9-3 shows the I-V curves of the Sb implanted ZnO thin films. The turn on voltage is about 1V. After annealing the leakage current becomes smaller. This is because diffusion of electrons and holes will reduce the potential of the p-n junction [13].
Figure 9-2 I-V curve (a) before; (b) after annealing (800°C) for TiN implanted ZnO thin films on n–Si.
9.3 PL study

Photoluminescence (PL) is the emission of light from a material under optical excitation. It includes fluorescence and phosphorescence. Unlike phosphorescence,
fluorescence does not involve a change in electron spin. Therefore it is short-lived (< 10⁻⁵ s). Phosphorescence is ordinarily observed at low temperatures.

Typically with intrinsic excitation, the low-temperature PL spectra of undoped ZnO single crystals are characterised by complex near-band-edge (NBE) spectra (E>3.37 eV), and neutral donor/acceptor bound-exciton complexes (D⁺X, A⁺X) near 3.36eV followed by LO (longitudinal optical) phonon replicas [14]. At lower energies, two electron satellites (TES) recombination and donor-acceptor pair (DAP) recombination at 3.22 eV are observed.

9.3.1 Experiment

After implantation as described in Section 9.2.1, the samples were further investigated by time-integrated and time-resolved photoluminescence experiments carried out by Dr. Gang Xiong and Yong Qiu at Wake Forest University, USA. The 4th harmonic of a Q-Switch YAG laser (266 nm, 0.45 mW, pulse width 3 ns) was used as the excitation source.

9.3.2 Results and Discussions
9.3.2.1 TiN Implanted ZnO single crystal

The PL spectra of the undoped sample are shown in Figure 9-4(a). The dominant peak at 3.360 eV is the luminescence of a neutral-donor-bound exciton (D\(^0\)X) complex. The phonon-assisted transitions of (D\(^0\), X) are located at 3.203 eV (D\(^0\)X + 2LO, second longitudinal optical phonon replica of donor bound exciton luminescence). The two-electron-satellite (TES) peak of D\(^0\)X centres at 3.314 eV. The calculated energy level of the donor (E\(_d\)) at 46 meV is very close to the literature reports [6, 15].

The Donor-acceptor peak (DAP) from the undoped sample at 3.232eV is several times weaker than its D\(^0\)X+2LO neighbour at 3.203 eV. The native DAP peak from the undoped ZnO crystal produced by Eagle-Picher, has been previously observed by K. Thonke et. al. [6], who suspected that contaminant N might be responsible.

The DAP luminescence intensity of the nitrogen-implanted sample prepared on the identical ZnO single crystal shows an enhancement of peak intensity as seen in Figure 9-4(b). Its intensity is stronger than the D\(^0\)X+2LO peak, and the one-phonon replica of DAP is obviously visible at 3.153eV. Because for both samples the DAP peak positions are the same, it’s believed that the same type of acceptors, most likely nitrogen at the oxygen vacancy (N\(_o\)), are responsible for the DAP transition at 3.232eV. In addition, the 3.232eV peak position, closely matches the reported DAP photoluminescence of nitrogen-doped ZnO films [15]. There is no evidence from these experiments and the literature showing that the Ti related defects are luminescent in this wavelength region.
Figure 9-4 (a): Luminescent spectra of an undoped ZnO single crystal; (b): Luminescent spectra of N-doped ZnO (Courtesy of Dr. Gang Xiong, Wake Forest University, USA).
9.3.2.2 Sb implanted ZnO

Sb doped ZnO thin films on Si shows some p-type tendency after a dose of about $1 \times 10^{16}$ ions/cm$^2$. The acceptor peak is located at 3.305 eV (375.17nm). Other peaks are assigned as a donor peak (369.0nm, 3.36 eV) and a DAP peak (380nm, 3.26 eV) [16]). These are consistent with the results of the I-V measurements.

![Figure 9-5 Luminance spectra of Sb implanted ZnO thin films.](image)

9.4 Electromagnetic Shielding Study of ZnO

9.4.1 Experiment
ZnO thin films were deposited on PEN (Polyethylene Naphthalate) or glass substrates by r.f. magnetron sputtering and high speed spin coating (Methodology in Chapters 3 and 10).

The electromagnetic wave shielding was evaluated between 8-12 GHz (radio frequency) using a TEM cell (Figure 9-6) and PNA series Network Analyzer (Agilent Tech. E8364A).

![Figure 9-6 TEM cell](image)

### 9.4.2 Results and Discussions

ZnO has previously been examined for its electromagnetic shielding properties [17]. The electromagnetic wave shielding effectiveness between 8.2~12 GHz is shown in Figure 9-7. The PEN and ZnO thin films on PEN show extremely small absorption between 8.2~12 GHz. Further investigations will be needed to confirm this, for example, at the different range of frequencies or using different ZnO materials.

Figure 9-8 shows the reflection effectiveness of ZnO thin films on glass substrates between 8.2~12 GHz. Both glass and ZnO thin films on glass show some shielding from
reflection, however the ZnO thin films on glass (Figure 9-8 b) have a little more reflection of waves between 8.2~12 GHz than glass.

