

# **Growth of Transparent, Conductive and Hydrophobic ZnO:Al Thin Films**

A Thesis submitted in partial fulfilment of the requirements for  
the award of the degree of

**Master of Science**

**in**

**Physics**

**Submitted by**

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**July, 2019**

## CERTIFICATE

This is to certify that the report entitled “**Growth of Transparent, Conducting and Hydrophobic ZnO: Al Thin Films**”, submitted by **Harpreet Kaur, Roll No. 301704010**, in partial fulfilment of requirements for the award of degree M.Sc. in Physics from School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala is a record of candidate own work carried out by her under my supervision and guidance. The work reported here has not been submitted, either in part or in full, for the award of any other degree in other institute or university.



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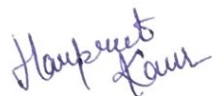
**Dedicated**

**To**

**My Family**

## DECLARATION

I hereby declare that the thesis report entitled "**Growth of Transparent, Conducting and Hydrophobic ZnO: Al Thin Films**" submitted by me in partial fulfilment of the requirements for the award of degree of **M.Sc. in Physics** from **School Of Physics And Materials Science** is a record of bonofide thesis report carried out by me under the supervision of **Dr. Bhaskar Chandra Mohanty**, Associate Professor, School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala. I further declare that work embodied in this report has not been and will not be submitted, either in part or in full, in any other institute or university for award of master and science or any other degree.



Harpreet Kaur

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## ABSTRACT

The increased demands of the cost effective solar cells have promoted the improvement of the materials used for its construction. Thin films of transparent conducting oxides (TCOs) form a key component of thin film solar cells and have been widely studied. Due to its high transparency and high electrical conductivity, aluminium doped zinc oxide (ZnO:Al) thin films have been routinely used as window layer in thin film solar cells. In this work, ZnO:Al thin films were deposited on glass substrates by RF magnetron sputtering at room temperature. ZnO:Al target with 2 wt% of Al and 98 wt% of ZnO was used as sputter source. The sputtering power was varied as 50, 100, 150, 200, 250 W for the deposition time 75, 60, 40, 30, 20 minutes respectively, in order to study effect of power on the structural, optical and electrical properties. The properties of the film were studied by XRD, UV-Visible spectrophotometer, field emission scanning electron microscope, Hall Effect measurements. Wettability is an important surface property which is often associated with self-cleaning character of the films, was studied from contact angle measurements. It was observed that irrespective of the deposition power, all ZnO:Al films showed very high crystallographic orientation along c-axis of wurtzite structure. All films showed very high visible transmittance (> 80%) and the lowest resistivity was found to be  $1.52 \times 10^{-3} \Omega \text{ cm}$ . More importantly, all the films were hydrophobic in nature with an average contact angle  $\sim 91.96^\circ$ .

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# Chapter 1

## Introduction

### 1.1 Zinc Oxide Thin Films

Zinc Oxide (ZnO) is an n-type semiconductor oxide, which crystallizes in the hexagonal wurtzite structure. It has a wide optical band gap ( $\sim 3.37$  eV) which provides it high transparency over the visible range. However, ZnO is found to have very high electrical resistivity, which can be reduced to the order of  $\sim 10^{-4}$   $\Omega$  cm by doping it with group III elements like aluminium (Al), boron (B) or gallium (Ga) [1]. Among all these impurity doped ZnO films, aluminium doped zinc oxide (ZnO:Al) films have been widely studied for various applications due to its low resistivity and high visible transmittance [2]. Furthermore, due to its low cost, non-toxicity, high chemical stability, abundance in nature, it has emerged as a promising transparent conducting oxide (TCO) material [2-4].

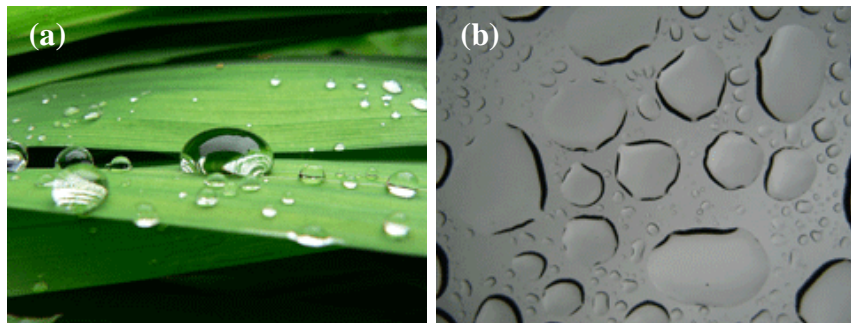
The TCO thin films have acquired considerable interest because they are the key element in a number of optoelectronic applications. Earlier indium tin oxide (ITO) was most commonly used TCO, but there were issues related to its toxicity, availability and cost [2, 5]. Due to a unique blend of optical and electrical properties, ZnO:Al thin films finds applications in numerous optoelectronic devices such as window layers of solar cells, organic light emitting diodes (OLED's), and flat panel displays [2, 3].

