

Structural, optical and electrical properties of undoped and co-doped Al/Ga ZnO thin films by spray pyrolysis

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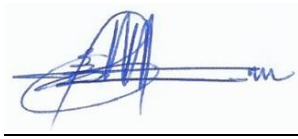
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STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF UNDOPED AND CO-DOPED Al / Ga ZnO THIN FILMS BY SPRAY PYROLYSIS

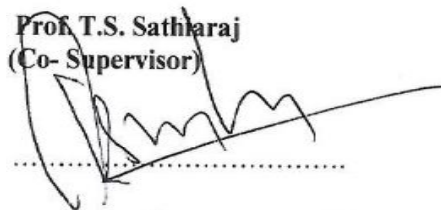
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Dedication

To my son Ortèl Theò and the young future researchers and innovators of Botswana.

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List of abbreviations and symbols

AFM	Atomic force microscopy
AGZO	Aluminum gallium doped Zinc oxide
ALE	Atomic layer Epitaxy
AZO	Aluminum doped Zinc oxide
CBD	Chemical bath deposition
CSP	Chemical spray pyrolysis
CVD	Chemical vapour deposition
DEA	Di-ethanolamine
F_M	Figure of merit
GZO	Gallium doped zinc oxide
ITO	Tin doped indium oxide
I-V	Current -voltage
LVDT	Linear variable differential transformer
2-MEA	2-methoxy ethanolamine
NIR	Near infrared
PVA	Polyvinyl alcohol
RAPET	Reaction under Autogenous pressure at Elevated Temperature
SEM	Scanning electron microscopy
SILAR	Successive Ion Layer adsorption and reaction
TCO	Transparent conducting oxide
Uv-Vis	Ultraviolet- visible
WD	Working distance

XRD	X-ray diffraction
ZAD	Zinc acetate dehydrate
k	Extinction coefficient
n	Refractive index
ρ	Resistivity
E_g	optical bandgap energy

Publications

Journal publication

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Abstract

Zinc oxide (ZnO) is a naturally occurring n-type semiconductor which is viewed as a promising candidate to replace indium tin oxide (ITO) in opto-electric applications, owing to its natural abundance and a wide bandgap (3.37). Synthesis of ZnO thin films via chemical spray pyrolysis technique is more convenient and cost effective compared to the mostly used deposition techniques such as magnetron sputtering which are highly expensive. Chemical spray pyrolysis provide easier way of doping the film by simply introducing dopant precursor ions into the starting solution. The doping of semiconductors with appropriate metals is generally one of the most effective ways of in research for developing sensitivity applications. In order to reduce resistivity of ZnO, more work have been done by doping ZnO with either group III or group VII elements using spray pyrolysis. Aluminum doped ZnO (AZO) and gallium doped ZnO (GZO) thin films have been extensively studied since they exhibit good optical transparency and a good electrical conductivity. Henceforth, there is a continuous search to explore other ways of further improving opto- electrical properties of ZnO through various doping techniques like co-doping.

In this thesis, aluminum and gallium co-doped ZnO (AGZO) thin films were grown by simple, flexible and cost-effective spray pyrolysis method on glass substrates, at a temperature of 230 °C. Effects of equal co-doping with aluminum (Al) and gallium (Ga) on structural, optical and electrical properties were investigated by X-ray diffraction (XRD), UV-Vis-NIR spectrophotometry and Current – Voltage (I-V) measurements, respectively. XRD patterns showed a successful growth with high quality polycrystalline films on glass substrates. The predominant orientation of the films is (002) at dopant concentrations ≤ 2 at% and (101) at higher dopant concentrations. Incorporation of Al and Ga to the ZnO crystal structure decreased the crystallite size and increased residual stress of the thin films, as well as decrease in surface roughness of the films with increasing doping concentration. All films were highly transparent in the visible region with average transmittance of 80 %. Increasing doping concentrations increased the optical band gap from 3.12 to 3.30 eV. A shift of the optical band gap was observed from 400 nm to 380 nm with increase in equal co-doping. Co-doping improved the electrical conductivity of ZnO thin films. It has been found from the electrical measurements that films with dopant concentration of 2 at% have lowest resistivity of $1.621 \times 10^{-4} \Omega \cdot \text{cm}$.

Chapter 1 INTRODUCTION

1.1 Transparent conducting oxides

Current scientific and technological research areas are dominated by study of nanomaterials which have a remarkable potential in generating novel materials with different structures and shapes[1][2]. One of the nanomaterials that have been of great interest for a wide range of technological fields associated with nanotechnology are the transparent conducting oxides (TCOs).

A transparent conducting oxide is a semiconducting material with dual properties of high electrical conductivity and optical transparency in the visible region. A semiconductor is a crystalline or amorphous solid with electrical conductivity ranging between that of an insulator and a metal. The properties of these TCOs are highly sensitive to presence of impurities at concentrations as low as 1 part in 10^{10} [3]. Introduction of very low concentrations of certain impurities (dopant elements) results in doped or extrinsic semi-conductivity with improved optical and electrical properties.

Undoped pure TCOs generally have large bandgap making them insulators at room temperature, hence a source of electron donor is essential in making these oxides conducting by increasing the free carrier density (electrons, ions and electron holes) in the conduction band. The physical properties of TCOs are determined by both the properties of the host crystal and the presence of impurities together with crystalline defects.

TCO devices can be incorporated as part of decoration in structural design to have multi-functionality. For instance solar cells can be made to serve as structure and at the same time as part of energy harvesting in windows of buildings. The devices needs to be optimized for the amount of light absorption necessary for power generation and the transparency essential for structural functionality. Figure 1.1 shows a semi-transparent solar cells integrated in windows of a building (Figure 1.1 (a)) [4] and as sunroof of an electric car (Figure 1.1 (b)) [5].

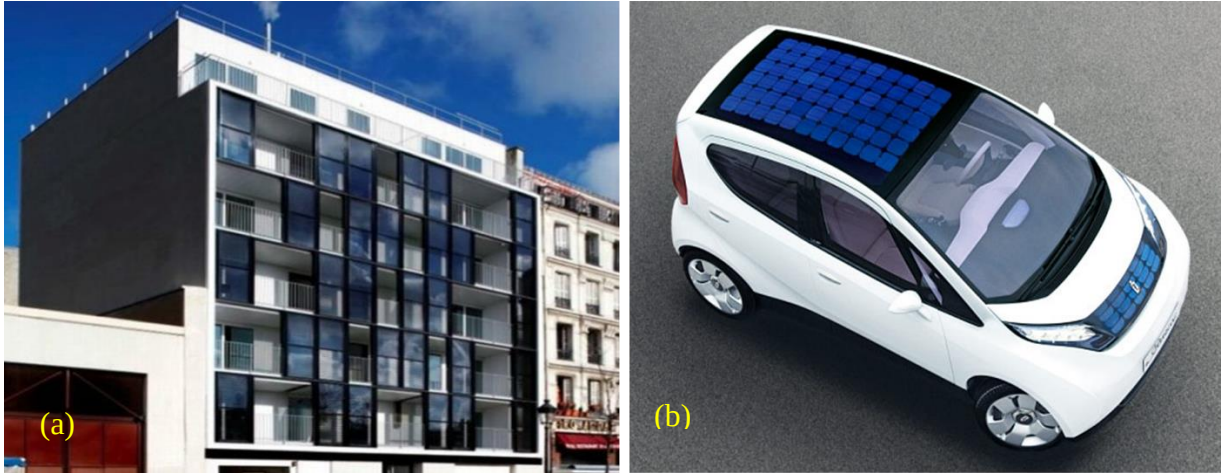


Figure 1.1: Applications of TCOs in solar cells (a) in windows of buildings and (b) sunroof of electric cars [4][5].

Various applications of zinc oxide based TCO thin films have been reported. These include applications in amorphous silicon solar cells, liquid crystal displays, gas sensors and energy efficient windows [6][7][8][9]. ZnO on its own has high electrical conductivity and this limitation is eliminated through doping. Singly doped ZnO thin films are more common than co-doped films. Co-doping is attained by using two different elements as dopants. Aluminum and gallium co-doped ZnO (AGZO) thin films are examples of co-doping. The ionic radii of Ga^{3+} (0.062 nm) and Al^{3+} (0.053 nm) are smaller than that of Zn^{2+} (0.074 nm) and hence Ga and Al have possibility to be co-doped into ZnO with minimal defects to the crystal structure. This doping method promise better opto-electrical properties compared to the singly doped films.

1.2 Problem statement

Conventional TCOs; indium oxide (In_2O_3) and tin oxide (SnO_2) based thin films currently dominate the TCO market immensely. However, production of thin films with these TCOs require rare raw materials such as indium, making them highly expensive[10]. Hence the search for inexpensive raw materials for sustainable production of thin films continues.

The most prominent methodologies for fabrication of ZnO based thin films are magnetron sputtering and pulsed laser deposition techniques[11][12][13][14]. These techniques requires highly expensive equipment which in turn requires highly skilled operation in order to produce

materials of good quality, hence, availability of these equipment in developing countries can be a limitation in research community.

Incorporation of foreign elements into a host lattice has been considered as a promising option to induce new functions in ZnO based films by enriching its opto-electrical functions for possible application in displays and optoelectronic devices. The effects of aluminum and gallium as single dopants in ZnO thin films has been extensively studied in literature [15][16][17][18]. However, there are few reports on co-doped aluminum and gallium ZnO (AGZO or GAZO) thin films produced by solution based methods[19]. Hence the effects of Al and Ga co-doped in ZnO can be investigated in order to broaden knowledge on these co-dopants ions.

1.3 Motivation and significance of the study

ZnO has emerged as the probable candidate in replacing the conversional TCO materials in optoelectronic applications owing to its advantages such as: (1) relatively cheap due to high natural abundance compared to other TCOs (See Table 2.1) [20]; (2) n-type semi conductivity with direct wide band gap (3.3 eV); (3) non-toxicity and (4) possible occurrence in many forms such as bulk single crystal, powder, thin film, nanowires, nanotubes etc.

ZnO based thin films can be grown by cost effective techniques, solution based methods such chemical spray pyrolysis and sol-gel. The solution base methods are advantageous in providing many varying doping routes, since dopant concentration can easily be manipulated during precursor solution preparation [21].

Aluminum has high reactivity hence when used as a single dopant, complications due to oxidation during film growth may occur. On the other hand, gallium is less reactive and more resistant to oxidation than Al. Therefore, synthesis of aluminum and gallium co-doped ZnO (AGZO) films, may be a good chance in incorporating the good properties of both Al and Ga in one film, by using a simple, inexpensive deposition method of chemical spray pyrolysis.

Understanding of the structure and morphology of thin films is essential as these properties determine the mechanical, electrical and optical properties of thin films. Deposition conditions have to be controlled to produce films with desired properties to suit intended application, hence careful control of the deposition conditions have to be addressed.

Transparent conducting oxides when used in solar cells aid in reducing environmental problems such as ozone depletion; increased danger of wildfires; extreme weather; loss of biodiversity and global spread of infectious diseases. These problems are accelerated by environmentally unfriendly human activities such as deforestation and combustion of fossil fuels for energy [22][23]. Solar energy is one of the renewable energy sources. Others include wind, hydro power and biofuels. With the exception of solar energy, renewable energy sources are geographically localized. Solar energy is free from environmental contaminants and has least risk compared to other sources like nuclear energy. For a semi-arid landlocked country like Botswana, the possible sustainable energy source is solar energy. Solar energy comes in the form of heat energy and light energy. The heat energy is mostly harvested by solar water heating systems while the light energy is converted into electrical energy using photovoltaic technology. Therefore solar energy is the most likely future candidate to substitute conventional energy storages which are mainly fossil fuels, in the form of natural gas, oil, and coal [24]. Additionally, conventional energy storages are non-renewable sources therefore excessive consumption will ultimately lead to resource depletion.

1.4 Aims and objectives of the present study

- Synthesize co-doped aluminum and gallium ZnO thin films by chemical spray pyrolysis (CPS) technique at lower deposition temperature (less than 300°C)
- Understand effects of varying dopant concentration on structural, optical and electrical properties of aluminum and gallium co-doped ZnO (AGZO) thin films.
- Establish optimum dopant concentration of AGZO thin films for probable application as transparent electrodes in solar cells.

1.5 Organization of the thesis

In chapter 2 the background theory of ZnO and its associated structural, electrical and optical properties will be presented. The general background of thin films will also be discussed. Additionally a review on structural, optical and electrical characteristics of aluminum and gallium doped ZnO thin films as well as their deposition techniques will be covered in this chapter.

Chapter 3 focuses on experimental methods. Machines, methods and procedures will be detailed: for example, AGZO precursor synthesis, thin film deposition and electro-optical measurements.

Experimental results, analysis and their discussion will be presented in chapter 4.

Chapter 5 summarizes the findings of the research work with recommendations for future work.

Chapter 2 ZnO AND AGZO FILMS:

BACKGROUND THEORY AND LITERATURE

REVIEW

Thin films have been around for more than a century as the first transparent conducting oxide was reported by a German physicist Karl Baedeker[25] in 1907. He coated a thin film of cadmium on glass and heated the sample in air by vacuum sputtering, obtaining cadmium oxide (CdO) thin film. The film had relatively high electrical resistance compared to the Cd metal and it was unstable over time as full oxidation occurred. This was the first demonstration of *n*-type TCO.

The discovery of CdO was followed by gradual development in thin film research leading to era of titanium oxide (TO) and tin oxide (SnO₂) [26]. Transparent conductive indium oxide was also made by pyrolysis from indium chloride. SnO₂ was developed for anti-static coatings and as a transparent electrode in electroluminescent panels. Aircraft windshields use TO as transparent heater films.

The most important TCO widely used for the last fifty years and today is tin doped indium oxide, In₂O₃: Sn, commonly known as indium-tin-oxide or ITO [27]. This TCO is used as a transparent electrode in nearly all flat panel displays, and this application currently dominates the global market for TCO thin film coatings [28]. ITO films has best characteristics required for thin film applications [29]. Despite this, indium remains the most expensive mineral for sustainable production of thin films due to its scarcity, as shown in Table 2.1 below. The forecasted market of non-ITO transparent conducting oxide is projected to reach \$ 8.1 billion in 2021, as illustrated in Figure 2.1 [30]. The 2015 estimated average free market price of bulk pure ITO powder ranges from 650 to 790 US \$ per kilogram, while that of zinc oxide powder ranges from 2.2 to 2.5 US \$ per kilogram [31].

Furthermore, deposition of ITO thin films mainly depends on expensive physical methods such as sputtering and vacuum evaporation [32]. These deposition methods require highly expensive equipment and highly sensitive environments to operate.

Table 2.1: Properties of ZnO and other TCOs compared to silicon [29] [33][34]

Property	In ₂ O ₃	SnO ₂	ZnO
Mineral name	—	Cassiterite	Zincate
Average amount of the metal in the Earth's crust (ppm)	0.1	40	132
Lattice parameter(s) (nm)	a:1.012	a:0.474 c:0.319	a:0.325 c = b:0.5207
Space group number	I ₂ 13 (no 199)	P4 ₂ mm (no 136)	P6 ₃ mc (no186)
Crystal structure	Cubic, Bixbyite	tetragonal, rutile	Hexagonal, Wurtzite
Band gap E _g (300K) (eV)	2.7(indir) 3.75(dir)	3.6(dir)	3.4(dir)

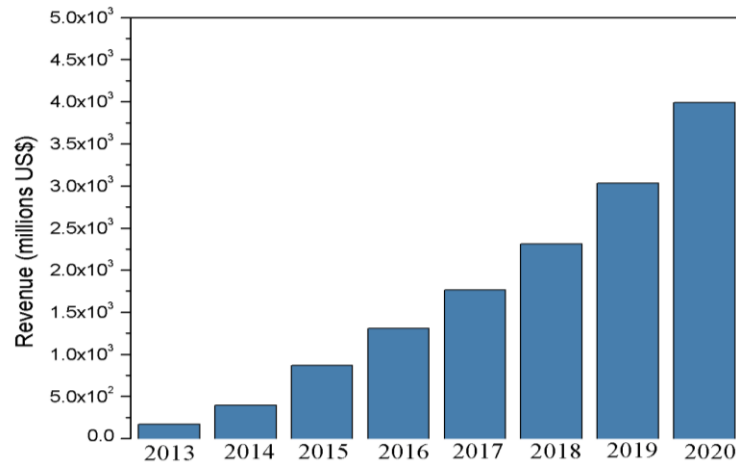


Figure 2.1: Non-ITO transparent conductor market revenue forecast [6].