(a) PEN substrate
(b) ZnO thin films on PEN

(c) PVA+PEO+1%wt ZnO on PEN

Figure 9-7 Absorption effectiveness of ZnO thin films on PEN between 8.2–12 GHz.
Figure 9-8 Reflection of glass and ZnO thin films on glass.

(a) Glass

(b) ZnO thin film on glass
9.5 Summary

Implanted ZnO thin films and single crystals have been investigated using photoluminescence (PL) and I-V characteristic experiments. In addition preliminary studies of electromagnetic wave shielding efficiencies of ZnO thin films was also carried out in the range 8.2 ~12 GHz.

From the I-V measurements, TiN and Sb implanted ZnO thin films show some p-n junction behaviour. The threshold voltage of this junction is about 1 V. After annealing the p-n rectifying ability becomes weaker, which may be attributed to the diffusion and interaction of holes and electrons.

TiN implanted ZnO single crystal and Sb implanted ZnO thin films show some p type PL characteristics. Enhanced peaks at 3.232 eV and 3.305 eV are assigned to DAP transitions and acceptor peaks, by investigating the energy level of the corresponding acceptor levels, and comparing these values with published results.

The PEN and ZnO thin films on PEN show extremely small absorption between 8.2~12 GHz. However, ZnO thin films on glass show a little more reflection of waves between 8.2~12 GHz than uncoated glass. Further investigations will be needed to study the electromagnetic shielding behaviour of ZnO, for example, at a different range of frequencies, or using different ZnO materials.
9.6 References


10 Nano-ZnO and Polymer Composites

10.1 Introduction

The degradation of polymeric materials is caused by various factors such as exposure to heat, UV light, irradiation ozone, mechanical stress and microbes. Degradation is promoted by oxygen, humidity and strain, and results in flaws such as brittleness, cracking, and fading [1, 2]. Fillers are widely used in polymer materials to improve characteristics to suit a particular commercial application. One such improvement is the addition of structural reinforcement materials [3]. Inorganic fillers can be added to polyamide 6 to increase rigidity and minimise heat distortion at high temperature for engineering applications [4]. Nanosized fillers have properties that are often significantly different from their counterparts with “ordinary size”. The introduction of nano-ZnO into polymers can improve the mechanical and optical properties of the polymers due to a strong interfacial interaction between the organic polymer and the inorganic nanoparticles. The nanoparticle's small size and large specific area make these particles of particular interest. Such nanocomposites are widely applied in coatings, rubbers, plastics, sealants, fibres and other applications [5-7].

Materials research that deals with synthesis, characterisation, and properties of organic/inorganic hybrid supramolecular materials is rapidly developing. These materials are most promising to fabricate substrates such as controllable molecular arrays and shapes for efficient intermolecular energy and electron transfer between the
organic moiety and the inorganic unit and to construct devices to combine superior electronic, magnetic, and optical properties [8]. Abdullah et. al. [9] have succeeded in producing ZnO/polymer composites with stable luminescence peaks down to 465 nm (blue region) by in-situ growth of ZnO nanoparticles in a poly(ethylene glycol) (PEG) matrix. Ali et. al. [10] reported a thin ZnO nanocomposite poly(styrene–acrylic acid) diblock copolymer film containing self-assembled ZnO nanoclusters on Si and SiO₂ surfaces. The approach holds promise for large area application in patternable nanocomposite films and stand-alone nanostructures on Si wafers. Zheng et. al. [11] examined the influence of ZnO nanoparticles on the crystalline structures of nylon-6. ZnO nanoparticles can induce the mesomorphic form in nylon-6 when it is cooled from the melted state and annealed from the amorphous solid. The inducing effect increases with decreasing ZnO particle size. The total crystallinity of composites containing ZnO is a little smaller than that of nylon-6 under the same crystallization conditions. Xiong [7] investigated poly(styrene butylacrylate) latex/ZnO nanocomposites. The tensile strength, UV and NIR (near infrared) shielding properties of the nanocomposite polymers increased, and the T_g first increased then decreased, with increasing nano-ZnO content.

Transparent conducting films deposited on polymer substrates have many merits compared to those deposited on glass substrates, such as lightweight, flexibility and small volume. They can be used in plastic liquid crystal displays, transparent electromagnetic shielding materials, flexible electro-optical devices, touch sensitive overlays and unbreakable heat-reflecting mirrors [12]. Therefore in the light of this interest a few interesting polymer / ZnO composites have been examined.
In this study preparation of polyvinyl alcohol (PVA), polyethylene oxide (PEO) and nano-ZnO composite films has been carried out, and their thermal, mechanical and optical properties have been studied.

10.2 Experimental

10.2.1 Materials

Polyvinyl alcohol (BP05) and polyethylene oxide (M.W 300,000, BDH) were used as polymer systems. A nano-ZnO dispersion in water with a mean size of 50 nm (30 wt.% ) was supplied by Nyacol Nano Tech. Inc. USA.