### 1.2 ZnO:Al thin films as window layer for solar cells

Solar cells are the photovoltaic devices that convert the solar energy into the electrical energy. A typical inorganic thin film based solar cell is made up of several layers such as topmost window layer, buffer layer, and the absorber layer. The efficiency of the solar cell is affected by number of parameters such as amount of incident light, dust or other impurities on cell surface, etc., besides the inherent cell design and properties of the absorber layer.

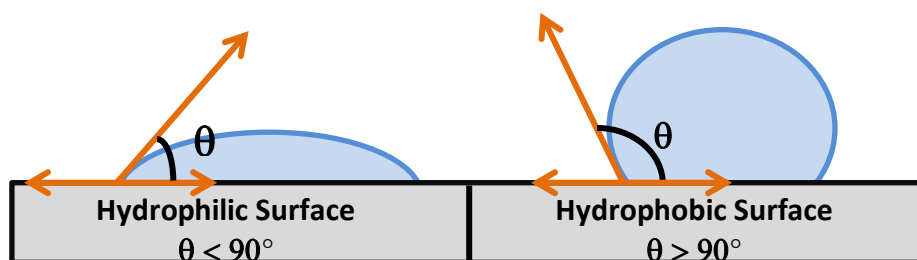
For high efficient solar energy harvesting, the amount of light entering the absorber layer should be maximum. This suggests that there should be minimum absorption of incident light by the window layer. Therefore, the window layer of solar cells is often made from transparent metal oxides allowing large amount of light to enter the absorber layer, and thus increasing its efficiency. Self-cleaning surfaces of the window layers are another important factor which helps in increasing the efficiency of the solar cell. Wettability is a property that depends on the surface energy and roughness, and helps in the cleaning of the surface [6]. It

is determined by the water contact angle ( $\theta$ ) which is defined as the angle between solid-liquid interface and liquid-vapour interface. A surface that provides non-wetting characteristics with water contact angle higher than  $90^\circ$  is called hydrophobic surface, for example: lotus leaf, as shown in **Figure 1.1(a)**. A surface that attracts water and has contact angle less than  $90^\circ$  is called hydrophilic surface, for example: glass, as shown in **Figure 1.1(b)**.



**Figure 1.1:** (a) Lotus leaf (hydrophobic surface), (b) Glass (hydrophilic surface) [7].

Both of these surfaces exhibit self-cleaning property through the nature of interaction of water on the surface. The hydrophobic surface exhibits self-cleaning property by forming round shape droplets of water that carries away the dirt. On the other hand, sheeting of water takes place on the hydrophilic surface, as shown in **Figure 1.2** [4].



**Figure 1.2:** Image shows hydrophilic and hydrophobic surface.

ZnO:Al as an important oxide semiconductor has attained considerable attention as promising material for window layer of thin film solar cell due to its unique properties such as wide band gap, low electrical resistivity along with the ability of self-cleaning.

### 1.3 Literature Review

In literature, one can find voluminous work on various characterisation of ZnO:Al thin films grown by a variety of techniques. The properties, especially the electrical and optical ones are strongly dependent on the processing of the films. In the followings, a brief review is presented on the growth, wettability, structural and optical properties of ZnO:Al thin films.

Patra et al. synthesized ZnO thin films by the sol gel method and studied the hydrophobic properties by contact angle measurement [4]. It was revealed that the films were highly transmitting and maximum hydrophobicity was found for the film with contact angle of  $114^{\circ} \pm 3^{\circ}$ .

Li et al. fabricated ZnO:Al thin films by two step layer process using atomic layer deposition technique and studied its surface properties [6]. The film was grown on ZnO:Al seed layer along (100) plane. The contact angle for ZnO:Al ALD was found to be  $110 \pm 4^{\circ}$  and for hydrothermally grown film was  $170 \pm 4^{\circ}$ .