The essential properties of ZnO crucial for opto-electrical applications are discussed under the forthcoming subtopics;

2.1 Crystal structure of ZnO

The mineral form of ZnO can be found in nature as zincite (as shown in Table 2.1). It grows in three different structures of wurtzite, rock salt and zinc blende [35]. The wurtzite polymorph is the most stable amongst the structures. The rock salt structure survive on high pressure while zinc blende structure is only achievable on pre-coated cubic surfaces. The hexagonal wurtzite structure is illustrated in Figure 2.1 below. The crystal structure can be described as having alternating planes composed of tetrahedral coordinated O^{2-} and Zn^{2+} ions, with sp^3 coordination stacked along c -axis. The bond is covalent but at the same time has ionic properties.

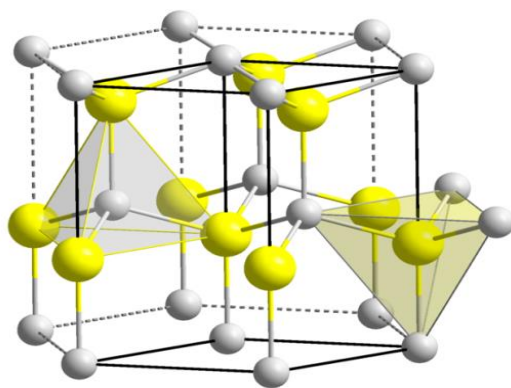


Figure 2.1: Wurtzite structure of ZnO ; Zn-yellow; O-grey [36]

The space group for this wurtzite structure is C_{6v}^4 by Schoenflies notation ($p6_3mc$ by Hermann-Mauguin notation) with three lattice constants $a = 0.325$ nm and $b = c = 0.520$ nm [37]. The tetrahedral coordination gives rise to a non-central symmetric structure, showing lack of inversion symmetry. This non-centrosymmetric character gives ZnO other properties of piezoelectricity (electricity generated due to pressure) [38] and pyro electricity (ability to generate a temporary voltage upon temperature fluctuations) [35].

Furthermore, the structure possesses polar surfaces in the basal plane. The alternating ions of Zn^{2+} (0001) and O^{2-} (000 $\bar{1}$) result in normal dipole moment and spontaneous polarization along the c -axis as well as divergence in surface energy. These different surfaces have different chemical properties that also influence the crystal growth along these planes [39].

The size of crystals of ZnO can be estimated by using the peak broadening in the x-ray diffraction pattern using the Debye-Schreer equation (discussed in chapter 4). A typical X-ray diffractogram of ZnO is shown in Figure 2.2[40]. The most characteristic peaks identifying ZnO crystals are labelled according to their miller indices, a notation system in crystallography for planes in crystal lattices. They uniquely identify the plane of a surface. Different materials have unique crystal lattices with specific plane orientations at certain angles. ZnO crystal is identifiable by the relatively more intense three peaks in angle range of $30^\circ > 2\theta > 36^\circ$ (the first three peaks in Figure 2.2).

At $2\theta = 34^\circ \pm 0.5^\circ$ the (002) peak is obtained and the orientation for this plane is a c-axis growth perpendicular to the substrate, giving the column structure, as shown in Figure 2.3(a). It is through this orientation that electric current can flow easily compared with other orientations. Growth of (002) plane as nanorods and nanowires has been important in developing solar cells[41][42][43]. Films with (002) orientation and small thickness are highly recommended for their high absorption, small diffusion length and higher recombination velocity. The (101) plane is observed at $2\theta = 36^\circ \pm 0.5^\circ$. It has a flat, c-axis growth parallel to the substrate with a pyramid-like structure Figure 2.3(b). The (100) plane appear at $2\theta = 32^\circ \pm 0.5^\circ$ and the corresponding orientation of this crystal plane is shown in Figure 2.3(c), with a c-axis growth parallel to the substrate (polygon structure).

It is noteworthy that the preferred plane orientations in ZnO based thin films are influenced by several factors including the type of substrate used as well as the deposition techniques of film growth. Chakrabarti and et.al [44] investigated the effects of substrate on preferred orientation of ZnO films by sol-gel method. Different types of substrates were used and the (002) was the most achieved orientation even under varying deposition temperature. The (101) plane appear to be a rare orientation to achieve probably due to the fact that the c-axis growth is on the edge or pointy hence less stable. Apparently the order of preferred orientation the preference of orientation (002) > (100) > (101) [45] with (002) orientation being the most stable.

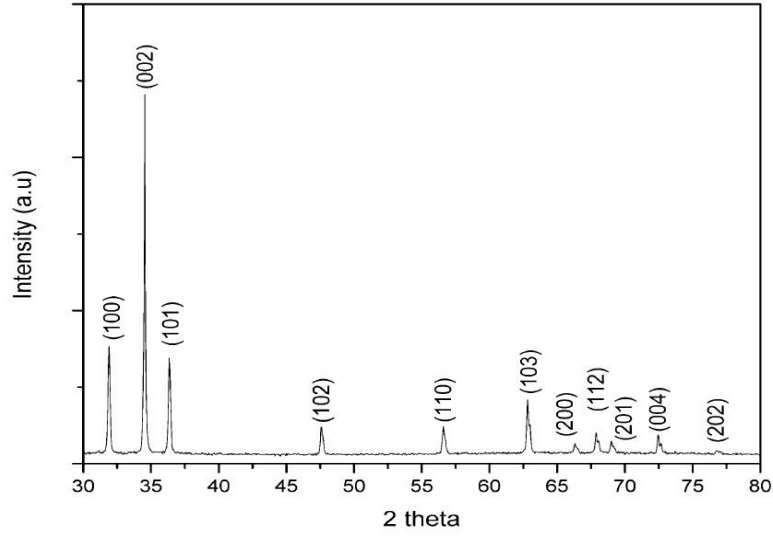


Figure 2.2: X-ray diffractogram of ZnO nanoparticles with peaks labelled by their respective miller indices [40]

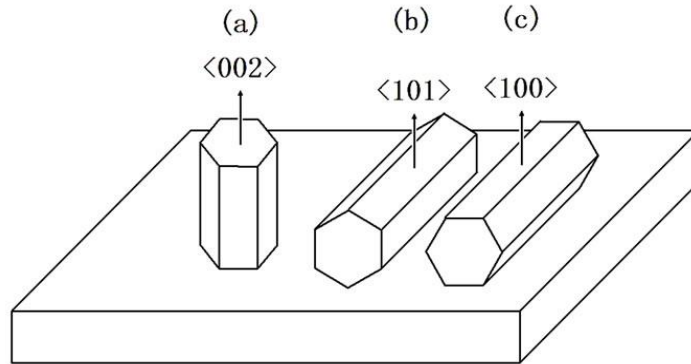


Figure 2.3: crystal growth orientation of ZnO films (a) c-axis perpendicular to the substrate for a columned structure;(b) c-axis growth parallel to the substrate for a pyramid-like structure;(c) c-axis growth parallel to the substrate for a polygon structure [46].

Surface topography and growth behavior of ZnO thin films strongly depends on the preparation method, deposition technique and the end point application in semiconductor devices [47]. For instance, in solar cell applications, surface texture should be such that it scatters light rays so as to increase the path length of light inside the solar cell. One of the smooth, coherent texture was reported using chemical vapour deposition (CVD) of SnO_2 : F film in 1990 [48]. The chemical stability of ZnO on top of the textured SnO_2 : F has been explained to be better than SnO_2 : F bare surface [49]. Yue-Hui et al [50] synthesized ZnO thin films with three different textures

for use as front electrodes in solar cells. They achieved textures as columnar polygonal, pyramidal and cratered ZnO thin films.

Morphological studies are investigated by variety of techniques including but not limited to; scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM) and stylus profilometry. The surface geometry acts as a contributing factor in the optical properties of thin films. Geometry includes film thickness, uniformity of the film thickness, and film surface roughness. These are all extrinsic factors therefore can be manipulated in the lab during thin film fabrication[51].

Figure 2.5 below embarks on exhibiting the relationship of SEM, XRD and AFM data with plane orientation of ZnO thin films [52]. From SEM images, preliminary observations shows that image (c) represent the (002) plane as the crystals shows the hexagonal shaped boundaries, which is a top view of the wurtzite structure as discussed in the previous Figure 2.3. The crystals have some spaces in between hence the surface is rougher, recording highest surface roughness of 216.6 nm. The XRD image in Figure 2.5(f) confirms (002) plane, as well as the complementary AFM image in Figure 2.5(i) showing surface roughness.

Similar inferences can be made for the (101) plane which has images in Figure 2.5 (b), (e) and (h) for SEM, XRD and AFM respectively. The SEM image shows edgy crystals (see Figure 2.4 (b)) with minimal spaces between crystals and the AFM image recorded surface roughness of 125.6 nm. The (101) plane exhibit a denser and compact crystals from its SEM image in Figure 2.5 (a), hence a small surface roughness of 11.6 nm is recorded by the AFM (Figure 2.5 (g)). This indeed shows how XRD, SEM and AFM techniques are interrelated in morphological studies of thin films.

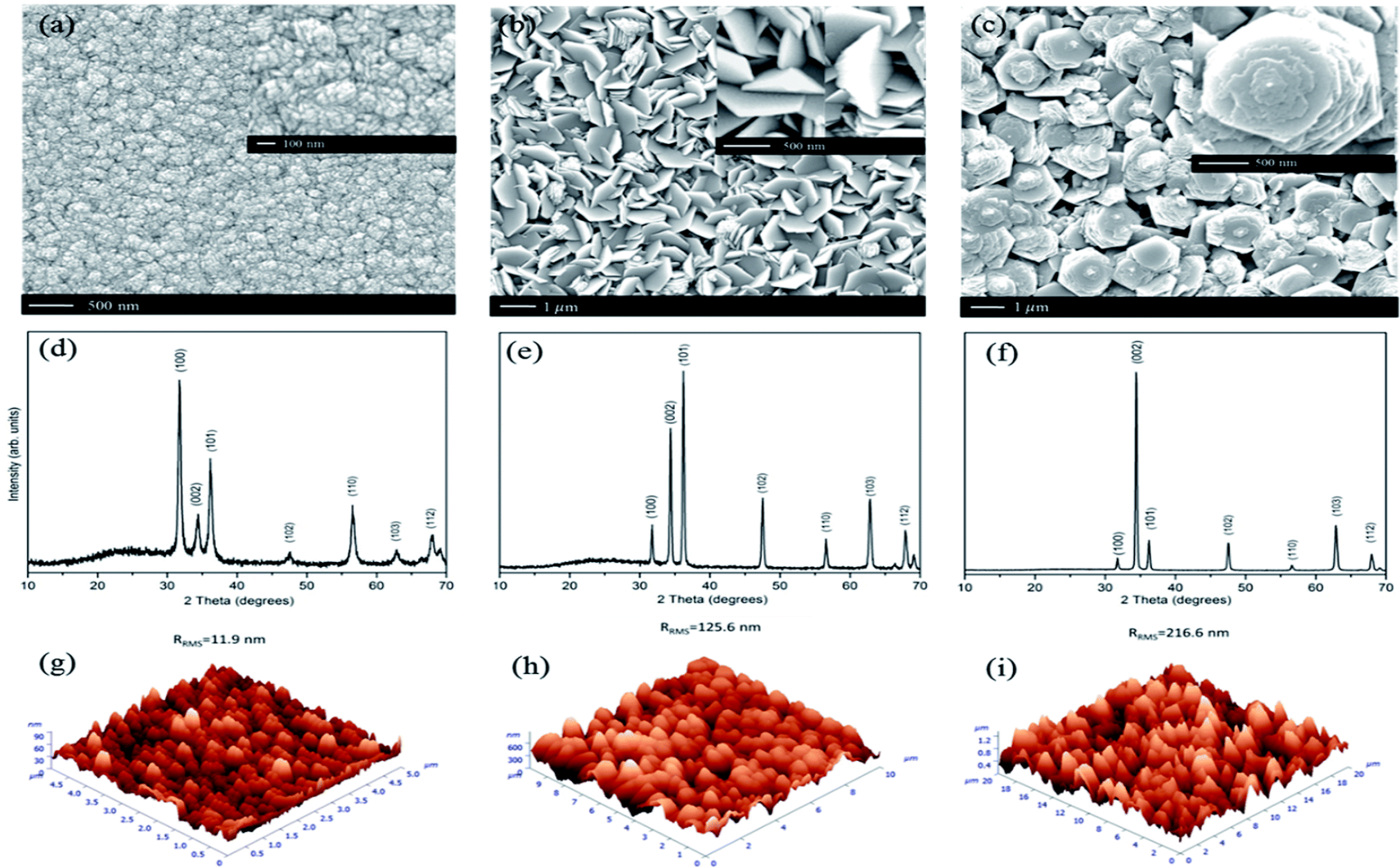


Figure 2.5: The relationship of SEM, XRD and AFM data with preferred plane orientation of ZnO thin films [52].

2.2 Electrical properties of ZnO

High electrical conductivity in a thin film is crucial as this is pivotal in opto-electrical applications of ZnO. ZnO is classified under semiconductors such as zinc selenite (ZnSe) and zinc sulphide (ZnS) and it remains a suitable candidate for a number of reasons discussed in this chapter. It is an *n*-type semiconductor with direct wide band gap ranging between 3.20 and 3.37 eV at room temperature [53]. This gives chances for optoelectronics in the blue and ultraviolet (UV) regions, including light emitting diodes, laser diodes and photo detectors [18][37][20][54].

The bandgap of ZnO (in Figure 2.6 (b)) can be altered by doping to yield *n*-type or *p*-type semi conductivity. The *n*-type conductivity of ZnO has been attained by doping with several elements including but not limited to group 13 elements (B, Al, Ga, In). The ions of these elements increase the number of valence electrons of the oxide and the excess electrons enter the conduction band of ZnO creating a donor level as illustrated in Figure 2.6(a) [55]. Group 15 elements (N, P, As, Sb) and Li [56][57][58] have been proven to yield *p*-type conductivity ZnO. This effect results in excess of positively charged holes in the valence band, causing a deficiency of electrons in the valence band. The valence band is not fully filled and now has an acceptor level as shown in Figure 2.6(c) below.

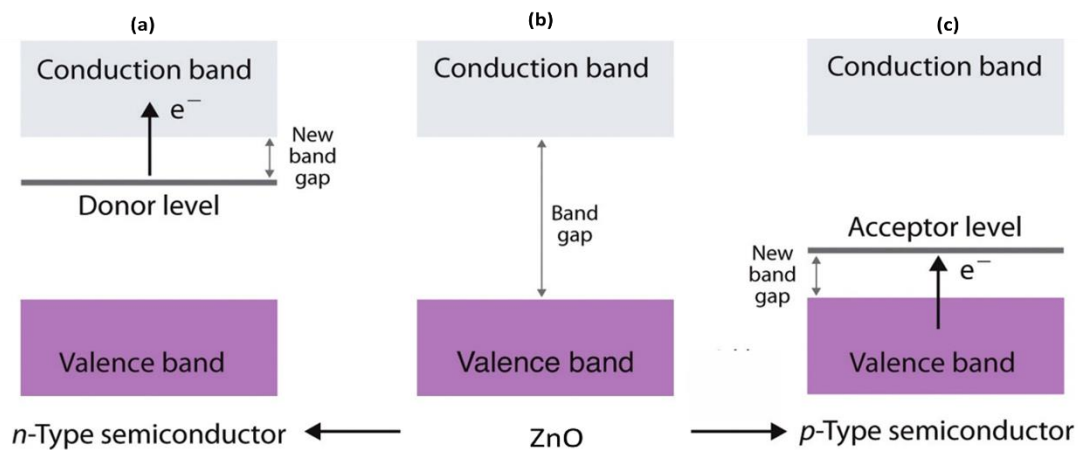


Figure 2.6: *n*-type and *p*-type doping of ZnO [55].

Undoped thin films are poor electric conductors, with resistivity (ρ) over $10^{10} \Omega \cdot \text{cm}$ [59]. The large band gap separating the valence electrons from the conducting band means that the

conduction band cannot be thermally populated at room temperature proving stoichiometric crystalline thin films to be good insulators. Electrical conductivity (σ) of n -type thin films depends on electron density in the conduction band and their mobility:

$$\sigma = \mu n e \quad (2.1)$$

where μ is electron mobility; n is its density and e is electron charge.

Electrical conductivity is intrinsically limited because electron density and mobility cannot be independently increased for practical thin films with relatively high carrier concentrations. At high electron density, carrier transport is limited primarily by ionized impurity scattering i.e., the Coulomb interactions between electrons and the dopants [9]. Higher doping concentration reduces carrier mobility to a degree that the conductivity cannot be increased. Moreover, it decreases the optical transmission at the near-infrared edge. In thin films carrier concentration is confined to a volume of the conduction band making it possible to have a thin film without free carrier concentration.