10.2.2 Preparation of Polyvinyl Alcohol / Polyethylene Oxide Nano-ZnO Suspensions

An aqueous solution containing equal proportions by weight of poly(vinyl alcohol) ([-C-C(OH)]_n-, PVA) and polyethylene oxide ([-C-C-O]_n-, PEO) was prepared by dissolving ~10 g of the polymers in 90 mL water in a 500 mL flask equipped with a heating mantle, magnetic stirrer and thermometer. Nano-ZnO suspension was added to PVA and PEO solutions (1:1) with continuous stirring at ambient temperature, to make 1, 3, 6, 9,
15 wt % nano-ZnO suspensions. Nano-ZnO suspensions in PVA solutions were not very stable because nano-ZnO particles have a high surface energy. Therefore, PEO has been used as a surfactant to improve the stability of the nano-ZnO suspension in PVA. To understand the effect of nano-ZnO on the stability of PVA/nano-ZnO suspensions, the resistivity was measured using a conductivity meter CDM230 (Radio Meter Analytical SAS, French).

### 10.2.3 Preparation of Polymer Films

The polymer films for Dynamic Mechanical Thermal Analysis (DMTA) and Differential Scanning Calorimetry (DSC) were prepared by casting the samples into molds. The films for the UV-VIS-spectra and Scanning Electron Microscopy (SEM) experiments were prepared by dipping or spinning the samples onto glass panels at 3000 rpm using a SPIN COATER WS-400B-6NPP/UTE (Laurell Technologies Corporation). The films were then dried at room temperature for more than 7 days prior to tests. The thickness of the dried polymer film and the polymer nanocomposite film was ~ 300 nm and ~500nm.
10.2.4 UV-Vis Spectra and Scanning Electron Microscopy

UV-Vis spectra were carried out on the Shimadzu UV-2101pc. The transmittance spectra were determined in the range of 250 -800nm wavelength. A Philips XL30S FEG was used for Scanning Electron Microscopy (SEM) observations.

10.2.5 Dynamic Mechanical Thermal Analysis

Dynamic Mechanical Thermal Analysis (DMTA) was carried out using a Rheometric Scientific apparatus to assess the visco-elastic properties of the films. It allows the determination of storage modulus $E'$ (elastic component) and loss modulus $E''$ (viscous component) as a function of temperature. Their dimensionless ratio, $\tan \delta$, is called the
damping or loss factor: \( \tan \delta = \frac{E''}{E'} \). The films were quickly cooled to -70°C and equilibrated for 3 min at that temperature and then heated to 95°C with a constant heating rate of 2°C/min under a nitrogen atmosphere. The stress required to maintain 0.005% strain at a frequency of 1 Hz.

Figure 10-2 Rheometric Scientific DMTA.

10.2.6 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a thermal analysis technique which is used to measure the temperatures and heat flows associated with transitions in materials as a function of time and temperature. Such measurements provide qualitative and quantitative information about physical and chemical changes that involve endothermic
and exothermic processes, or changes in heat capacity. DSC measurements using a DSC Q100 (TA Instruments) were performed in the temperature range from -80 °C to 120 °C or 230 °C with a heating rate of 10 °C per minute. The samples, with typical mass of the order 3 mg, were contained in aluminium pans and heated in an atmosphere of flowing, oxygen-free nitrogen.

![Figure 10-3 TA Instruments DSC Q100.](image)

### 10.3 Results

#### 10.3.1 Resistivity of PVA/Nano-ZnO Suspensions

The samples used for resistivity measurement were PVA/nano-ZnO suspensions. Figure 10-4 shows the resistivity of the suspensions as a function of ZnO concentration. With increasing concentration of ZnO the resistivity decreases initially at a faster rate, then slows down. ZnO has a very low solubility product constant \( K_{sp} = 3 \times 10^{-17} \) \([13]\). The
conductivity of the suspensions mainly comes from the surface charging of the ZnO particles. The fast drop of resistivity at the initial stage (Figure 10-4) reflects more significant aggregation of 3 or higher wt% nano-ZnO PVA suspensions compared to a 1 wt % nano-ZnO PVA suspension.

Figure 10-4 Resistivity of PVA/nano-ZnO suspensions with different ZnO concentrations.

10.3.2 Morphology of Composite Polymer Films

Figure 10-5 presents the SEM images on the surface of PVA/PEO/1 or 3 wt% ZnO films on glass. Here PEO has been used as surfactant to improve the stability of nano-ZnO particles. In Figure 10-5 (a) almost all nano-ZnO particles were dispersed into the PVA/PEO/1 wt% ZnO film. As nano-ZnO content was increased, agglomerates of ZnO nanoparticles with sizes of 400-600 nm were observed, as shown in Figure 10-5 (b).
This suggests that higher ZnO concentrations lead to agglomeration of nano-ZnO particles as evidenced in the resistivity data in Figure 10-4.