Shinde et al. has grown ZnO thin films on glass substrates using chemical bath deposition method (CBD) [8]. They studied the change in structural, optical and electrical properties of the ZnO films, after giving the heat treatment at 623 K for 2h in air. After the heat treatment, structural properties showed elongation along highly preferred c-direction, and the band gap decreased from 3.7 to 3.2 eV. The resistivity was found to be of the order of  $10^3 \Omega \text{ cm}$  for annealed film which confirmed the semiconducting nature of the film. Wettability test revealed the contact angle of  $72.28 \pm 1.5^{\circ}$  confirming the hydrophilic nature of the film.

Papadopoulou et al. studied the changes in the wetting states of the ZnO thin films, deposited on silicon (Si) substrates by pulsed laser deposition [9]. It was found that the surfaces of the thin films were photosensitive. The wetting behaviour was fully reversible from hydrophilic to hydrophobic state, studied as a function of time, through alteration of UV illumination and dark storage.

Choa et al. studied the effect of Al doping concentration and substrate temperature on the surface wetting properties of the ZnO:Al thin films prepared by radio-frequency magnetron sputtering [10]. It was found that resistivity was the lowest for the 2% aluminium doping concentration and film surface may either be hydrophilic or hydrophobic depending on the growth temperature. It suggested that 2% Al doping is critical concentration to determine changes in electrical as well as surface properties.

Tarwal et al. deposited ZnO thin films on the glass substrates by spray pyrolysis technique (SPT) at 723 K and studied its properties by varying the solution concentration from 0.1 to 0.4 M [11]. The films were found to have c-axis preferred growth orientation, high transmittance of about 85%, 3.25 eV energy band gap and hydrophobic in nature.

Kim et al. fabricated hydrophobic ZnO:Al thin films by optimising the Al concentration and deposition time [12]. It was revealed that as the doping level increased, the resistance decreased from 305.81 to 32.40  $\Omega$ . Deposition time of 90 min and doping concentration of 4 mM was optimum for the growth of ZnO:Al nanorods based window layer.

Patel et al. have grown nanostructured ZnO thin films on glass substrates by RF magnetron sputtering [13]. The structural, optical and wetting properties of the ZnO films were studied by depositing two sets of films; one by varying sputtering power and keeping substrate temperature constant at 300 °C, other by varying substrate temperature and keeping power constant at 90 W. The contact angle measurements were done using the two different liquids: - ethylene glycol and water. Highest contact angle was 97.6° for water and 75.6° for ethylene glycol, found for the film deposited at 150 W. It was revealed that as substrate temperature was increased from 200 °C to 600 °C, the value of contact angle increased up to 99.2 °C and 79.1 °C for water and ethylene glycol respectively.

Kim et al. synthesized ZnO:Al thin films at room temperature by pulsed laser deposition on three different substrates: - fused quartz (FQ), polyethylene terephthalate (PET), polyethersulfon (PES) [14]. The ZnO:Al films preferred c axis orientation and were optically transparent (~ 90%). The resistivity of the films was of the order of  $10^{-4}$   $\Omega$  cm for PET and PES substrates. Changes in the polymer surfaces were observed when the plasma treated thin films exhibited decrease in the contact angle after exposing them to the plasma.

Nakajima et al. prepared self-cleaning, transparent and superhydrophobic boehmite (AlOOH) thin films coated with TiO<sub>2</sub> of by spin coating at 1500 rpm [15]. The surface and optical properties were studied by preparing six different boehmite films with varying TiO<sub>2</sub> concentration. The contact angle of the film with 2 wt% of TiO<sub>2</sub> was 140°. The film shows degradation from the hydrophobic behaviour as the concentration of TiO<sub>2</sub> is increased beyond 55 wt%.

Huang et al. coated the carbon nanotubes (CNTs) with ZnO thin films by cathodic vacuum arc technique at working pressure of  $4.2 \times 10^{-5}$  Torr [16]. Wettability properties were studied by the measuring of contact angle using a 0.5  $\mu$ l drop and the surface was found to be

superhydrophobic as the drop rolled off from the surface. The wetting properties were found to be reversible under dark storage and UV irradiation.

Feng et al. deposited ZnO nanorods onto the glass wafers by sol-gel method and studied the reversibility of the wetting states of ZnO films guided by variation of dark storage and UV illumination [17]. It was revealed that the wettability state changes from superhydrophobic to super-hydrophilic upon UV irradiation and the same was reversible when the ZnO film was kept in dark storage.