2.3 General optical properties of ZnO

ZnO thin film must reveal very low absorption coefficient in the near UV-Vis-NIR region of the electromagnetic spectrum for better performance in optical devices and solar cells [60]. Transmission in the near -UV region is limited by the bandgap (E_g), as photons with energy larger than E_g are absorbed [61]. Ideally, a wide bandgap thin film should not absorb photons in the transmission 'window' in the UV-Vis-NIR region. However, there are no ideal thin films, and even if such films could be deposited, reflection and interference would also affect the transmission. Hence 100% transparency over a wide region cannot be obtained [62].

The optical properties of ZnO thin films; transmittance (T), reflectance (R) and absorption (A) are determined by its refractive index n , extinction coefficient k , E_g and geometry. T , R and A are intrinsic and depend on the chemical composition and the solid structure of the material whereas the geometry is extrinsic [63]. There is a negative correlation between the carrier density and the IR absorption edge, but there exist a positive correlation between the carrier density and the UV absorption edge, as E_g increases at larger carrier density (Burstein-Moss

effect). As a result, the ZnO thin film transmission boundaries and conductivity are interconnected. The width of the visible transmission window of a ZnO film deposited on a transparent substrate is affected not only by the optical parameters of the ZnO but also by the optical properties of the substrate [44]. Refractive index (n_{sub}) of the most common substrates are around 1.45 for fused silica and around 1.6 for various glasses. Extinction coefficient of the substrate (k_{sub}) is generally $<10^{-7}$. Hence light absorption would take place only in the film, where generally $k_{film} > k_{sub}$. Band interferences (fringes) in ZnO can be observed in films with thickness above 100 nm, producing maximal and minimal values of T when either the wavelength or thickness is varied [64]. The transmittance curves for different thickness of ZnO films on glass substrates had shown that the interference fringes increases with increasing film thickness while the refractive index and extinction coefficient decreases as wavelength increases[65].When k_{film} is closer to 0, the peak transmission (T_{max}) is equal to the transmission of the substrate. Hence assuming that the sample is in air, $T_{max} = 90\%$ and 93% for thin films deposited on glass and fused silica, respectively.

The single quantity that can describe the absorption and refraction of light through a medium is termed the complex refractive index given by the equation:

$$n_c = n + ik \quad (2.1)$$

where n is the refractive index describing the velocity of light (v) in the medium since

$$n = c/v \quad (2.2)$$

where c is the speed of light in vacuum and k is the extinction coefficient which describes the attenuation of light wave as it passes through a material. The absorption coefficient (α) of the material can be determined from k using the equation:

$$\alpha = \frac{4\pi k}{\lambda} \quad (2.3)$$

where λ is the wavelength of transmitted light.

2.4 Other key properties of ZnO

ZnO possess free exciton binding energy of 60 meV [66] [67][68], which is relatively higher than of other similar semiconductors (compared to GaN-25 meV [3], ZnS- 40 meV, and ZnSe- 22 meV). This large exciton binding energy indicates that efficient excitonic emission in ZnO can persist at room temperature and at higher temperatures. This makes ZnO a promising material for optical devices that are based on excitonic effects [82]. The high thermal conductivity of ZnO makes it useful as an insulating additive. For example it is added to rubber in order to increase the thermal conductivity of tyres. This also increases the appeal of ZnO as a substrate for homoepitaxy or heteroepitaxy (e.g. for growth of GaN, which has a very similar lattice constant) [69][70]. High thermal conductivity also helps in overheating problems as it offers high efficiency of heat removal during device operation [61].

Semiconductor device fabrication processes greatly benefit from the amenability to ‘low-temperature wet chemical etching’. It has been reported that ZnO thin films can be etched with acidic, alkaline as well as mixture solutions [71]. The possibility of low-temperature chemical etching adds great flexibility in the processing, designing and integration of electronic and optoelectronic devices [72].

2.5 Review on AGZO thin films

AGZO thin films can be easily grown on glass substrates with advantages of simple processing of procedures of ZnO, such as easy etching with acid or base. A vast number of reports are available in literature, in which optimizing the electrical properties of ZnO using a variety of doping atoms and concentrations is discussed [73][74][75][76][63].

Numerous reports have proved Ga and Al as successful dopants for ZnO thin film synthesis since doping yield thin films with low resistivity and high transparency comparable to conventional ITO films [19][77][78][17]. The ionic radii of Ga^{3+} (0.062 nm) and Al^{3+} (0.053 nm) are smaller than that of Zn^{2+} (0.074 nm) and it can be hypothesized that Ga and Al have possibility to be co-doped into ZnO with minimal defects to the crystal structure.

The effects of Ga and Al as singly doped ZnO thin films on the electrical and optical properties remain broadly studied in literature [17-21]. GZO and AZO films generally have lower stability in humid environments when compared to ITO. Nevertheless, Minami et al. showed that thin

films of AZO and GZO with thickness greater than 200 nm are relatively stable and consequently suitable for applications such as LCDs and touch panels [27].

Singly doped Gallium doped ZnO (GZO) and Aluminum doped ZnO (AZO) thin films have been studied using different deposition techniques in recent years [79][80][81]. AZO films have excellent conductivity and chemical stability, and they have been the most favorable TCOs for application in amorphous solar cells, SnO_2 : F (Asahi U-Type) [82]. AZO thin films have limitations such low thermal stability and degeneration problems during extended exposure to ambient air conditions, due to high reactivity of Al [83][84][18] .

On the other hand, GZO thin films survive well in humid environments and more resistant to oxidation compared to AZO [34-38]. GZO thin films has better transparency and conductivity in the near infrared region [85]. AZO and GZO thin films have higher doping concentrations and large grain size, making them to have better electrical properties when compared co-doped AGZO thin films. However, AGZO films had shown superior transmittance in the near-infrared (NIR) region and conversion efficiency in solar cell applications when compared to AZO and GZO films under similar conditions [86]. Liu et al. [87] demonstrated that AGZO thin films have superior electrical properties compared to AZO and GZO thin films and that the lowest resistivity of AGZO thin films is $8.12 \times 10^{-4} \Omega\cdot\text{cm}$. In addition, AGZO thin films were found to have a higher average transmittance than the other two thin films in the wavelength range 300 –1000 nm.

Effects of thickness on the properties of AGZO thin films were investigated by Seo et al. [88] and they recorded average transmittance of 94.8% in the visible region with an optimized thickness of 200 nm. Shin et al. [14] fabricated AGZO thin films with different Al/Ga concentrations by using pulsed laser deposition. They showed that doping 1.5 at% Al/Ga in AGZO thin films resulted in the lowest electrical resistivity of $2.18 \times 10^{-4} \Omega\cdot\text{cm}$ and a transmittance of 85 %. Henceforth, improvements in various properties of ZnO can be expected in AGZO thin films, making a promising alternative economical doping procedure for device applications.

2.5.1 Deposition techniques of AGZO films

The choice of deposition method is very crucial. Any two given transparent conducting oxide films with the same chemical compositions can possess significantly different characteristics depending on their techniques of deposition. For example, for photovoltaic applications, the TCO layer must attain very low surface roughness in order to make a good contact. In this case, deposition techniques such as DC magnetron sputtering would be suitable, where a smooth film is deposited on the substrate.

Deposition of AGZO films is entirely dominated by physical methods, mainly magnetron sputtering [24-32]. Such techniques comprises of costly equipment and complicated procedures. Sputtering (DC or RF) techniques involve use of expansive targets which inhibits mass production of thin films. Other physical deposition techniques such as pulsed laser deposition (PLD) and molecular beam epitaxy (MBE) have abilities of producing high quality films but they are not recommended for mass production due to high cost. AGZO thin films have not been investigated by chemical spray pyrolysis, there are only reports on sol-gel [25, 42] and electron spinning [48]. Chemical deposition methods are advantageous due to their simplicity and cost effectiveness. The chart in Figure 2.7 below shows the chemical solution based methods that have been used in ZnO thin films synthesis; sol-gel [21], spray pyrolysis [89], Chemical Bath Deposition (CBD) [90], Cathodic electrodeposition [91], Aqueous precipitate synthesis [92] and self-assembly. Gas phase methods include Atomic Layer Epitaxy (ALE) [93], Reaction under Autogenous pressure at Elevated Temperature (RAPET) [41], Successive Ion Layer adsorption and reaction (SILAR) [94] and chemical vapour deposition (CVD) [95].

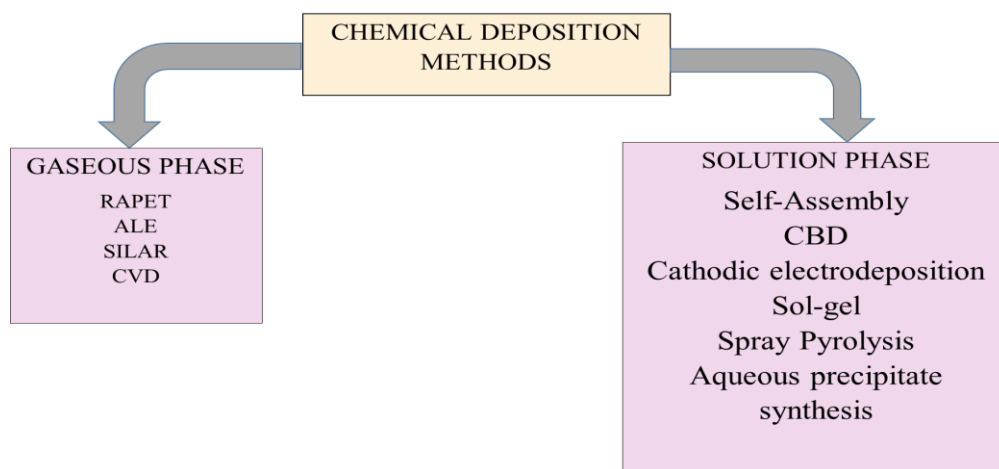


Figure 2.7: Chemical deposition techniques commonly used for ZnO thin film deposition.

The most studied chemical deposition methods for ZnO deposition are sol-gel and spray pyrolysis [21][96]. They offer advantages such as production of high quality films in large scale; excellent control of stoichiometry, low cost of the apparatus and raw materials [63]. Spray pyrolysis is much more advantageous over sol-gel as it does not use organic additives such as polyvinyl alcohol (PVA) or diethanolamine (DEA) additives needed for gel formation [21][97]. Films grown from these additives are prone to many defects like cracking during annealing. Spray pyrolysis can be implemented in a standard laboratory. Therefore, Chemical spray pyrolysis deposition method can be used extensively as much as physical methods have been employed in deposition of AGZO thin films, as there are no significant discrepancies in optical and electrical properties between the two deposition techniques (Table 2.1). For example, above 85 % optical transmittance for AGZO films deposited on glass by sol-gel was recorded by Ebrahimifard et al.[19] and the same optical transmittance was obtained when depositing AGZO films on polymers by r.f sputtering[12].

2.6 Summary

This chapter have discussed the history of thin films and their applications. Much focus was directed to ZnO thin films. Their general properties have shown economic sustainability when compared to other thin films in the market. ZnO films have wide range of applications in opto-electrical devices when used as transparent conducting oxides. Various deposition techniques have been explored for production of co-doped ZnO films, as summarized in Table 2.2. Spray

pyrolysis emerges the most economic and flexible deposition technique for growth of doped ZnO thin films. Thin film fabrication processes require controlled and optimized deposition parameters in order to attain films of desired morphology, optical and electrical properties for a particular thin film application.

Table 2.2: Investigation of AGZO thin films with different deposition methods.

Deposition method	$T_{substrate}$ (pre-post annealing temperature °C)	Precursor reagents (optimum at% achieved)	T_{av} (%) Visible region	E_g^{opt} (eV)	ρ ($\Omega.cm$)
Sol-gel dip coating [19]	300-500 / glass	Zn(CH ₃ COO) ₂ .2H ₂ O 1at% Al(NO ₃) ₃ .9H ₂ O	>85	3.20-	-
Sol-gel spin coating[98]	200-500 / glass	Zn(NO ₃) ₂ .6 H ₂ O Ga(NO ₃) ₃ .8 H ₂ O In(NO ₃) ₃ .4.5 H ₂ O	>97	3.35-3.82	-
Sol-gel spin coating [99]	450-550 / glass	Zn(CH ₃ COO) ₂ .2H ₂ O NaCl 8 mol% MgCl ₂ 1-3 mol%	~70	3.29	-
Radio frequency magnetron	Room temp/ glass	98 wt% ZnO 1.8 wt% Ga ₂ O ₃	>86	3.52	1.87 x10 ⁻³ -
Radio frequency magnetron sputtering[101]	Room temp & 200 / glass	98 wt% ZnO 1.8 wt% Ga ₂ O ₃ 0.2 wt% B ₂ O ₃	>85	BGZO-RT 3.58 BGZO-AN 3.67	BGZO-RT 1.9x 10 ⁻³ BGZO-AN 0.9x10 ⁻³
Radio frequency magnetron sputtering [12]	Room temp / Fused quartz (FQ) & cyclo olefin polymer (COP)	96.785 wt%-ZnO 0.215 wt%-Ga ₂ O ₃ 3.000 wt%-Al ₂ O ₃	>85	-	3x10 ⁻³ - 4.07 AGZ/FQ 4x10 ⁻³ - 5.73 AGZ /COP
Direct current magnetron sputtering [102]	350 / glass	98 wt% - ZnO 1 wt% -Al ₂ O ₃ 1 wt% -Ga ₂ O ₃	>82	-	3 x 10 ⁻⁴

(The sign - means no values mentioned in the study)

Chapter 3

METHODOLOGY

Despite numerous reports on synthesis and fabrication of doped ZnO thin films, it is a rare case to reproduce same results by following a given procedure because the properties of thin films are highly sensitive to doping and they are influenced by numerous deposition parameters such as spray distance to substrate and atomization pressure which, have to be optimized simultaneously. Even the fumes in the lab can subject the thin films to non-intentional doping hence altering their properties.

3.1 Synthesis

This chapter discusses the experimental methods under synthesis and characterization subtopics. The synthesis part comprises of the precursor, substrate and deposition methods for thin films while equipment is discussed under characterization. The detailed experimental procedures which were used for the synthesis of AGZO thin films are elaborated under the following subtopics:

3.1.1 Precursor Synthesis

Precursor synthesis for this work was adapted from several authors [89][103][104]. The precursor salts in solution were dissolved by means of ultrasonic bath instead of using a laboratory hotplate to heat the solutions, as commonly done in other studies [105]. The salts were weighed accurately using an analytical balance. Analytical grade reagents were used for this synthesis. Zinc acetate dehydrate (ZAD), (Sigma Aldrich 99.5%) was used as a source of zinc ions. Aluminum acetylacetonate (Sigma Aldrich, 99%) and gallium acetylacetonate (Sigma Aldrich 99.99%) were used as dopants sources. The organic salts were dissolved in a solution made from mixing deionized water and ethanol, with a volume ratio of 10 mL: 90 mL, respectively, at room temperature, using an ultrasonic bath. Small amount of glacial acetic acid (5 mL) was added to the aqueous solutions to act as complexing agent and prevent precipitation of zinc hydroxides. Equal doping concentration (constant doping) was used; that is, a sample of AGZO 3 at% (at% refers to atomic percentage) denotes 1.5 at% Al; 1.5 at% Ga; and 97 at% Zn. The doping concentrations were varied from 0 to 6 at%, hence an array of seven solutions was made. The total concentration of the precursor solutions was kept constant at 0.1 mol/dm³.

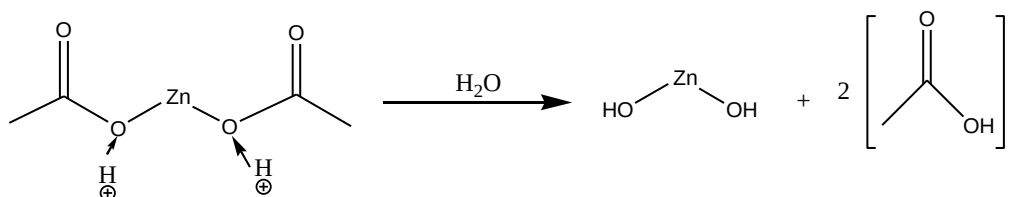
An example calculation of the required amounts is shown in Table 3.1 for the preparation of a sample of 100 mL solution of 0.1 mol/dm³ AGZO 3 at%. The atomic percentages were converted to mass in respect to total moles of 0.01 in solution. Thus, to make 100 mL of 0.1 M AGZO 3 at% one makes a solution containing 2.1291 g of ZAD, 0.05506 g gallium acetylacetonate and 0.0486 g of aluminum acetylacetonate.

Table 3.1: Sample calculations for preparation of AGZO solution at 3 at%.