![Figure 10-5 SEM images of (a) PVA/PEO/1wt%ZnO, (b) PVA/PEO/3wt%ZnO](image)

10.3.3 UV-Vis Spectra
The UV-Vis transmission of nano-ZnO/PVA/PEO suspensions is shown in Figure 10-6. The PVA and PEO films have very limited UV absorbance. The absorbance in the UV region is enhanced with the addition of nano-ZnO due to its high energy gap. Nano-ZnO particles not only absorb UV light, but also scatter visible light. Thus 1 wt% nano-ZnO PVA/PEO suspensions have a better transmission of visible light compared to higher ZnO concentrations. Higher nano-ZnO content will promote aggregation in the PVA/PEO solutions to affect UV absorption and scatter visible light.

![Figure 10-6](image)

**Figure 10-6** Transmission spectra of Nano-ZnO and polymer films deposited on glass by high speed spin coating.

### 10.3.4 DMTA of Composite Polymer Films
Storage moduli $E'$ spectra of PVA and its nano-ZnO composite are shown in Figure 10-7. For PVA the value of $E'$ varies only slightly with temperature in the range -80 to 20°C. At higher temperatures there are two ‘step’ decreases in $E'$ with onset temperatures in the vicinity of 40 and 60°C. At about 80°C the magnitude of $E'$ is still high and although the scans did not extend beyond about 90°C it is likely that the $\alpha$-transition (glass transition) of PVA occurs above 90°C, as expected for DMTA determination of $T_g$. Addition of PEO to PVA decreases $E'$ up to about 20°C, but $E'$ is nearly constant up to about 60°C due to the crystallinity of the PEO component of the film. A significant increase in the $E'$ value of the composite is clearly seen with the addition of 1% ZnO to the PVA/PEO mixture; however further addition of ZnO sharply decreases $E'$. That decrease is attributed to the formation of aggregates of ZnO particles in the mixture with 3% ZnO which, perhaps surprisingly, results in reduced stiffness of the film. Incorporation of ZnO in the polymer films has another notable effect, in that $E'$ exhibits a single step with onset temperature about 70°C.

Loss moduli $E''$ spectra of PVA and its composites are presented in Figure 10-8. In pure PVA, a slight peak at around 45°C is observed. With the addition of PEO, a significant peak is observed at around 70°C. This is due to the melting of PEO. The addition of nano-ZnO particles into PVA/PEO composites decreases the melting point. However the addition of 1wt% ZnO into PVA/PEO composites significantly increases the $E''$ value (viscosity), on the other hand addition of more nano-ZnO particles decreases the $E''$ value due to agglomeration of ZnO nano particles.

Mechanical loss factor spectra of PVA and its composites are shown in Figure 10-9. From -70°C to about 20°C, no significant change in tan $\delta$ is observed. Above about 20°C the curves start to deviate with pure PVA showing the highest tan $\delta$ value. The
temperature (70-80°C) corresponding to the peak in tan δ is taken as the glass transition temperature. In pure PVA, the β (segmental) transition is seen here at around 51°C, followed by the α transition peak at around 72.5°C. The introduction of PEO into PVA virtually eliminates the β transition. That effect is not the result of plasticisation by PEO because the α transition temperature of the PVA/PEO blend is not significantly different from that of PVA. It may be the case that PEO inhibits segmental motions of the PVA chains through strong hydrogen bonding interactions between the polar groups on the PVA and PEO chains. The PVA/PEO blend has the smallest tan δ value at temperatures close to the α transition temperature. The introduction of nano-ZnO particles into PVA/PEO blend increases both the magnitude of tan δ, and (for 1% ZnO) the transition temperature: the glass transition temperatures of PVA/PEO blend and its 1 and 3% wt nano-ZnO composites are around 74, 78 and 73°C, respectively. The increase in T_g of the nanocomposite polymer may be attributable to strong interfacial interaction between the nano-ZnO particles and the polymer matrix. However, when the nano-ZnO content is further increased, agglomeration of the particles occurs, reducing the interfacial area between the particles and the polymer matrix.

Figure 10-7 Storage moduli spectra of PVA/PEO and nano-ZnO composites.
Figure 10-8 Loss moduli spectra of PVA/PEO and nano-ZnO composites.

Figure 10-9 Mechanical loss factor spectra of PVA and its composites.

10.3.5 DSC
The glass transition temperature ($T_g$) and melting point ($T_m$) values of PVA and PEO are shown in Table 10-1.

Table 10-1 Glass transition temperature ($T_g$) and melting points ($T_m$) of PVA and PEO. (*These data are from the DSC experiment)

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA [14]</td>
<td>85, ~48° (with moisture, dry 68°)</td>
<td>180-230, 190°*</td>
</tr>
<tr>
<td>PEO [15]</td>
<td>-45 to -53</td>
<td>60, 66°*</td>
</tr>
<tr>
<td>PVA/PEO</td>
<td>48° (with moisture)</td>
<td>63° (PEO), 199° (PVA)</td>
</tr>
</tbody>
</table>