Fang et al. synthesized ZnO: Al nanorod films onto SiO<sub>2</sub> substrates with precoated layer of ZnO [18]. The synthesis involved two processes: - first the deposition of the ZnO seed layer by RF magnetron sputtering, secondly the deposition of ZnO: Al on the ZnO seed layer by chemical solution method. It was revealed that the ZnO: Al films were grown along the c-axis preferring (002) plane. The contact angle was measured using deionised water and increased from 133.4° to 137.4° as the doping concentration of aluminium (Al) increased from 0% to 5 %.

Xiong et al. deposited ZnO:Al films on the glass substrates by pulsed DC sputtering with 2 kW of DC power at 200 °C, followed by the etching of the sputtered films to form the textured surface [19]. Large deflection was found for the peak along (002) plane indicating the c- axis orientation of the thin films. The resistivity and carrier concentration were found to be  $8.32 \times 10^{-4} \Omega \text{ cm}$  and  $6.64 \times 10^{20} \text{ cm}^{-3}$ , respectively. The contact angle was found to be 79° for as-deposited film, 94°, 103° and 86° for films etched for 60, 90, 120 s respectively. It was revealed that upon etching the films change their behaviour from hydrophobic to hydrophilic due to the textured surfaces.

#### **1.4 Motivation and objective**

The brief literature presented above shows that although many deposition techniques have been successfully employed to prepare the ZnO:Al thin films, in each case the deposition parameters strongly influence the properties, especially the wettability. Considering that sputter deposition has been recognised as an attractive technique for preparing films on large area substrates with superior control on process parameters, in this work, it was attempted to prepare the ZnO:Al thin films by RF magnetron sputtering and to study the effect of RF power on various properties of the films.

## Chapter 2

### Experimental Techniques

This chapter presents a brief description of the experimental techniques used for the deposition of the thin films and their characterization.

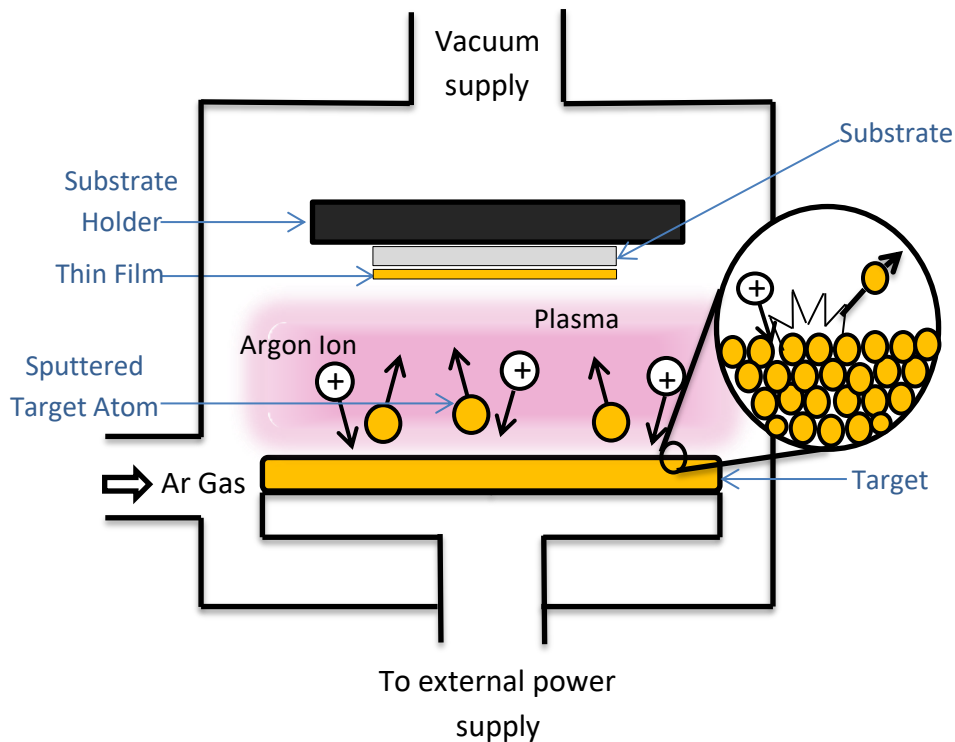
#### 2.1 Deposition of thin films by sputtering

Sputtering is a physical vapour deposition technique to deposit thin films. In this technique, the surface of material to be deposited (known as target) is bombarded with high energy positive ions. The particles are ejected by the mechanism of momentum exchange between the surface atoms and energetic particles. The deposition takes place by the condensation of the ejected species onto the substrate. The deposition process is affected by a number of parameters which includes sputter power, deposition time, substrate temperature, working pressure, etc.