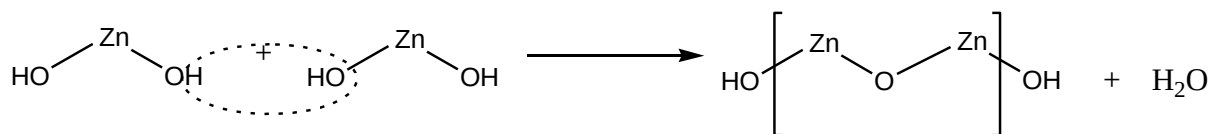
$M_r \text{ ZAD} = 219.51 \text{ g/mol}$ 97 at% of total moles in solution = $0.97 * 0.01 \text{ mol} = 0.0097 \text{ mol}$ Mass of salt required $0.0097 \text{ mol} * 219.51 \text{ g/mol} = \underline{2.1291 \text{ g}}$	$M_r \text{ Ga (acac)}_3 = 367.05 \text{ g/mol}$ 1.5 at% of total moles in solution = $0.015 * 0.01 \text{ mol} = 0.00015 \text{ mol}$ Mass of salt required $0.00015 \text{ mol} * 367.05 \text{ g/mol} = \underline{0.05506 \text{ g}}$	$M_r \text{ Al(acac)}_3 = 324.31 \text{ g/mol}$ 1.5 at% of total moles in solution = $0.015 * 0.01 \text{ mol} = 0.00015 \text{ mol}$ Mass of salt required $0.00015 \text{ mol} * 324.15 \text{ g/mol} = \underline{0.0486 \text{ g}}$
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3.1.2 Thin film formation

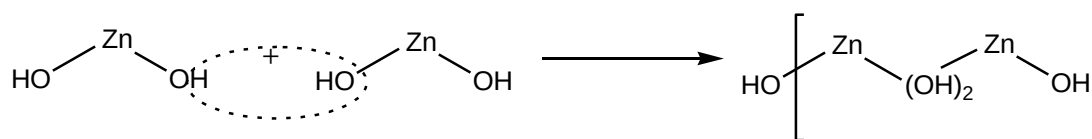
For easier understanding of the thin film formation, the dopant cations (Al and Ga) are omitted in the following illustrations. The proposed general mechanism starts with hydrolysis of zinc acetate dehydrate precursor solution [106];



After hydrolysis of zinc acetate molecules, the hydrolyzed species undergo poly-condensation to make an inorganic polymer (oligomer) through elimination of water molecules:



During poly-condensation, ololation process (formation of hydroxo bridges) is possible when the coordination of the metallic center (Lewis acid center) is not fully satisfied. The reaction kinetics of ololation are usually faster than oxolation (formation of oxygen bridges).



The fast ololation reaction is not favorable under organic additives such as carboxylic acids or functional alcohols, as they act as chelating ligands and modify the reactivity of precursors [107]. Nonetheless, the general predictions of various reaction mechanisms between central metal cations with various ligands are currently under research [106]. The final step would be subjection of the colloid into spray pyrolysis system where upon calcination, the organic solvents and ligands are vaporized, leaving behind dense films of inorganic oxides.

3.1.2.1 Proposed mechanism by others

Ions from the spray are absorbed on the substrate surface upon which they may diffuse away or may bond with other neighboring ions. For achievement of quality crystalline films, there must be sufficient surface diffusion to allow ions to migrate to the thermodynamically stable sites and minimize their surface energy within the time needed to deposit a monolayer of atoms. All phase transformations in film formation involve the processes of nucleation and growth. The initial process for film formation involve condensation of sufficient vapour atoms on the substrate. Growth depends on the size of vapour atoms; they will either grow in size or dissociate into smaller entities. Repeated exposure of the substrate to the incident vapour result in formation of small but highly mobile clusters or islands [108]. The next stage involves merging of the islands by coalescence as illustrated in Figure 3.1. Spanhel and Anderson [109]

reported two possible ways of describing growth of ZnO films: Ostwald ripening and aggregation. The formed stable clusters rapidly combine to yield next most stable aggregate. Primary aggregates further rapidly combine to give most stable secondary aggregate and so on. On other similar studies, Meulenkamp [110] also suggested that the particle growth in colloid systems could be explained by two standpoints. The first being Ostwald ripening where large particles grow at expense of smaller particles. The second point describe growth rate basing on addition of reactive precursors available in solution to already existing particles. The rate of particle growth depend on concentration of precursors or dissolved species and their reactivity, which depend on their particle surface atoms and the solution composition.

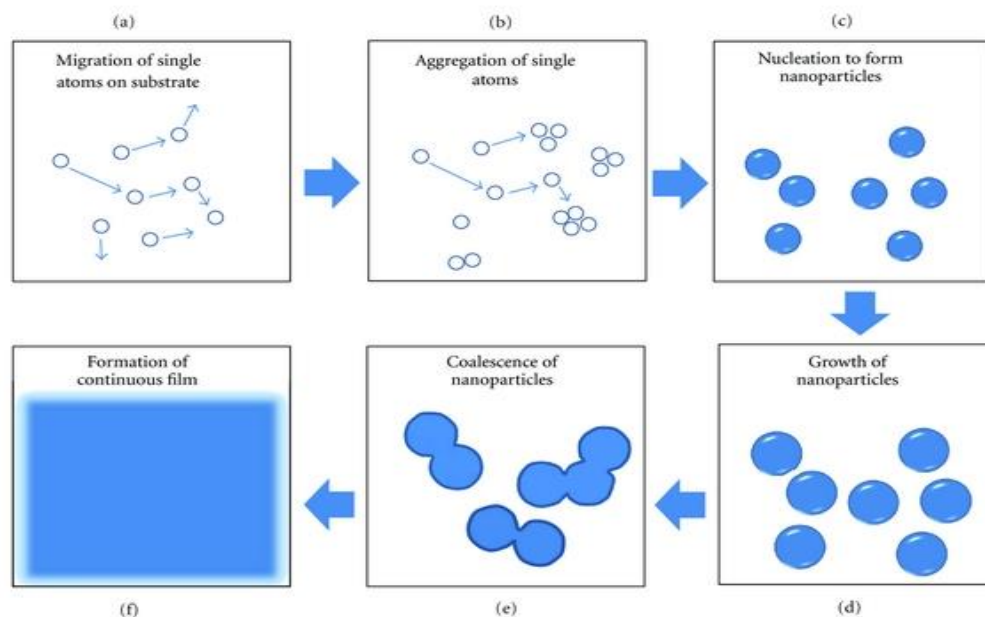


Figure 3.1: Schematic of thin film growth. The processes include (a) migration of single atoms on the substrate, (b) aggregation of single atoms, (c) nucleation to form nanoparticles, (d) growth of nanoparticles , (e) coalescence of nanoparticles, and (f) formation of continuous film.[111].

When Clusters from the colloid are allowed to diffuse on a given substrate, they will try to minimize the substrate free energy(G). Free energy is a convenient measure of feasibility of the reaction. It is defined as follows

$$G = H - TS \quad (3.1)$$

where H is the enthalpy, S is the entropy and T is the absolute temperature. When a system changes from initial to a final state under constant temperature due to chemical or physical processes, the free energy changes accordingly with changes in entropy and enthalpy. Systems naturally tend to minimize their free energy and successively proceeds to lower G values and even negative value G , until it is no longer possible to reduce G further. At $G = 0$, the system is at equilibrium and there is no longer driving force for change, then it can be explained by change in chemical free energy per unit volume, ΔG_v . The two main thermodynamic parameters that determine growth mechanism of most deposition processes are substrate temperature, T_s , and the supersaturation, S which are included in the following equation [112]:

$$\Delta G_v = -\frac{kT_s}{\Omega} \ln\left(\frac{P}{P_e}\right) = -\frac{kT_s}{\Omega} \ln(S) \quad (3.2)$$

P is the pressure of the arriving atoms and P_e is the equilibrium vapor pressure at the substrate temperature T_s , S is the vapour supersaturation defined by $S = \left(\frac{P}{P_e}\right)$ and Ω is the atomic volume. When there is no supersaturation, $S=0$ and $\Delta G_v=0$, the nucleation and growth are impossible. Hence any level of gas phase supersaturation generates a negative ΔG_v , which make nucleation possible. A supersaturated solution/vapour is not at equilibrium ($\Delta G_v \neq 0$) and in order to relieve the supersaturation, equilibrium shift ($\Delta G_v = 0$), and the solution crystallizes. Therefore a supersaturated solution/vapour is required for crystallization to occur, which involves nucleation and growth.

3.1.3 Substrate preparation

Often when characterizing thin films, only the material making the film is the one mentioned, however, their physical properties are mostly influenced by the deposition technique used and also the compatibility with the lattice parameters of the substrate. Material and orientation of the substrate material introduces effects on the nucleation and growth dominated microstructure of a thin film [113].

Methods of substrate cleaning involve, chemical wetting, physical wet and dry cleaning methods. On this work standard chemical wetting method was used, which comprises of acid, base and solvents. This method was appropriate as the glass substrates were uncoated, hence simply removal of dirt on the surface was sufficient. The microscopic glass slide substrates (thickness of 1.35 ± 0.1 mm) were cut into 25 mm x 25 mm pieces with a glass cutter, cleaned thoroughly by soaking them overnight in concentrated nitric acid, thereafter ultrasonically cleaned with acetone, 2-propanol and finally deionized water. Standard ultrasonic baths like the one used in this work, operate at frequency of 40 kHz. This leads to a standing wave pattern within the ultrasonic bath, cleaning the substrate vigorously in certain spots and leaving other spots not cleaned at all (similar effects as on ultrasonic aluminum foil test [114]). This effect was reduced by periodically moving the glass substrates during ultrasonic cleaning.

3.1.4 Thin film Deposition

The spray pyrolysis method developed by Chamberlin et al. [25] was modified and used for the deposition of the thin films. Spray pyrolysis is a procedure by which thin film is deposited by spraying a precursor solution on a heated substrate, where decomposition of the solution leaves the desired oxide layer while the volatile solvents evaporates [105]. The solvents are selected such that they are volatile at the deposition temperature. There have been numerous studies on spray pyrolysis since the pioneering work by Chamberlin and Skarman [115] on CdS films for solar cells. Figure 3.2 gives the typical spray pyrolysis setup.

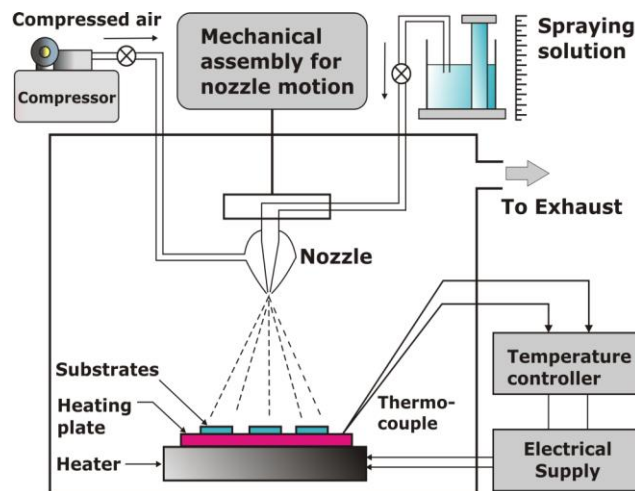


Figure 3.2: schematic diagram for spray pyrolysis technique [116].

The prime requisite for obtaining good quality thin films rely on the optimization of preparative conditions such as substrate temperature, spray rate and concentration of the solution [21]. The key parameters to consider for spray pyrolysis are the atomization technique, aerosol transport (carrier gas, pressure and distance), type of the substrate, deposition temperature and the chemical composition of the precursor solution [117].

Efforts have been made for improving the performance of the atomizing mechanism, and different types of nozzles are commercially available currently [118][119]. The carrier gas used determines the oxidizing influence of the atmosphere in which the pyrolytic reaction takes place, hence influencing the cation oxidation number in the final film [120]. The rate at which droplets reach the substrate rely much on the pressure in the nozzle thus influencing both the growth rate and the cooling rate of the substrate.

Substrate temperature influences many parameters; aerosol transport towards the substrate, solvent evaporation, possibility of droplets impacting the surface, the dynamics of their spreading and the precursor decomposition pathway. The overall morphology and composition of the film is also influenced by the substrate temperature. The type of substrate used is mainly related to its heat capacity. Substrates with low heat capacity and conductivity are cooled much faster by the spray than those that have large heat capacity [121].

For this work, customized spray pyrolysis unit was built, with all necessary components as shown in Figure 3.2. Compressed ambient air was used to atomize precursor solution, maintaining pressure between 3.0 and 3.5 Bar. An automated syringe pump was used to provide a flow rate of 3 mL/min during deposition of films. The nozzle to substrate distance was maintained at 26 cm. The deposition temperature was monitored by a digital multimeter fitted with K-type thermocouple, and maintained at 250 ± 4 °C. Post annealing was done at the same temperature of 250 ± 4 °C for 1 hour, in order to decompose the organic substituents into final AGZO films. The flow chart shown in Figure 3.3 below shows the summary of steps followed in deposition process. The pump syringe had a 30 mL capacity hence a 100 mL volume of precursor solution consequently resulted in four loops of coating, with 5 minutes pre-annealing in between spraying cycles.

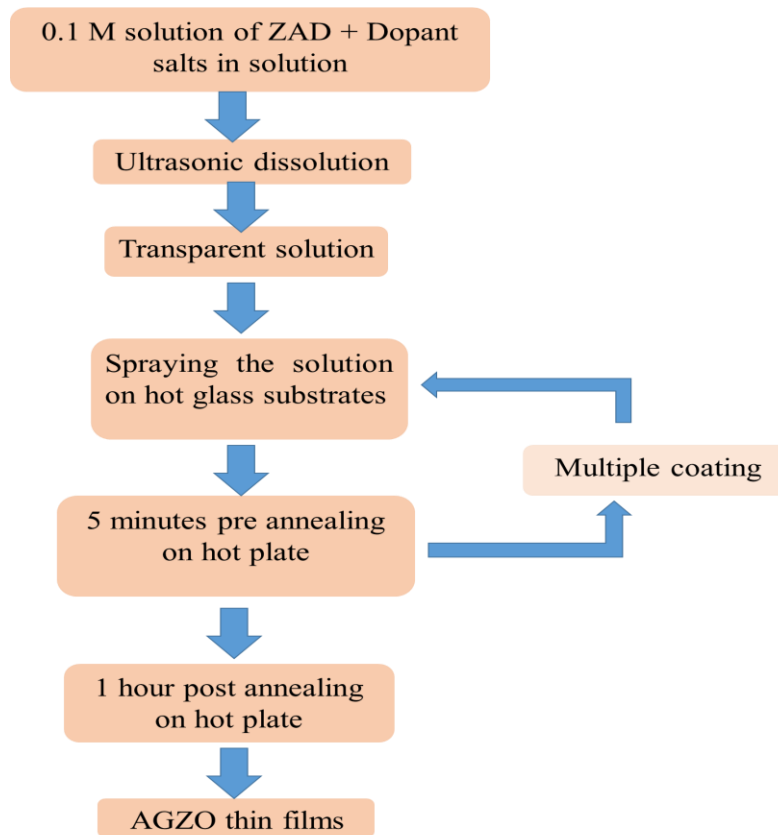


Figure 3.3: Flow chart for preparation of AGZO thin films.

3.2 Thin film characterization techniques

Several characterization techniques can be used in analyzing thin films. These include film thickness measurements, morphological, optical, electrical mechanical characterizations. Each characterization involves specialized equipment. Characterization can be taken as quality assurance process in thin film technology. The fabricated films have to possess certain properties for specialized purpose. For example dye sensitized solar cells requires thicker films (more than 1 micron) while films for transparent electrodes require thickness ranging in nanometer scale.

3.2.1 Film thickness

Physical properties of a thin film are highly dependent on their thickness. Determination of film thickness is therefore a fundamental task in thin film technology. The methods include gravimetric, optical and direct methods. Gravimetric methods are based on the determination

of mass making it prone to uncertainties during use of micro analytical balances and time consuming procedures. Optical methods comprises use of expensive equipment like ellipsometry and Nomarsky interferometer in optical microscopes. Direct methods utilize the use of mechanical profiling or by observation in microscopes. In stylus profilometry the film has to exhibit a step on a plane substrate. A diamond stylus (tip curvature of approximate 10 μm) is pulled along the surface at constant velocity. The step height is measured by a pick-up system.

In this work, the film thickness was measured using stylus profilometer (KLA Tencor D 100, USA). The instrument takes measurements electro-mechanically while moving the sample beneath a diamond tipped stylus. The stylus is mechanically coupled to the core of a Linear Variable Differential Transformer (LVDT). The stage moves the sample beneath the stylus with respect to the user's set parameters; scan length, speed and stylus force. As the stylus moves over the surface of the sample, surface variation causes the stylus to be translated vertically. Electrical signal corresponding to the stylus movement are produced as the core position of the LVDT changes. The LVDT scales an alternating current (AC) reference signal proportional to the position change, which in turn, is conditioned and converted to digital format through a high precision, integrating, analogue to digital converter. In order to get film thickness, a scratch is made on the film by etching with a dilute acid. Figure 3.4 shows a snapshot of the stylus tip about to scan the scratched area. This scratch groove will be picked by the stylus and change in height recorded.