The DSC measurement was taken on PVA, PEO and PVA/PEO, as shown in Figure 10-10 (a). The glass transition of PVA appears at around 48°C (the expected magnitude is reduced by plasticisation by water in the polymer film), and $T_m$ is about 190°C. The repeat scan gives $T_g$ at 68°C, the film having been dehydrated in the previous heating cycle. $T_g$ from DSC is characteristically lower than the value from DMTA because the measurements are made under different conditions. PEO shows relatively sharp melting at ~66°C, but no apparent glass transition because of its high degree of crystallinity. The first DSC scan for PVA/PEO blend shows $T_g$ of about 48°C which is, as in the case of PVA film, affected by the presence of water in the film. The scan shows two melting transitions at 63°C and 199°C that are attributed to PEO and PVA, respectively. In Figure 10-10 (b), PVA/PEO and its composites show melting points around 60°C (PVA/PEO: 60.4°C; PVA/PEO/1% wt ZnO: 59.6°C; PVA/PEO/3% wt ZnO: 56.3°C). The introduction of nano-ZnO particles slightly decreases the PEO melting point of the PVA/PEO composites. This is because nano-ZnO particles may decrease the interaction of polymer matrix at temperatures near the melting point.
Chapter 10

(a)

-100 -50 0 50 100 150 200

Temperature (°C)

-100 -50 0 50 100 150 200

Heat Flow (mW)

-100 -50 0 50 100 150 200

Temperature (°C)

PVA

48 °C

190 °C

PEO

66 °C

199 °C

PVA/PEO

63 °C
10.4 Summary

Thin films of poly(vinyl alcohol)/poly(ethylene oxide) blend can be easily modified by incorporation of ZnO nanoparticles prior to film casting. A possibility yet to be explored, is that similarly modified blown film can be made. The properties of the cast films are significantly modified by inclusion of 1 wt% ZnO nanoparticles. The introduction of 1 wt% nano-ZnO into PVA and PEO significantly increased their UV absorption, storage moduli, and affects the interactions of the polymer matrix itself. At higher nanoparticle loading, the particles tend to aggregate, to an increasing extent as
the nanoparticle content increases. PVA/PEO/nano-ZnO composites exhibit very small transmittance in the 260-300 nm UV region, but in the case of the 1% ZnO composite very high transmittance at wavelengths longer than about 300 nm. Consequently, they may be of use as optically transparent UV absorbing film materials.

10.5 References


15. [http://www.findarticles.com/p/articles/mi_m0EEH/is_5_29/ai_n14711723](http://www.findarticles.com/p/articles/mi_m0EEH/is_5_29/ai_n14711723).
11 Concluding Remarks

11.1 Background

ZnO is a wide band gap semiconductor with a range of both current and potential applications. However the development of p-type ZnO has proved to be particularly difficult [1, 2]. This is partially due to compensation by donors with low formation enthalpies. Most of the basic aspects of how to reliably produce p-type ZnO and control the basic stoichiometry are still not well understood. These have intensified interest in this material for applications in UV light emitters, varistors, transparent electrodes, high-power electronics, surface acoustic wave devices, piezoelectric transducers, and chemical and gas sensing. Recent improvements in fabrication of ZnO-based semiconductors have been demonstrated in the control of background conductivity in n-type doping, and initial p-type doping success has been reported [3]. There are fewer reports studying the relationships of microstructure and properties of ZnO thin films.

The work reported in this thesis has involved addressing a series of issues in an attempt to advance the understanding of the control of ZnO properties, particularly those of sputtered thin films. The issues can be summarized as:

- processing (changes in deposition conditions; annealing; implantation), composition, microstructure, electronic, optical and electromagnetic shielding properties of ZnO thin films deposited by magnetron sputtering;
• ion implantation as a method to dope Al, Ag, Sb, Sn and TiN into ZnO thin films or single crystals; to develop conducting, transparent oxide films and/or p-type semiconductor for potential device applications;

• the relationships between the microstructure and composition and the resulting electronic, electrical and optical properties of various ZnO thin films, for example, effects of d-spacing, X-ray density, residual stress, doping and temperature, on the resistivity of magnetron sputtered ZnO thin films.

11.2 Processing, Microstructure and Properties of Magnetron Sputtering ZnO Thin Films

Magnetron sputtering is a suitable method to rapidly deposit dense ZnO thin films. Zinc oxide thin films were prepared by d.c. (direct current) and r.f. (radio frequency) magnetron sputtering on glass substrates. The r.f. discharge has a higher plasma density in front of the substrate and a lower deposition rate for the same discharge power compared to d.c. sputtering. ZnO films produced by d.c. sputtering have a high resistance (> $10^5 \, \Omega \cdot \text{cm}$), while the films produced using r.f. sputtering are significantly more conductive (9.0x$10^{-3}$ - $10^2 \, \Omega \cdot \text{cm}$). The reported resistivity of sputtered ZnO thin films is in the range of $10^{-4}$ to $10^5 \, \Omega \cdot \text{cm}$ [4, 5]. While the more conductive films have a compact nodular surface morphology, the resistive films have relatively porous surfaces with columnar structures growing vertically from the substrate. Compared to the d.c. sputtered films, r.f. sputtered films have a microstructure with smaller d-spacing (< 0.261 nm), lower internal stress (< 0.70 GPa), higher band gap energy (> 3.15 eV) and
higher density (> 5.66 g/cm³). Smaller inter-atomic spacing stretches the electronic spectrum due to the increased overlap between atomic wavefunctions which is believed to be responsible for the higher band gap in r.f. sputtered films. The electrical resistivity of ZnO films follows a linear relationship with the inverse of their density and thickness, with d-spacing and stress.