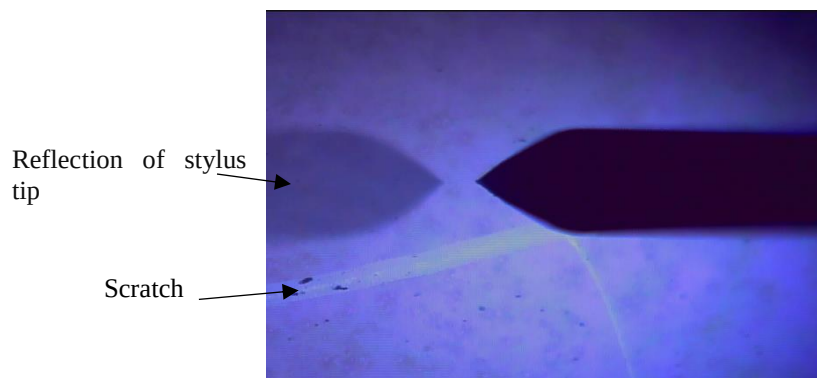


Figure 3.4: Image of stylus tip about to scan the scratched area for film thickness measurement.

3.2.2 Surface topography

Surface morphology of thin films is characterized by several microscopic techniques involving scanning tunneling microscopy, field emission scanning electron microscopy and atomic force microscopy. Through these techniques surface texture and roughness can be quantified. Topographical data of thin films can be deduced from the secondary electrons emitted from the very top of the surface.

The structural features deeper under the surface such as grain boundaries, phase boundaries and composition can be deduced when higher energy is used in scanning electron microscopy (SEM). Scanning electron microscopy is one of the most useful and versatile technique for the investigation of surface topography, microstructure features, etc.

The working principle involves the use of the scattered secondary electrons as a finely focused electron beam impinges the surface of the sample [122]. The electrons are produced by a thermal emission source, such as heated tungsten filament, or by using field emission cathode. To create SEM image, the incident electron beam is scanned in a raster pattern across the sample surface. Several detectors can be introduced in the SEM specimen chamber, like the secondary electron detector and energy dispersive spectrometer (EDS) or wavelength dispersive spectrometer (WDS). The electron gun is kept free from contaminants by a vacuum system, which is made up of a mechanical pump and a diffusion pump. The vacuum keeps electron beam from dispersing randomly in the chamber.

As the electron beam hits the sample surface at around 50 eV, secondary electrons are emitted from 5- 50 nm below the surface at lower energy around 20 eV. They are detected by the secondary electron detector in the chamber. Intensity of the emitted electron signal is displayed as brightness on a cathode ray tube. Figure 3.5 shows a primary electron beam with interaction volumes with the film (sample). The higher the interaction volume the lower the image resolution, hence secondary electrons give higher resolution than backscattering electrons [118]. The sample must be electrically conductive to give higher resolution by secondary electron imaging.

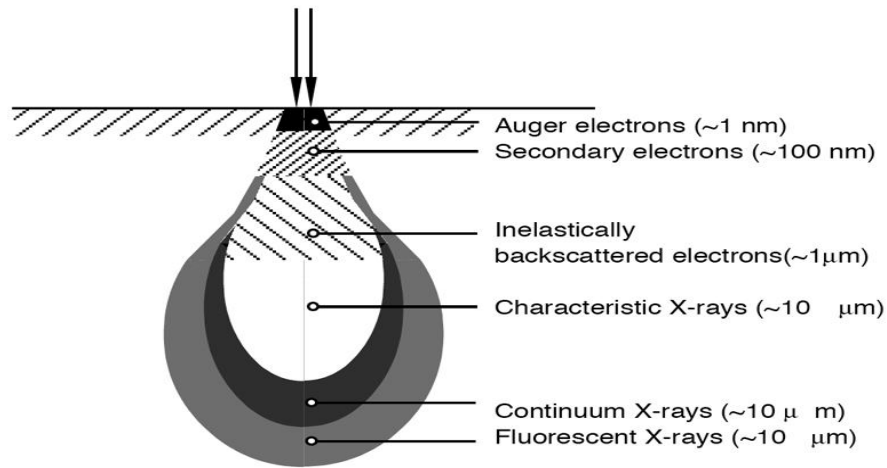


Figure 3.5: Primary electron beam showing interaction volumes of various scattering types [123].

Figure 3.6 shows a schematic of a SEM column [124]; the electron beam is aimed towards the substrate through an aperture and its size and shape are changed by electromagnets. Magnetic fields or electrostatics focus the electron beam. Electromagnets produce magnetic fields that adjust the electron trajectory as current is applied to the coil [122]. When current is adjusted, it changes the position of the focal point of the beam. Electron beam then passes through a condenser lens which takes the wide beam coming out of the aperture, condensing and collimating it. Then the beam is sent through objective lenses which focus the beam into fine point at the substrate surface and supply demagnification. After the objective lenses, the beam passes through a final aperture referred to as “real” aperture. Apertures prior to the real aperture are referred to as virtual apertures and they perform common task as real apertures of excluding the scattered electrons.

The working distance (WD), the distance between the sample and the real aperture, can affect the depth of the field in the image and the resolution of the image. A higher WD results in more depth of the field, which makes more of image focus. High WD is useful in taking images of samples with lot of height variation in their topography while smaller WD is ideal for flat samples as higher resolutions can be attained.

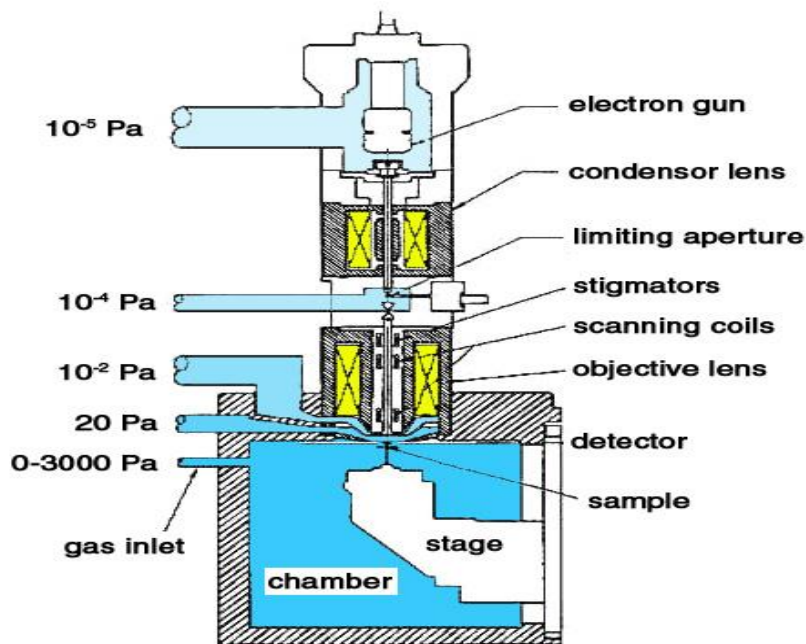


Figure 3.6: Schematic diagram for column of an SEM [119].

For this study the topographical images of the AGZO films were taken with FE-SEM JSM-7100F (JEOL, USA) scanning electron microscope. This SEM has the high vacuum with capabilities of accelerating voltages between 0.5 and 30 kV. It uses field emission cathode which is capable of imaging at 3.0 nm resolutions at 30 kV, 8 nm at 3 kV and 15 nm at 1kV. The chamber working pressure was kept at 3.0×10^{-5} Pa. Images were taken at 50 000 X magnification at WD between 8 nm and 10 nm. It was at this magnification that the crystals of the AGZO films were clear and detailed for grain size and shape comparisons. The samples were cut to fit size of the stub and mounted with carbon adhesive paste. Coating was not necessary as the films were highly conducting and the carbon paste attached to the sample gave electrons a way to escape and thus preventing electron charge build up.

Another imaging technique used in determination of topography and other properties of surfaces is the atomic force microscope (AFM). This technique is non-destructive as there is no radiation involved as compared to the techniques discussed above and non-conducting surfaces like polymers and biological samples can be analyzed. The instrument works on the principle that when a tip, integrated to the end of a spring cantilever, is brought within the interatomic separation between the tip and the sample, interatomic potentials are developed between the

atoms of the tip and those of the sample. As the tip moves across the surface, the interatomic potentials force the cantilever to bounce up and down with changes in the contours of the surface. Hence, measuring the deflection of the cantilever, the topographical features of the surface can be mapped out [125]. Three dimensional images are achieved by recording cantilever motion in the Z- direction as a function of sample's X and Y position. AFM can be operated in three modes; contact mode, non-contact mode and tapping mode. Figure 3.7 shows the schematic diagram of the main components of AFM [126].

For this work Bruker Dimension Edge AFM with scanAsyst[®] (Germany) was used to characterize the AGZO samples. The instrument uses Nanoscope v 5.12 software for both real time and post capture image processing. It was housed on a vibration isolation table and images were acquired using tapping mode under ambient conditions, using triangular pyramidal-tipped cantilevers (DNP-S, Veeco, UK), with nominal tip diameters of 20 nm and nominal spring constants of 0.58 N m⁻¹.

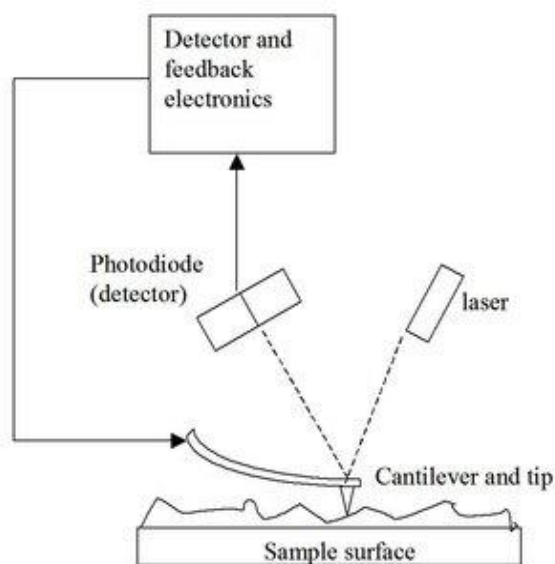


Figure 3.7: schematic diagram of the AFM [121].

3.2.3 X – ray diffraction

X-ray diffraction is used in studying the crystal structure of materials, which include the estimation of the crystallite size and orientation of crystal planes (miller indices). The technique

is one of the most important aspects of material science and engineering as many properties of materials depend on their crystal structures. X-rays are electromagnetic radiation with wavelength around $1 \text{ \AA}$, just about the size of an atom, hence used for characterization of crystalline materials and determination of their structure. The main component of XRD unit is called goniometer. The goniometer comprises of X-ray tube, sample holder, monochromator and a detector. The left arm holds the X-ray tube and the right arm holds the monochromator and the detector. Monochromator transmits a mechanically selectable narrow band of wavelengths suitable for the working of the diffractometer. The goniometer arms moves in an arc position during scanning maintaining the angles ($2\theta/\theta$), as shown in Figure 3.8 below.

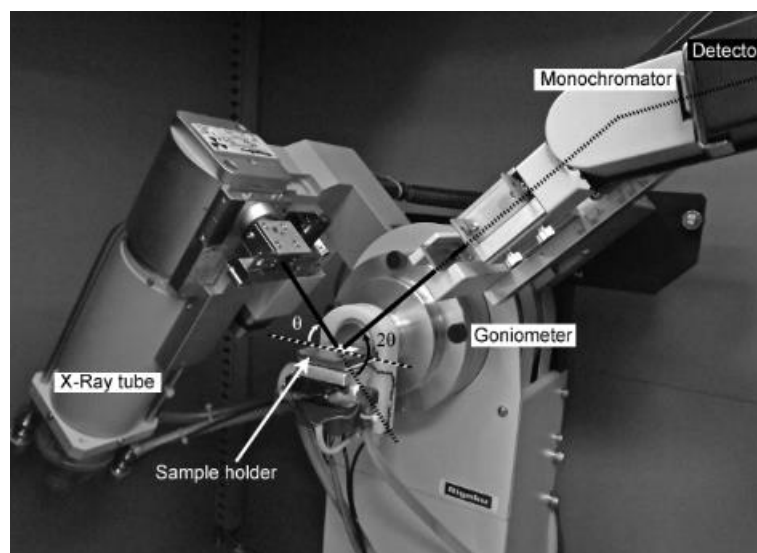


Figure 3.8: Schematic diagram of the goniometer of an X-ray diffractometer [127].

The X-rays are generated by accelerating electrons at a metal source at several keV, causing the core electrons (K shell or $1s$) in the metal target to be knocked out by energized electrons. As the valence electrons (from L ($2p$) or M ($3p$) levels) fall into the vacancies in the core shell, X-rays are emitted [128].

The commonly used metal target is copper, preferred for its high melting point and an excellent thermal conductor. The X-rays produced have well defined wavelengths that corresponds to the energy difference between the two shells (i.e. K and L shells) of the metal target, hence they are called characteristic X-rays. This characteristic X-rays are sent to the sample and cause the

atoms and electrons of the sample to scatter X-rays, forming new waves that constructively interfere with one another in certain directions according to Bragg's law below;

$$n\lambda = 2d_{hkl} \sin \theta \quad (3.3)$$

where d_{hkl} is the lattice spacing of the crystal, θ is the Bragg's angle of incidence, λ is the wavelength of Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) from a copper target, or Mo K α radiation ($\lambda = 0.7107 \text{ \AA}$), hkl denotes the miller indices of a particular plane. If the wavelengths of the X-rays have similar size to the interatomic spacing (d_{hkl}) of the sample's planes, the waves diffract and scatter, carrying information about material's individual atoms and their arrangement [127].

Crystalline samples are easy to measure since they scatter strongly in certain directions. The unit cell of the crystalline sample scatter the X-rays in the same direction if the path length difference (when equation 3.3 is satisfied). Other scattered rays will experience destructive interference and will be out of plane with each other. The average size of the crystallite (Dp) is also determined from XRD pattern using the Debye-Scherrer equation [129] :

$$Dp = \frac{0.9\lambda}{\beta \cos \theta} \quad (3.4)$$

where β is full width at half maximum (FWHM).

In this work, XRD was performed on the sprayed samples of AGZO using diffractometer (Bruker D8 Advance) with Cu K α emission ($\lambda=1.54105\text{\AA}$) with high efficiency linear detector of Lynx Eye type. The samples were scanned between 30° and 70° at a scan speed of $1^\circ/\text{min}$ in 0.01844 increments, at 40 keV and 40 mA. The scanning mode used was coupled ($2\theta/\theta$). The AGZO samples on glass substrates were mounted with a prestick into the sample holder to prevent them from slipping during rotation.

3.2.4 Optical characterization

Spectral region in the visible and adjacent (near UV and near IR) ranges is of importance in Uv-Vis spectroscopy. Analysis in this region is commonly associated with solutions but solids and gases can also be studied. The optical properties of thin films are determined using uv-vis

spectrophotometer. Spectrophotometer used in this study was Lambda 750 (Perkin Elmer, USA). The equipment is easy to operate, non- destructive to sample, gives quick and accurate results. It is a double beam spectrophotometer consisting of tungsten-halogen and deuterium (190-3300 nm) light sources, two sample holders (reference and test sample), a diffraction grating with double monochromator used to separate the different wavelengths of light, and a photomultiplier detector (R955).Figure 3.9 shows the schematic diagram of a double beam spectrophotometer, showing the path of rays with arrows [130].

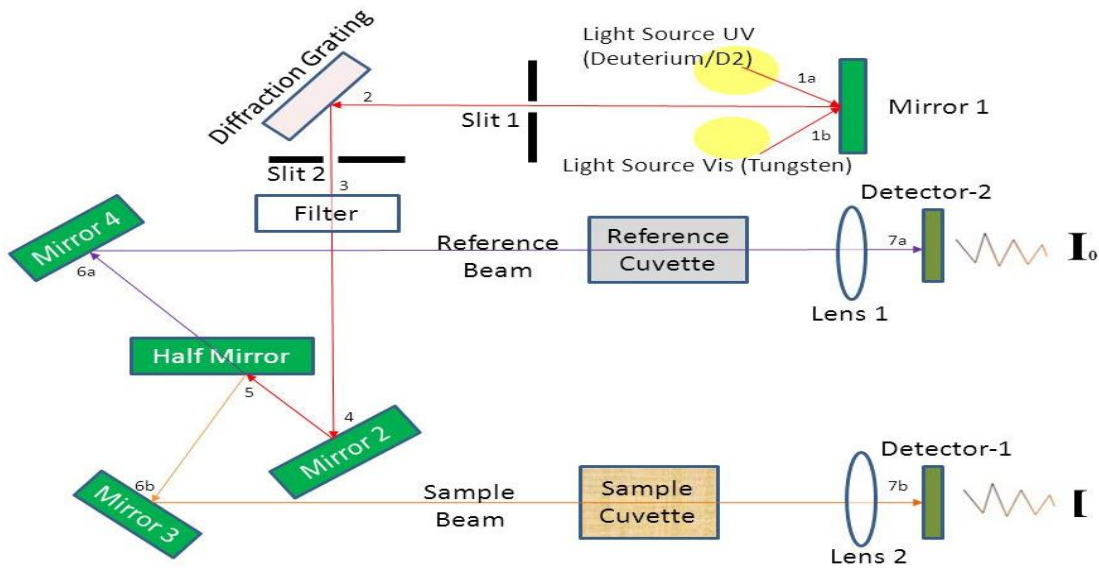


Figure 3.9: Schematic diagram of double beam Uv-Vis spectrophotometer [123].

The light is split into two beams before it reaches the sample, one beam for the reference sample and the other beam passes through the sample. The reference beam intensity was taken as 100% transmission (0 absorbance). The AGZO samples were analyzed on the visible range (wavelength range of 300 to 800 nm). With thin films, no sample preparation is required. The optical constants, refractive index n and extinction coefficient k of the films can be computed from transmittance, reflectance and absorbance data from the spectrophotometer.

The absorption coefficient (α) is independent of the intensity of light and related on the properties of materials as expressed in equation 2.4 discussed in optical properties of ZnO,

section 2.3. From equation 2.4, the optical band gap energy of films can be calculated from Tauc equation:

$$(ah\nu)^n = A (h\nu - E_g) \quad (3.5)$$

where $h\nu$, A and E_g are photon energy, relation constant and optical band gap, respectively. For direct band gap semiconductors like ZnO, $n = 2$, and $n = 0.5$ for indirect band gap semiconductors.

3.2.5 Electrical characterization

The common simple technique used for electrical characterization of thin films is the four point probe. This technique uses separate pairs of current carrying and voltage sensing electrodes to make more accurate measurements for low resistance values. The four springy tungsten wires are arranged in a line, equidistant from each other, usually 1 mm apart. A circuit diagram for this technique is illustrated in Figure 3.10 below.

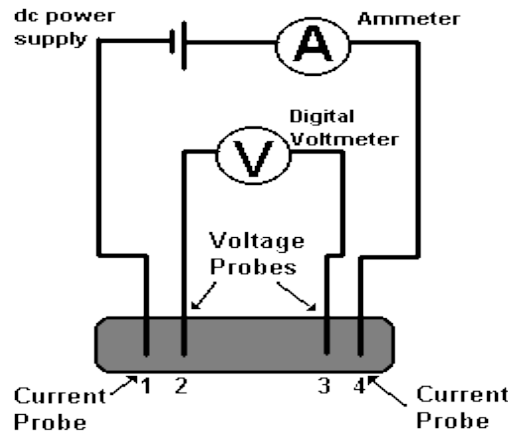


Figure 3.10: Circuit diagram for four point probe technique [131].

Surface resistivity of a material is independent of its physical dimensions. The Ohm's Law for circuit theory states that the resistance of a material is the applied voltage divided by the current drawn across the material across two electrodes, expressed as follows:

$$R = V / I \quad (3.6)$$

where R is the resistance (Ohms, Ω), v is voltage (Volts, V) and I is the current (amperes, A). The electrical resistance is proportional to the sample's length while resistivity is inversely proportional to the sample cross sectional area:

$$R = \rho l / A \quad (3.7)$$

Where ρ is the resistivity, A is the cross-sectional area, l is the length.

For thin film with thickness d , much bigger than the distance between the probes (1 mm), with measurements done far from the edge of the substrate, resistivity is given by:

$$\rho = \pi V d / I \ln 2 \quad (3.8)$$

which reduces to

$$\rho = 4.53 dV / I \quad (3.9)$$

The four point probe system used in this study comprised of two Keithley197A autoranging microvolt digital multimeters, for voltage and current, an EZGP-4303 power supply and a signatone table, where the substrate was held under the four probes of spring tungsten contacts.

3.3 Summary

Fabrication of aluminum and gallium co-doped ZnO thin films was carried out using chemical spray pyrolysis technique. The acetate salts of Zn, Al and Ga were used in preparation of precursor solutions, with mixture of ethanol and water as solvent. Thin film characterization was done using several techniques comprising of stylus profiler, field emission scanning electron microscopy, atomic force microscopy, X-ray diffraction, UV-Vis spectroscopy and four point probe.

Chapter 4 RESULTS ANALYSIS

This chapter reports and discusses co-doped AGZO thin films grown by chemical spray pyrolysis. The co-doping effects are discussed in relation to the morphological, optical and electrical properties of the thin films. The AGZO thin films were grown under same conditions (deposition temperature, pressure, annealing time etc.).

4.1 X-ray diffraction analysis

Figure 4.1 shows XRD patterns of AGZO films with doping concentrations of 0 to 6 at%. The diffractograms did not show other peaks that correspond to either Ga or Al or their complex oxides which suggests that the films do not have any phase segregation or secondary phase formation. The pattern for AGZO 0 at% shows only one prominent peak, while upon doping, more peaks were observed indicating polycrystalline lattice structures.

Strong peaks corresponding to (002) plane are observed on AGZO 0 to 2 at% films, thereafter the preferred orientation peak becomes the (101) plane above 2 at% doping. The (101) orientation is not common for doped ZnO films grown under similar conditions as in this study. The most common orientation for ZnO films is the (002). This plane has the densest atomic packing and minimum surface energy [132][133][134][45]. Chakrabarti et al [44] investigated substrate dependence of preferred orientation in sol-gel-derived zinc oxide films. They used soda-lime glass, quartz glass, Corning 7059 glass, p-type Si (100) and polycrystalline alumina substrates. The dominant orientation was the (002) orientation among all the substrates. Paul et al [135] undertook comparative study on opto-electrical properties of Al, Ga and In doped ZnO thin films. They used a polymer substrate, (polyetherimide) at deposition temperature of 250 °C and they recorded preferred orientation on (101) plane.

The absence of the (002) peak above doping concentration of 2at% can be attributed to that the dopant ions (Al and Ga) were inducing more strain in the ZnO lattice structure as the solubility limit of these ions was being exceeded. The maximum solubility limit of Al and Ga in ZnO have been studied to be around 2 at% [135]. Another factor contributing to this change in preferred plane orientation can be that the deposition temperature for this study was too lower and coupling with increasing concentration, atoms lack sufficient energy to move to the

kinetically favorable (002) plane[136] . Li et al [137] demonstrated that the (002) orientation present the fastest growth velocity, subsequent to that the wurtzite structure lacks inversion symmetry, hence an inherent asymmetry allows anisotropic growth along c-axis.

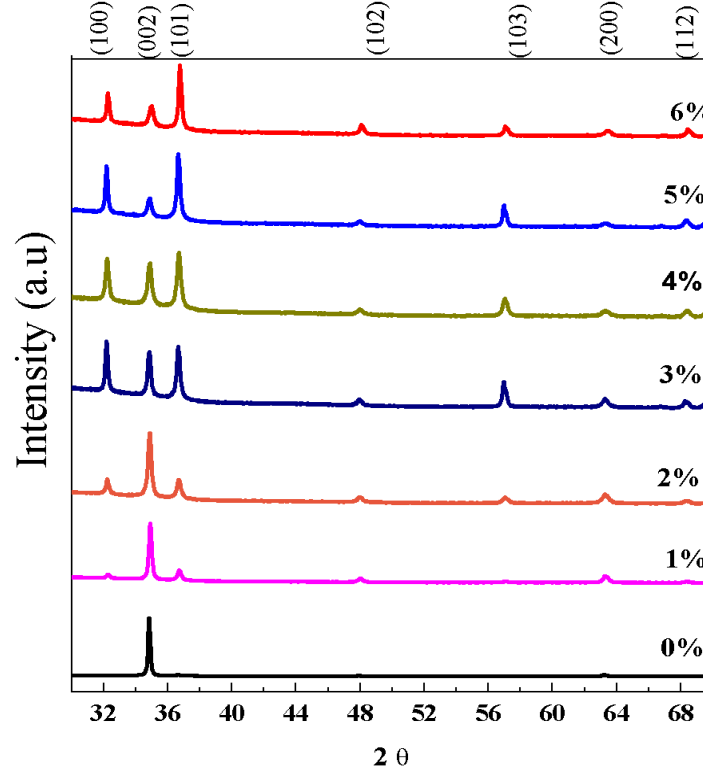


Figure 4.1: XRD patterns of undoped ZnO and AGZO films with different doping concentration of Al and Ga.

Figure 4.2 shows the diffractograms for (002) and (101) peaks. A clear peak shift towards the right of the diffraction line (reference line drawn) was observed at both (002) and (101) planes. This peak shift was also observed by Jeong et al. [138] and they attributed this shift of the (002) diffraction peak position to residual stress in the film, caused by the difference in ionic sizes between Zn^{2+} (0.074 nm) and Al^{3+} (0.054 nm). Based on the calculations presented in Table 4.1 on lattice strain (ϵ), the same effects are suspected. Co-doping ZnO with Al and Ga induced lattice strain on the films.

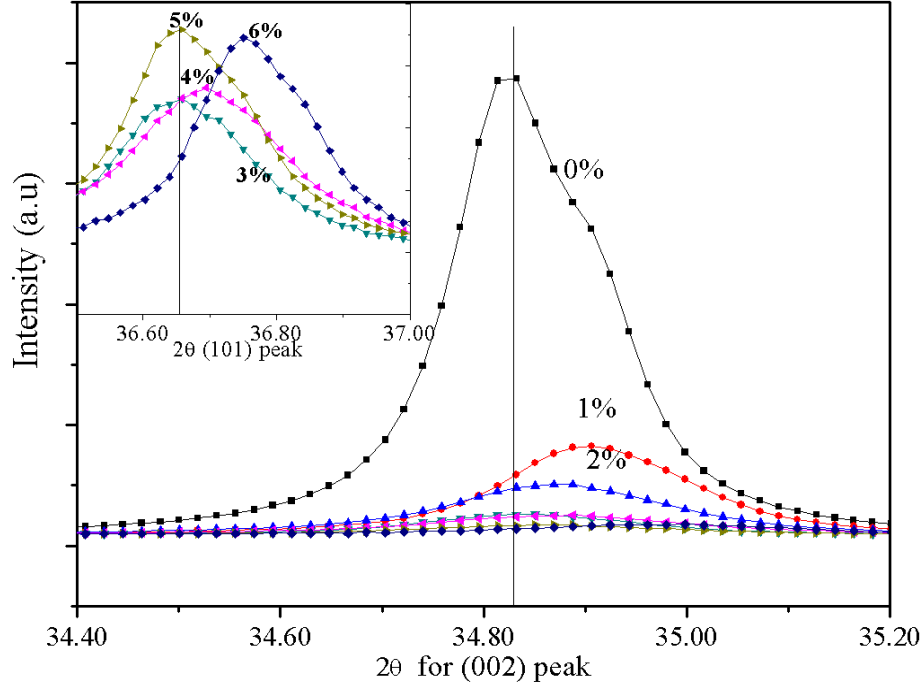


Figure 4.2: Diffractogram for (002) and (101) (insert).

Doping with Al/Ga did not produce a significant change in the lattice parameters since comparing with AGZO 0 at% films, the lattice parameters are approximately equal, with $a = 3.22 \text{ \AA}$ and $c = 5.20 \text{ \AA}$ as presented in Table 4.1. For the bulk ZnO the lattice parameters are, $a = b = 3.25 \text{ \AA}$ and $c = 5.21 \text{ \AA}$ (From Table 2.1). The overall effect of the lattice parameters is summed up by the calculated lattice constant, μ which shows presence of lattice strain and residual stress in the films. (Table 4.1).

Lattice strain (ϵ) [63] and the dislocation – density (δ) [139] were calculated using equations:

$$\epsilon = \frac{\beta}{4 \tan \theta} \quad (4.1)$$

$$\delta = \frac{1}{D^2} \quad (4.2)$$

where β is full width at half maximum (FWHM) in radians, and θ is Bragg's angle. Crystallite size, D_p was calculated using equation (4). The lattice parameters a and c were calculated using equation [63]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (4.3)$$

where d_{hkl} is the inter planar spacing obtained from Bragg's Law and h , k and l are the Miller indices denoting the plane.

Table 4.1: The inter-planar spacing (d), crystal size, lattice parameters, lattice constant (μ), dislocation density (δ), lattice strain (ϵ), film thickness (t) and Surface roughness (R_{rms}) of the AGZO thin films.

Al + Ga (at%)	crystal size (nm)	Lattice parameters		$\mu = \frac{c}{a}$	δ (10^{-4} nm $^{-2}$)	ϵ (10^{-2})	t (nm)	R_{rms} (nm)
		a (Å)	$b = c$ (Å)					
0	53.3727	3.2219	5.2000	1.6139	3.5135	13.7734	98	4.0823
1	47.3247	3.2200	5.2000	1.6149	4.4712	15.6127	120	3.2477
2	43.5735	3.2219	5.2000	1.6139	5.2728	18.4785	143	3.2011
3	39.9147	3.2200	5.2000	1.6149	6.2823	19.3613	138	2.9215
4	33.5023	3.2200	5.2000	1.6149	8.9156	21.9746	193	2.9152
5	32.2756	3.2190	5.1489	1.5995	9.6044	22.4644	208	1.1219
6	31.4128	3.2190	5.1489	1.5995	10.143	23.4151	213	1.1638

As doping concentration increases from 0 to 6 at%, the crystal size is decreased (Figure 4.3). This can be attributed to the positioning of doping atoms in the crystal structure of ZnO. At low doping concentrations below 1 at%, Al^{3+} (0.054 nm) and Ga^{3+} (0.062 nm) ions are likely to substitute the Zn^{2+} (0.074 nm) ions as their ionic radii are smaller than that of Zn at higher doping concentrations, this substitution of ions becomes limited due to solubility limit of the host material, ZnO. Hence the decrease of crystal size will eventually become constant as doping concentration is increased [19]. This trend of doping effects on crystallite size has been observed in several studies with different deposition methods [76][140][141][142]. Ohyama et al. [132] observed similar trend for Al-doped and Sn-doped ZnO thin films. Comparing the dislocation density between undoped and AGZO thin films, the small deviations suggests minimal distortions during doping. Larger crystallite size and smaller δ values indicate good crystallinity of AGZO films.

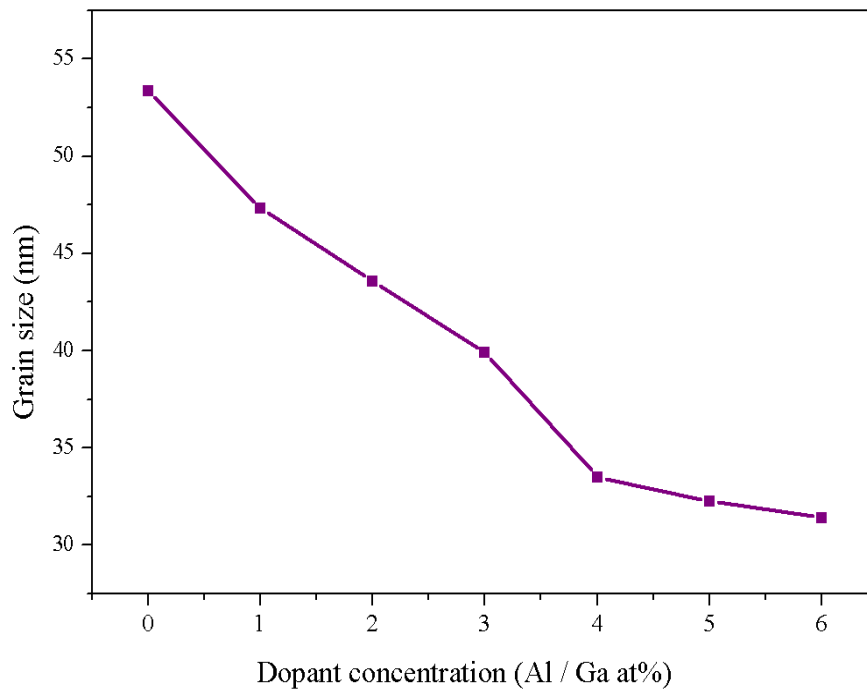


Figure 4.3: Effects of dopant concentration on grain size of AGZO films.