During this research, conductivity (σ) change with temperature has been found to follow the Arrhenius equation. However two distinct regimes are observed. This study suggests that in different temperature regimes, the conduction mechanism in sputtered n-type ZnO thin films is controlled through charge transport in the conduction band, or through electronic hopping between the nearest neighbour donor levels. The activation energies of the charge transport are a few times those of hopping because of the ease of hopping compared with charge transport [6-8]. There are different energy barriers for the different conduction mechanisms. This dual conduction mechanism may be also suited for other wide band gap semiconductors such as GaN because they have similar carriers and crystal structures.

To interpret the conductivity behaviour of ZnO thin films, it is assumed that the resistivity of these films comes from the sum of grain boundary resistivity $\rho_G$, lattice resistivity $\rho_L$, impurity resistivity $\rho_I$ and porosity resistivity $\rho_d$, i.e.

$$\rho = \rho_G + \rho_L + \rho_I + \rho_d \quad (1)$$

The conductivity of ZnO thin films is primarily determined by the degree of nonstoichiometry (Zn rich defects) which can be changed by substituting Zn$^{2+}$ with Al$^{3+}$.
and introducing extrinsic defects. \( \rho_L \) and \( \rho_I \) are related to the nonstoichiometry of the ZnO thin films. Though the oxygen content in the samples varied from 46.8 at. % to 49.8 ± 2 at. %, their resistivity varied from \( 9.0 \times 10^{-3} \) to \( 2.7 \times 10^6 \ \Omega \cdot \text{cm} \), implying that not only the composition, but also other factors such as the microstructure and porosity have significant influences on the conductivity of the films.

The post-deposition annealing of ZnO films has been found to alter the film’s microstructure and properties. Annealing alters the distribution of oxygen defects, reduces the stress of the thin film and causes grain coarsening and recrystallization. For initially dense films, annealing can increase the porosity. In addition, the conductivity of poorly conductive samples is often improved after annealing. However, annealing in nitrogen or air does not improve the conductivity of samples with high conductivity prior to annealing. Annealing at lower temperatures (less than 200°C) does not have much effect on the crystal structure, but at higher temperatures (more than 300°C) and in different atmospheres it has a large effect on these ZnO thin films. Annealing in air, especially at higher temperature (> 300°C), increases the oxygen content and the porosity of thin films, leading to an increase in resistivity, however under N\(_2\) annealing also often improves the film transparency and conductivity. The resistivity of as-grown films can decrease from \( 10^2 \) to \( 10^{-4} \ \Omega \cdot \text{cm}^{-1} \) after annealing in nitrogen due to less porosity and better contact of grains.

For ZnO films of thickness between 200-500 nm, optical transmission is very high (about 90%). The films show good UV absorption, however, limited electromagnetic shielding efficiency between 8.2~12 GHz. Further study will be required to understand this effect, for example, in other frequency ranges or using implanted ZnO thin films to vary the effective band gap.
11.3  Implantation and Characterisation of ZnO Thin Films and Single Crystals

Ion implantation is widely used for introducing conduction carriers into semiconductors, to realise selective-area doping, electrical and optical isolation, dry etching, and ion slicing. However the modification of properties due to implantation of polycrystalline materials is significantly more complex than that for single crystal materials [9-11]. The behaviour of both forms of ZnO has thus been investigated. Ion implantation introduces dopants, and causes displacement collisions and defects. It modifies the composition and crystalline structure of the films, affecting both the optical and electronic properties.

ZnO thin films were prepared by r.f. magnetron sputtering deposition on glass, Si or polymer substrates. Low energy ion implantation was employed to dope ZnO thin films with Ti, N, Sb, Al, Sn and Ag. Single crystal ZnO samples were also implanted in parallel with ZnO thin films to compare their properties such as implant depth profiles and the impact on properties such as photoluminescence. Structural, electrical and optical properties of implanted ZnO were characterised with SEM, SIMS, XRD, conductivity, Hall and optical measurements. TRIM calculations and SIMS confirm that lighter elements implant deeper than heavy elements under the same implantation conditions. After implantation, the ZnO crystal structure shows damage in varying degrees. XRD measurements indicate that the implanted ZnO films are partly amorphous and grain sizes of the implanted ZnO thin films become smaller (a larger (~25-55%) FWHM of the 002 peak) compared to the unimplanted samples. In the micrographs a coarsening of the film surface after implantation is observed. The columnar structure is dislocated or disrupted, and grain size becomes smaller, in agreement with the XRD patterns after implantation. Improvement in conductivity is
observed following the implantation of poorly conductive samples. However, deterioration in conductivity is seen as a consequence of implantation in samples that are initially highly conductive.

It is known that annealing can help to recover the damaged crystal structure and photoluminescence of implanted ZnO [12-14]. This research confirms that after annealing of the implanted ZnO thin films, the disrupted structure recrystallizes into a coarse columnar morphology, and the d-spacing becomes smaller, presumably due to the reduction in stress of the implanted films. At the same time the larger grain sizes of the implanted films observed in the smaller FWHM after annealing, can decrease the resistivity arising from the grain boundaries. The decrease in resistivity after implantation and vacuum annealing may be also attributed to the enhancement of the oxygen deficiency or zinc excess in the films, which may be exaggerated during the vacuum annealing process, owing to the increased mobility and out-gassing of oxygen in the film.

From the SIMS results, the depth profile of the implanted elements often exhibits a Gaussian profile. Generally speaking dopants such as Ti and Sb diffuse more easily in the thin film than in the single crystal samples. The depth profiles of Ti and N co-implanted into ZnO thin films exhibit that the lighter element N penetrates further compared to Ti. The depths of the N and Ti peak concentrations are around 20-30 nm at an accelerating voltage of 40 kV. The boundary between the ZnO film and Si substrate is easily identified before annealing. N piles up at the interface, however, comparison of the $^{133}$Cs$^{48}$Ti$^+$ and the $^{49}$Ti$^+$ signal suggests that the Cs adduct at the interface may be associated with an interfering molecular ion. The diffusion of N in the Ti and N co-implanted ZnO thin film is not significant after annealing. In the Ti and N co-implanted ZnO single crystal, N shows some mobility. Hence, it is proposed that the N occupies an
O site in the N-doped ZnO thin film, but an interstitial site in the ZnO single crystal in the presence of Ti. The implanted Sb profiles in the ZnO single crystal do not have a Gaussian shape under these implantation conditions. After annealing at 800 °C for 1h, diffusion and loss of Sb to the gas phase were observed. However, in the ZnO thin film recrystallization and residual defects in the film make Sb diffuse more easily, forming a very broad plateau in the depth profiles.

Implantation can also enhance the refractive index and extinction coefficient in the UV region, and affect the band gap of ZnO thin films [15-17]. A shift in the band gap for the implanted ZnO thin films has been observed. An increase in band gap by Al doping can be attributed to the increase in carrier concentration of the Fermi level due to the Burstein-Moss effect and blocking of energy transitions. A red shift (decrease) in the band gap is caused by the exchange energy due to electron–electron and electron–impurity interactions. Transmission for undoped and Al doped ZnO films is very high (about 90%). The transmittance of the implanted ZnO films decreases gradually for the Al, Ag, Sn, and Sb doped samples, reaching a value of about 70% for Sb-doping. Ellipsometric spectra of implanted ZnO thin films have also been measured. It has been found that considering a simple air/roughness/ZnO-M (layer 1)/ZnO (layer 2)/glass model for the doped films and utilizing a generalized form of the Lorentz harmonic oscillator expression for the effective dielectric function of ZnO, all the features in the ellipsometric spectra of the films can be described well. The Lorentz model is appropriate for films constituting of a mixture of crystalline and amorphous phases.

The $E_g$ values obtained from the FB model (Chapter 8) are much lower than those from the optical measurements because FB model is not well suited to the crystalline ZnO thin films. The $E_g$ results are somewhat different from the ones from the LOA model due to some errors from the linear fitting of optical measurements.
From the I-V measurements, TiN and Sb implanted ZnO thin films show some p-n junction behaviour. The threshold voltage of this junction is about 1 V. After annealing the p-n rectifying ability becomes weaker, which may be attributed to the diffusion and interaction of holes and electrons. A TiN implanted ZnO single crystal and Sb implanted ZnO thin films show some p type PL characteristics. Enhanced peaks at 3.232 eV and 3.305 eV are assigned to DAP transitions and acceptor peaks, by investigating the energy level of the corresponding acceptor levels, and comparing these values with published results [18, 19]. The level of implantation to achieve p-type ZnO is still high and the effect is weak at this stage.

TiN or Sb Implanted ZnO thin films or single crystals both show photoluminescence. The transmittance of ZnO thin films and single crystals are more than 70%. They show different diffusion behaviours and defect levels. The photoluminescence spectrum indicates that the as-grown ZnO crystal has a very low concentration of native defects and is much closer to its ideal stoichiometry.