4.3 Morphological analysis

The topographical analysis of the thin films were investigated using two different techniques; namely atomic force microscopy and field emission scanning electron microscopy. The results are discussed in detail under the following subtopics;

4.3.1 AFM analysis

The root-mean-square surface roughness (R_{rms}) and the morphologies of the AGZO films measured by AFM are shown in Table 4.1 and Figure 4.4, respectively. Surface roughness decreases as doping concentration is increased. This trend is consistent with the decreasing crystal size upon increase in doping concentration. The Al and Ga ions improves the surface flatness and reduces the average grain size. This is clearly shown in the 2D and 3D micrograms presented in Figure 4.4 below. Furthermore, this is corroborated by the SEM analysis. The images in Figure 4.5 shows gradual decrease in crystallite size as doping concentration is increased, since there is increasing number of nucleation centers during incorporation of dopant ions into ZnO [143].

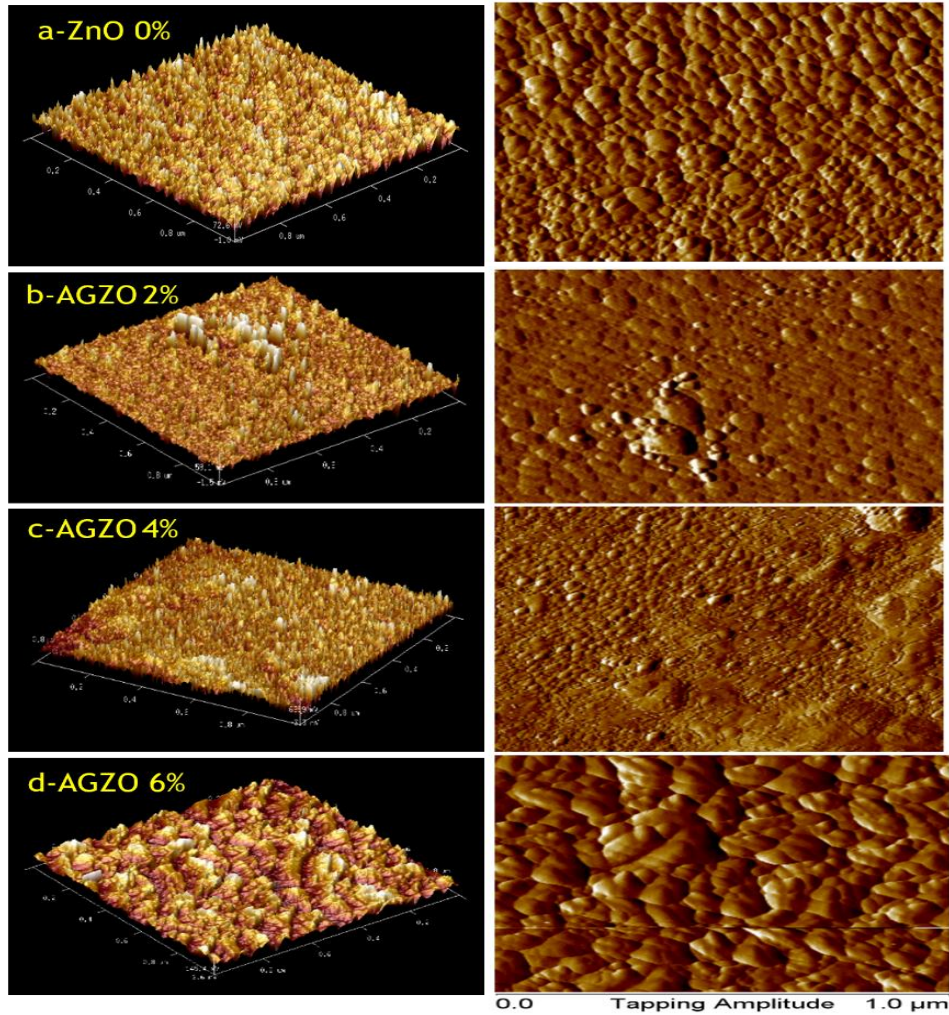
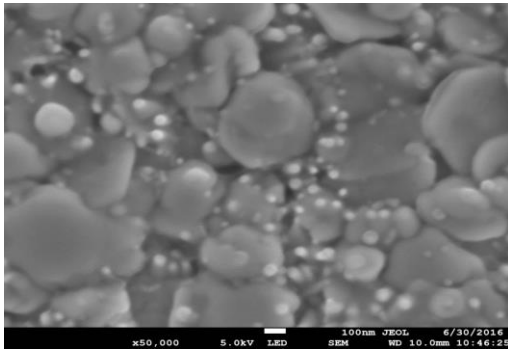


Figure 4.4: AFM micrograms of AGZO films at different doping concentrations.

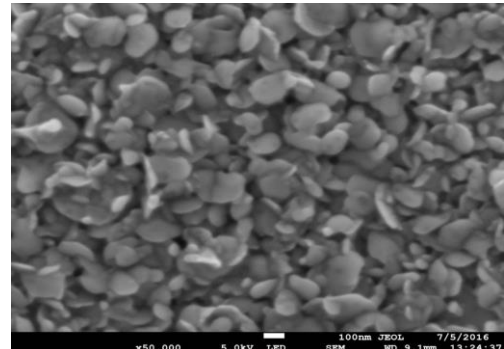
4.3.2 SEM analysis

Figure 4.5 shows SEM images taken at 15 kV at a magnification of X50 000. The images are arranged from (a) to (f) with respect to doping concentration increase; from 0 at% to 6 at%. There is clear indication of decrease in crystal size as doping is increased, which resonates well with the XRD data. The images show that undoped ZnO, AGZO 1 at% and AGZO 2 at% have well defined grains with clear boundaries, this are the (002) oriented planes. Images for the rest of the films show elongated and blurred overlapping boundaries which shows change in

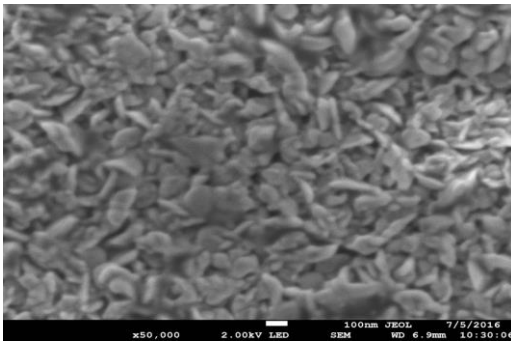
preferred orientation from (002) plane to (101) plane. This shows that dopant concentration has a great influence in morphology of thin films.



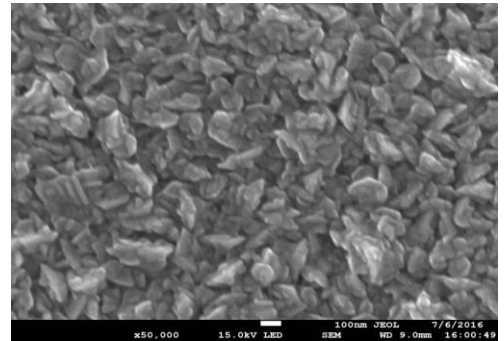
(a) AGZO 0 at%



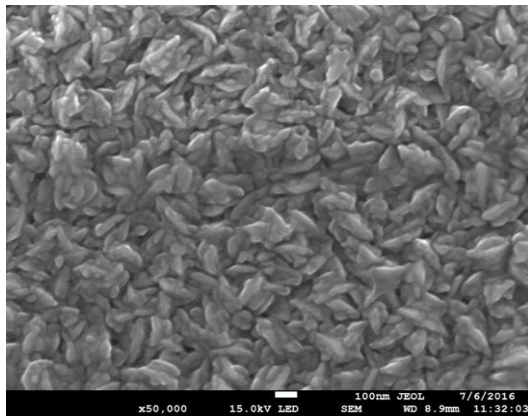
(b) AGZO 1 at%



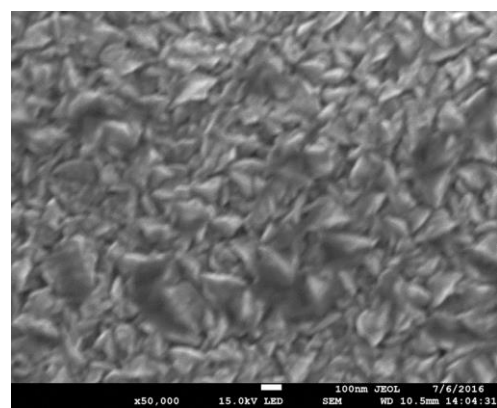
(c) AGZO 2 at%



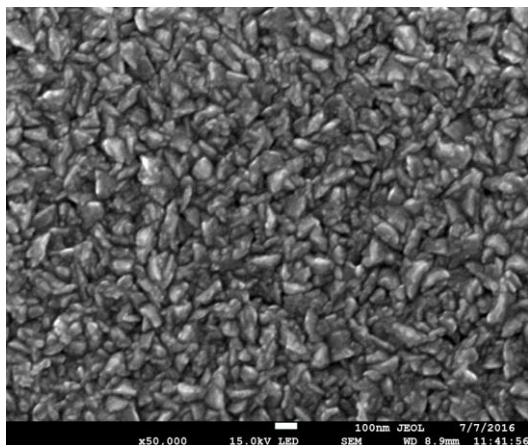
(d) AGZO 3 at%



(e) AGZO 4 at%



(f) AGZO 5 at%



(g) AGZO 6 at%

Figure 4.5: SEM images for AGZO thin films at X 50 000 magnification.

4.4 Optical analysis

The transmittance spectra for the AGZO films was studied in the visible region with wavelength range from 300 to 800 nm, as shown in Figure 4.6 below. The data indicates that the films are transparent in the visible region with an average transparency of 80 %. Doping clearly increased the optical transparency of the AGZO thin films. Number of interference fringes (wavelike region of the spectrum) increase with the doping concentration, as well as increasing film thickness. The values of film thickness were presented in Table 4.1. The AGZO 0 at% spectrum shows no significant fringes as it recorded the least film thickness of 98 nm.

The observed interference fringes result from decrease in refractive indices of films (shown in Figure 4.7) and variations in film thickness as doping concentration is increased. This can suggest that the films had low light scattering [41]. The transmittance peak in the UV region (295- 370 nm) just before the absorption edge which is common in GZO and AZO thin films is absent in the co-doped AGZO samples [23] and this can be attributed to that either of the dopants is showing dominance as a result of constant co-doping . All the films show absorption edge around 380 nm which is a common characteristic of ZnO [23]. As dopant concentration is increasing, the absorption edge shifts to shorter wavelength (shown with an arrow in Figure 4.7), and this shift can be attributed to the decrease in the particle size. Similar observations were inferred by Mahdhi et al. [42] and Rao et al. [34] in their respective studies.

The transmittance data for the thin films was used to extract the optical constants n and k by spectra simulation using a commercially available software, CODE (SCOUT 2) [46][47], over wavelength range of 300 to 800 nm. With the thickness data from surface profiler, the simulated results are presented in Figure 4.7 and 4.8. The extinction coefficient (k), represent the photon energy loses and is related to the crystalline quality and surface morphology of the films. Extinction coefficient decreased with wavelength, varying from 0.55 to 0.02. Co-doping lead to lower extinction coefficient resulting in little optical loss in the visible region [48].

In Figure 4.8 , the variation of refractive index n with wavelength (λ), ranges from 1.6 to 2.2. For AGZO 0 to 1 at% doping concentration, there is increase in the $n(\lambda)$ value but after that the refractive indices decreases with increasing doping concentrations. This inverse relationship of doping concentration with refractive index is attributed to the fact that as doping

concentration increases, the crystallite size decreases and light transverse easily through smaller crystals, hence giving lower refractive indices.

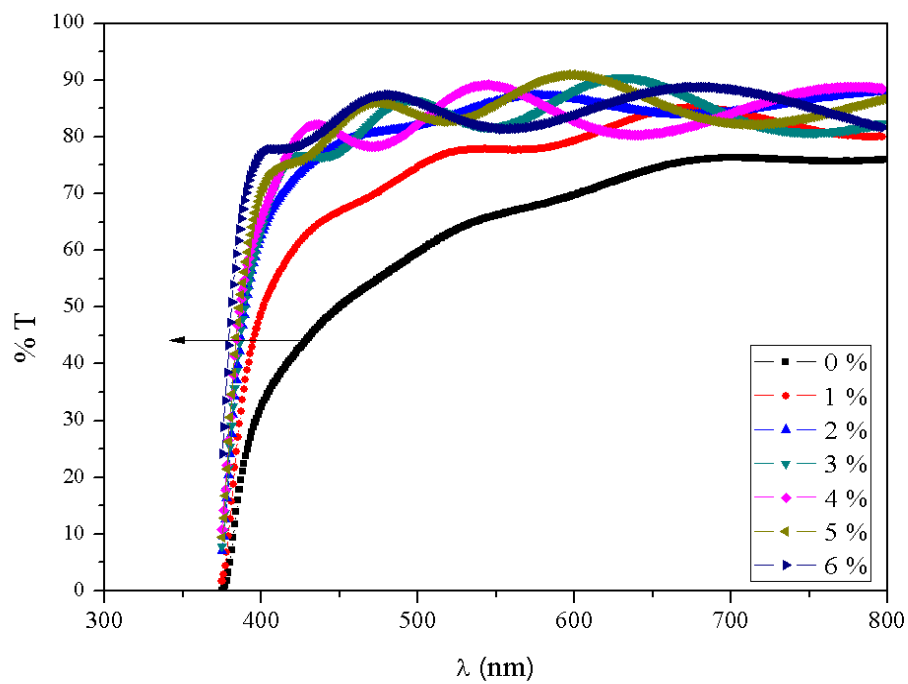


Figure 4.6: Transmittance spectra for AGZO thin films with different doping concentrations.

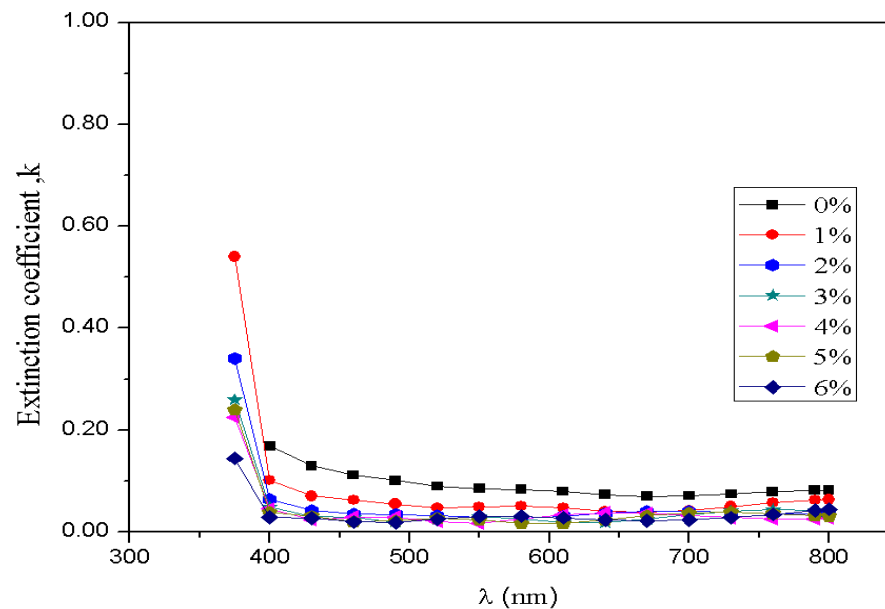


Figure 4.7: Variation of extinction coefficient $k(\lambda)$ with wavelength λ for AGZO (0 - 6 at %) films.

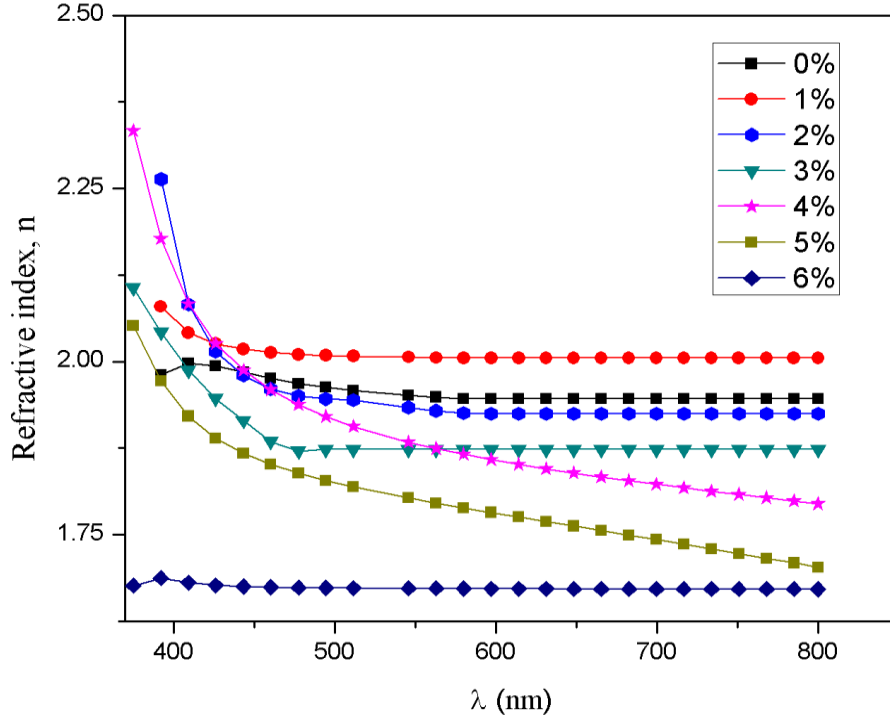


Figure 4.8: Variation of refractive index $n(\lambda)$, with wavelength λ , for AGZO (0 - 6 at%) films.