### 11.4 Nano-ZnO Polymer Composites

In contrast to sputter deposited ZnO thin films, a series of nano-ZnO composites were prepared by blending a PVA, PEO water solutions with a nano-ZnO suspension and then casting into thin films by spin coating. Their UV and thermo mechanical properties were then tested. The composites were characterised by SEM, UV-Vis spectra, DMTA and DSC etc. The introduction of nano-ZnO into PVA and PEO significantly increased
their UV absorption, storage moduli, and affects the interactions of the polymer matrix itself. The introduction of nano-ZnO particles into PVA/PEO blend increases both the magnitude of tan δ, and (for 1% ZnO) the transition temperature: the glass transition temperatures of PVA/PEO blend and its 1 and 3% wt nano-ZnO composites are around 74, 78 and 73°C, respectively. The increase in Tg of the nanocomposite polymer may be attributed to strong interfacial interaction between the nano-ZnO particles and the polymer matrix [20, 21]. However, when the nano-ZnO content is further increased, agglomeration of the particles occurs, reducing the interfacial area between the particles and the polymer matrix. PVA/PEO/nano-ZnO composites exhibit very small transmittance in the 260-300 nm UV region due to UV absorption of nano-ZnO, but in the case of the 1% ZnO composite very high transmittance is observed at wavelengths longer than about 300 nm. Consequently, they may be of use as optically transparent UV absorbing film materials.

11.5 Summary

In this thesis, the processing, microstructure and properties of sputtered ZnO thin films are examined. For comparison to the sputtered ZnO thin films, ZnO single crystal samples and nano-ZnO polymer composite thin films have also been studied.

A conduction mechanism for the ZnO thin films is suggested. This conduction mechanism may be also suited for other wide band gap semiconductors such as GaN. The experiments show that the conductivity of implanted or annealed ZnO thin films has
differing behaviour between high and poorly conducting samples. The relationship of
microstructure and properties (electric, electronic and optical) of as deposited, annealed
and implanted ZnO thin films has been studied and is discussed predominantly in terms
of the impacts on density and grain boundary area. The annealed diffusion behaviour
and ellipsometry of implanted ZnO thin films have been studied. The implanted ZnO
thin films show some p type tendency and evidence of photoluminescence. Nano-ZnO
and the polymer composites have been shown to have excellent mechanical and good
UV barrier properties.

11.6 References


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in processing and properties of ZnO. Progress in Materials Science, 2005. 50(3): p. 293-
340.

4. Quaranta. F., Valentini, A., F.R.Rizzi and Casamassima, G., Dual-ion-beam


12 Recommendations For Further Research

During the course of study, the potential for further development in specific fields of study was identified. However, they were not pursued because the goals of these projects diverged from the main objectives. This chapter highlights such areas.

12.1 Develop a Good Conductive p Type ZnO and Study its Thermal Behaviour

The implanted ZnO has shown some p type tendency. It is difficult to develop a good conductive and stable p type ZnO, more investigative work is needed using different dopants and processing methods such as Molecular Beam Epitaxy (MBE) using dopant Sb.

12.2 Further Investigation of Magnetic Shielding Properties of ZnO Thin Films in the Range of Frequency (0.1-1 GHz)
Chapter 12

The magnetic shielding of ZnO thin films was carried out in the radio frequency range of 8-12 GHz. In the other frequency ranges further investigation will be required to understand the electromagnetic shielding properties of ZnO thin films or doped ZnO thin films. A new test facility is needed to carry out this experiment.

12.3 SIMS Investigation on the Interface between Thin Film and Substrate

The SIMS depth profiles of the ZnO thin films show complex behaviour at the film and substrate interface. Further investigation is needed to determine the migration of species at the interface and examine the potential for impurity species to “precipitate” at this interface.

12.4 Raman Spectra Study of Sputtered ZnO Thin Films

In order to examine the relationship of defects and conductivity of ZnO thin films, the Raman spectra (Figure 12-1) have been measured using blue 488nm laser in the range of 5000-100 cm\(^{-1}\) for magnetron sputtered ZnO thin films under different preparation conditions (Chapter 3). It was found that some of ZnO thin films showed weak photoluminescence at certain infrared wavelengths. Thus not many clues have been
found in the relationship between Raman spectra and conductivity of these ZnO thin films. Further investigation may be needed to understand the relationship between microstructure (defects and chemical bonds) of ZnO thin films under different processing parameters and Raman Spectra.

Figure 12-1 Raman Spectra of Magnetron Sputtered ZnO Thin Films.

12.5 Develop a Potential Application of ZnO in the Timber and Polymer Industries
ZnO is a cheap, safe and good UV blocker. It can also improve the mechanical properties of polymer composites. Thus there is potential for further development of ZnO as a UV protection system, especially in the polymer industry. The experience in this work suggests more work is needed to control dispersion of ZnO particles in the polymer matrix. Based on the experience with TiO₂, parallel development of the technologies may be needed to develop a possible application in the timber and polymer industries.
Appendix

List of Publications

Papers


Conferences


18. J. Lee, Z. Li, A. Asadov, M. Hodgson, T. Ashida, J. Metson and W. Gao, Microstructure and conductivity of ZnO thin films prepared by magnetron


Figures

Conductivity increases with increased doping

Figure A-1 Conductivity of Different Materials (S/cm, Ω$^{-1}$.cm$^{-1}$, Source: Synthetic Metals, 125 (2002) 11-22)

Figure A-2 Standard profile of film orienting to c-axis calculated by ‘Rietan 2000’

SIMS of Sb Implanted ZnO Single Crystal and XPS Measurement of Sputtered ZnO Thin Films (See following copies).