The Tauc equation (equation 3.5) [36] was used to calculate the optical band gap energy of the films and the absorption coefficient α derived from transmittance, T using the Beer-Lambert law [44]:

$$\alpha = \frac{1}{t} \ln \frac{1}{T} \quad (4.4)$$

where t is the film thickness.

The Tauc plot of $(ah\nu)^2$ versus $h\nu$ and extrapolation of linear part to the $h\nu$ axis yields the band gap value as shown in Figure 4.9. Values of band gap energy obtained from the Tauc plot are plotted against varying doping concentrations (insert in Figure 4.9). Upon doping, the band gap increased from 3.10 eV to 3.29 eV, as illustrated in Table 4.2. Generally increasing dopant concentration increases the band gap which is observed in the AGZO samples. This change in band gap can be explained by the Burstein-Moss shift; doping increases electrons density in the conduction band and more energy is required to excite electrons from the valence band to

conduction band [43]. The band gap of the material is related to the excitation of the electrons from the top of the valence band to the bottom of the conduction band. This results in elevation of the Fermi level into the conduction band of the degenerate semiconductor due to the increase in the carrier density, which results in the band gap broadening [45].

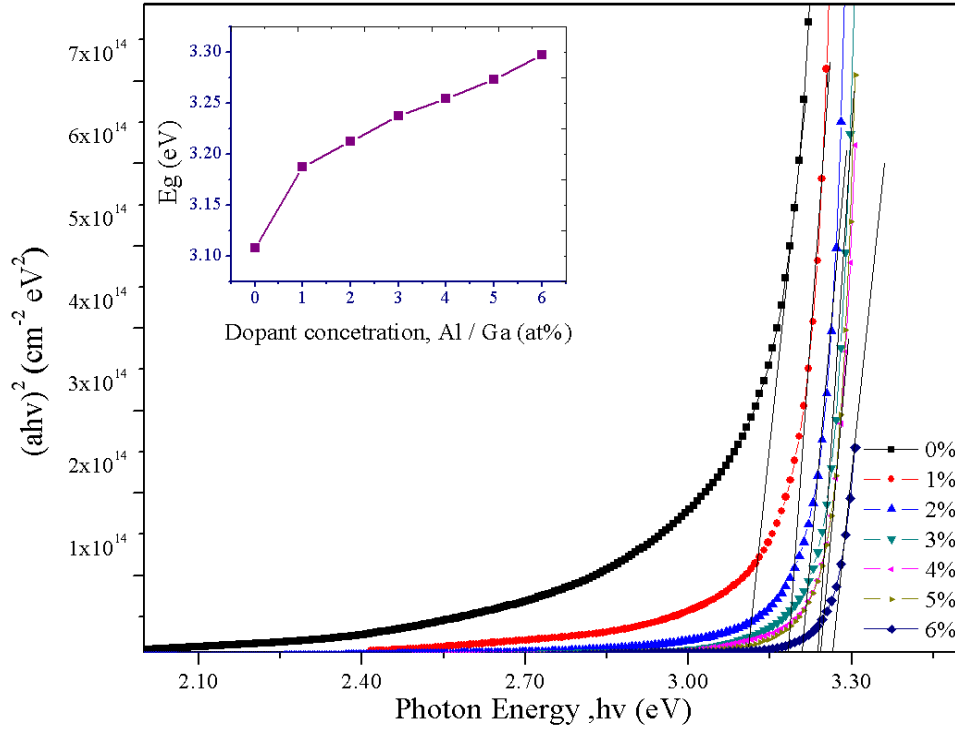


Figure 4.9: Variation of $(ahv)^2$ versus hv of the AGZO thin films (Tauc Plot). Insert shows band gap as a function of Al and Ga dopant concentration.

Absorption coefficient at photon energy below the band gap (tail absorption, < 3.0 eV) depends exponentially on the photon energy. This absorption region can be used to characterize the structural properties of materials as it is sensitive to the width of the defect states of the material or low crystalline materials. The region is often described by the Urbach empirical rule which is given by the following equation:

$$a = a_0 \exp\left(\frac{hv}{E_{Urb}}\right) \text{ for } hv < E_g \quad (4.5)$$

where a_0 is a constant and E_{Urb} is the Urbach energy. Taking the logarithm of the two sides of the above equation, a straight line equation is deduced as follows

$$\ln a = \ln a_0 + \left(\frac{h\nu}{E_{Urb}} \right) \quad (4.6)$$

Hence the band tail energy (E_{Urb}) can be obtained from the gradient after plotting $\ln a$ against photon energy ($h\nu$). The calculated E_{Urb} values are presented in Table 4.2 were obtained from the gradients of the linear plots shown in Figure 4.10 (A line of best fit on the first ten points was used). The graphs shows slight change in the slope as doping increases, this is shown from the calculated values of the steepness parameter, β which is defined in the following equation:

$$\beta = \frac{K_B T}{E_{Urb}} \quad (4.8)$$

where K_B is the Boltzman constant and T is the temperature (300 K). The steepness parameter characterizes the steepness of the straight line near the absorption edge owing to the electron/phonon or exciton/phonon interaction [144]. The results of AGZO films steepness parameters are given in Table 4.2. The steepness parameters increases with the decreasing Urbach energy. This can be explained as that the dopant elements altered the width of the localized state in the optical band.

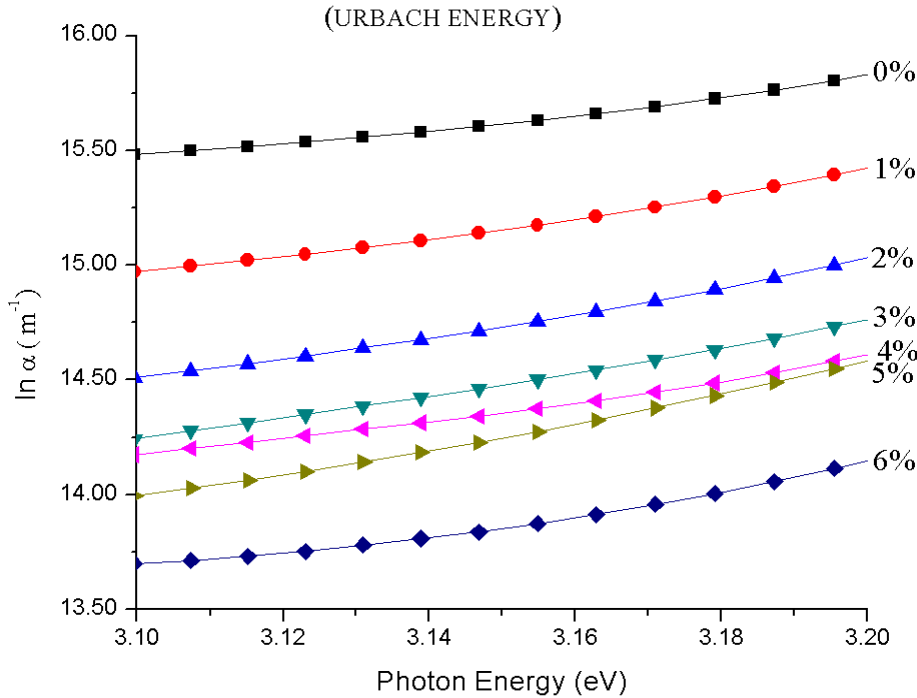


Figure 4.10: $\ln (\alpha)$ versus photon energy ($h\nu$) plots of the AGZO thin films.

Table 4.2: Values of optical bandgap, resistivity, figure of merit, Urbach energy and steepness parameter for AGZO films.

Sample	E_g (eV)	ρ ($\Omega.cm$) $\times 10^{-3}$	F_M (Ω^{-1}) $\times 10^{-5}$	E_{Urb} (meV)	Steepness parameter (β) $\times 10^{-3}$
AGZO 0 at%	3.1074	1.0523	0.0542	1544	1.6744
AGZO 1at%	3.1873	0.0116	0.0957	1485	1.7409
AGZO 2 at%	3.2120	0.0016	2.0103	1437	1.7990
AGZO 3 at%	3.2372	0.0118	1.0284	1422	1.8180
AGZO 4 at%	3.2542	0.0182	1.3672	1417	1.8244
AGZO 5 at%	3.2735	0.0212	1.4713	1396	1.8519
AGZO 6 at%	3.2975	0.0300	1.3937	1368	1.8898

4.5 Electrical analysis

The electrical properties of doped AGZO films drastically improved in comparison with undoped thin films. the resistivity of AGZO films are shown in Figure 4.11. The four point probe measurements of current (I) and resistance (R) were used to calculate resistivity (ρ), using the equations (3.7) and (3.8) [49]:

$$\rho = \left(\frac{\pi}{\ln 2} \right) \cdot R_s d$$

Table 4.2 shows the calculated resistivity values for the AGZO films. Increasing dopant concentration results in decreasing resistivity and the minimum value obtained at Al + Ga = 2 at%. Pure ZnO films exhibit high electrical resistance as they have contributing intrinsic defects such as interstitial zinc atoms and oxygen vacancies. The valance shell of ZnO has Zn (3d) and O (2p) orbitals. The conduction band includes Zn (4s) and Zn (4p) atomic orbitals [50]. The trivalent donor dopants (Al and Ga) increases electron density in the valence bands. The increased electrons leads to formation of new energy levels in the conduction band. Therefore,

excess electrons of Al and Ga are placed in the reconstructed conduction band and result in electrical conductivity [51].

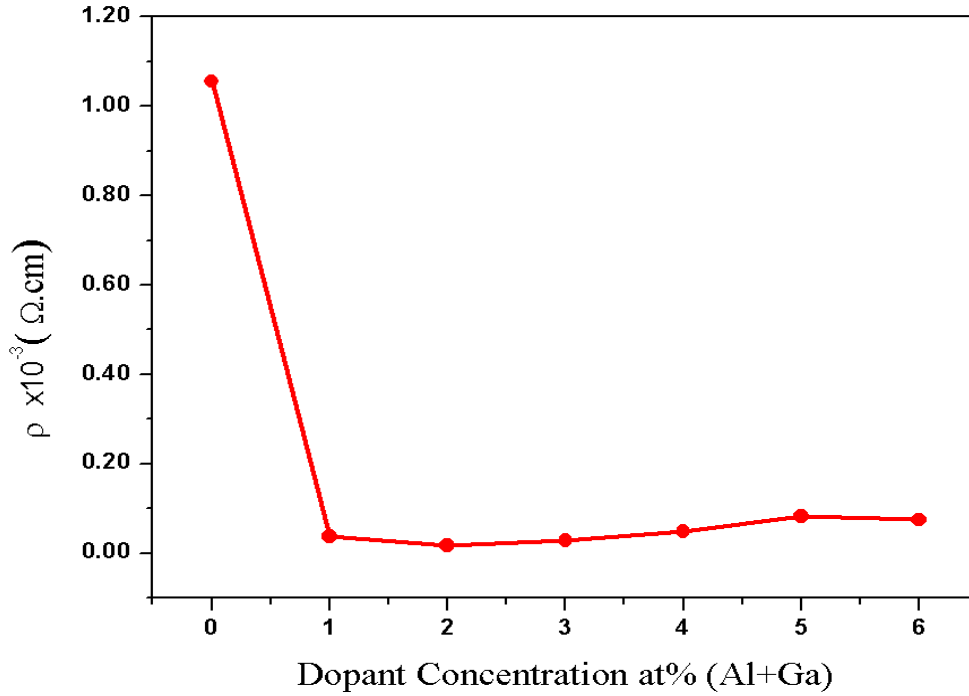


Figure 4.11: Resistivity of AGZO films with varying dopant concentrations.

Comparing the oxide bond lengths of Al (1.92 Å) and Ga (1.82 Å), Ga will have higher Madelung constant compared to that of Al and this may give edge for Ga to be more substituted over Al in AGZO samples [52]. The chance of this process is higher in high total doping contents, where there are lower substitutional positions in those samples [19]. Substitution of Ga with Al in AGZO at 2 at% is more effective, giving rise to more stable AGZO and denser electron concentration, which finally decreases the electrical resistivity.

As doping concentration increases from > 3 at%, the resistivity increases. This can be understood from the fact that at higher doping concentrations, lattice strain increases the efficiency of scattering mechanism, being phonon scattering and ionized impurity scattering, which in turn increases resistivity. This is consistent with the structural studies as the lattice strain of the AGZO films is found to be increasing (shown in Table 4.1) with increase in doping concentration. These inferences are consistent with recent studies of Muchuweni et al. [53], where they recorded lowest resistivity at 1 at% GZO films. Slight increments in resistivity at

higher doping levels, 3-6 at% are observed. The increase in resistivity with higher doping concentrations is due to scattering mechanism of electron-electron interactions [54].

In order to rate performance and degree of quality of the thin films, the ratio of electrical resistivity (ρ) to absorption coefficient (α) was calculated. This ratio is termed Figure of merit (F_M). The calculated values for F_M are presented in Table 4.2 and the equation below was used:

$$F_M = \frac{1}{\alpha\rho} \quad (4.9)$$

The larger the value of F_M the better the performance of a TCO thin film. From Table 4.2, a larger F_M value was recorded at 2 at% doping ratio. AGZO 2 at% thin film recorded lowest resistivity, implicating that it has highest conductivity hence it has best performance relative to other thin films. The lowest value of F_M was obtained at AGZO 0 at%, proving the fact that undoped ZnO has poor conductivity hence it has lowest performance as a TCO. The electrical characterization results conforms to both morphological and optical data which showed that the optimum doping ratio for AGZO is at 2 at%. This optimal doping ratio was recorded by R. Ebrahimifard et.al [19], using sol-gel technique.

4.6 Summary

The effects of co-doping concentration of aluminum and gallium on ZnO thin films were analyzed under the subtopics; morphological, optical and electrical properties. Film thickness of range 100-200 nm was recorded. The morphological studies revealed transition in preferred plane orientation of thin film crystals from (002) plane (at doping ratio of ≤ 2 at%) to (101) plane (at doping ratio of ≥ 3 at%). The AFM and SEM images complemented this mentioned transition in preferred plane orientation. Thin films with doping concentration of 2 at% had suitable properties for applications as transparent electrodes in solar cells.

Chapter 5

CONCLUSION

In addition to the intrinsic properties of ZnO, the specific extrinsic properties can be enhanced to improve performance of the ZnO thin films. Deposition temperature, cost and environmental impact are other factors that can influence the choice of transparent conducting oxide for any particular application. This thesis showed the possibility of fabrication of ZnO thin films via simple and cost effective method with probable application in solar cells. Transparent conducting thin films of aluminum and gallium co-doped ZnO were successfully prepared by spray pyrolysis at 230 °C. XRD results showed that the ZnO thin films have a hexagonal wurtzite structure. Doped samples were polycrystalline with well-defined sharp peaks. Preferential orientation was observed at (002) plane for doping concentrations of 0 – 2 at% and subsequently shifted to (101) plane at dopant concentrations ≥ 3 at% due to favorable lower deposition energies and increased electron concentration. All doped films recorded average transmittance of 80 %. Co-doping increased band gap from 3.10 – 3.29 eV which can be attributed to the Burstein-Moss effect. The optical constants, extinction coefficient and refractive index agree well with the structural properties of the thin films. Co-doping improved optical transparency of thin films leading to lower values of extinction coefficient. Optimal dopant concentration of 2 at% (1at% Al + 1at% Ga) showed lower resistivity of $1.621 \times 10^{-4} \Omega\text{.cm}$, with Figure of merit of 2.0103×10^{-5} .

To broaden understanding of the AGZO films, future studies will focus on the surface composition, work function and the electrochemical properties of these films. The surface chemistry and structure of TCOs have been shown to affect key parameters that impact the performance of contacts such as work function. Also exposure of ZnO to different gases has been demonstrated to change the surface conductivity and work function over time due to charge transfer and band-bending at the interfacial sites. Therefore, detailed characterization of the surface both before and after various surface pre-treatment can provide insight into the effects of AGZO co-doping in the formation of organic/oxide heterojunctions.

Chapter 6

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