Sputtering process is carried out in a high vacuum chamber, which is pumped using a combination of rotary and turbo molecular pump. The target is connected to the negative potential (cathode). The substrate is positioned above the target in the substrate holder and is maintained at ground potential. An inert gas mostly argon (Ar) is introduced into the chamber after it reaches to the base pressure of the order  $10^{-6}$  mbar. The inert gas is ionized due to the high voltage supply, which exhibits dense plasma in the chamber, maintained throughout the deposition process. The inert gas ions make a series of collisions with surface of the target and dislodge the atoms. The ejected atoms are made to condense on the substrate to form a film. The sputter yield (number of atoms/ions ejected from the target per incident ion) depends on the binding energy, characteristics of incident ion, target material composition and the sputtering power. Excellent adhesion of the film on the substrate is acquired from sputtering due to the higher kinetic energy of the sputtered particle. Magnetron sputtering deposition utilises magnetron sources behind the target to confine the electrons from the plasma close to the surface of the target, leading to high density plasma, increased deposition rates.

Sputtering technique exhibits several advantages over other vacuum coating techniques, for example, high deposition rate, high purity films, uniformity on large area substrates, sputtering of any metal, compound or alloy, etc. Depending on the type of power

used sputtering process can be divided into two categories: RF (Radio frequency) and DC (Direct Current). **Figure 2.1** illustrates the sputtering process in a vacuum chamber.



**Figure 2.1:** Schematic of the sputtering process in the vacuum chamber

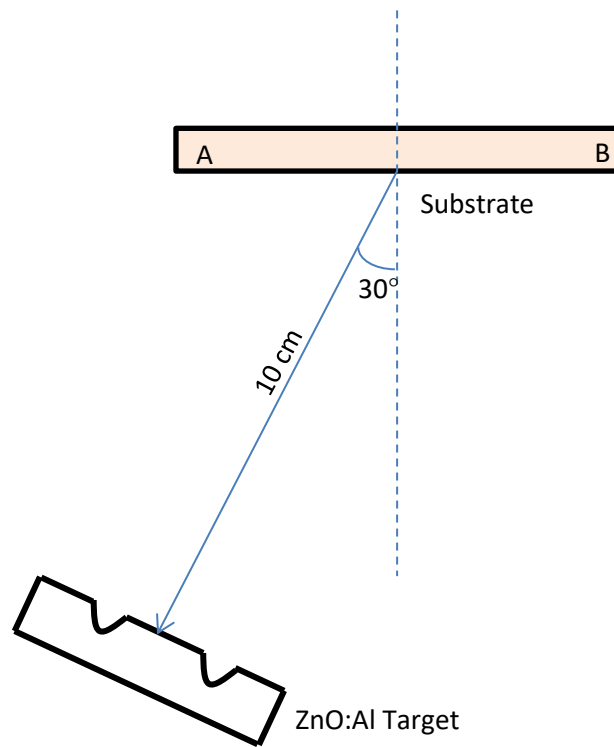
### 2.1.1 RF Magnetron Sputtering

In RF magnetron sputtering, the power is delivered at radio frequencies typically at 13.56 MHz. It is widely used to deposit films on insulating materials, where the charge remains localised, once the ions strike the target. This leads to the accumulation of the positive charges which further prevents the bombardment of ions. Application of RF power overcomes this problem by providing sufficient energy to the electrons oscillating in the alternating field to cause ionising collisions, maintaining self-sustained discharge.

### 2.2 Growth of ZnO:Al thin films

The ZnO: Al films were deposited on soda lime glasses using an oxide target (with purity 99.99%, mass ratio of ZnO/ Al<sub>2</sub>O<sub>3</sub> is 98:2), by RF magnetron sputtering at room temperature. The substrate to target distance was about 10 cm. The substrates were placed at an inclined angle of 30° with respect to the normal of the surface of the target. **Figure 2.2** illustrates the configuration of the sputtering system [21]. The substrates were initially rinsed

in acetone, followed by ultra-sonication using deionized water for five minutes, then cleaned with ethanol and isopropyl alcohol, and finally dried by hot air blow before loading into the chamber [5, 20]. The sputtering was carried out at different RF powers 50, 100, 150, 200, 250 W for different deposition times 75, 60, 40, 30, 20 min respectively, at 13.56 MHz in pure Ar atmosphere. The time was varied to prepare films of similar thicknesses.



**Figure 2.2:** Sputtering configuration of the RF magnetron sputtering system used for the fabrication of ZnO:Al films.

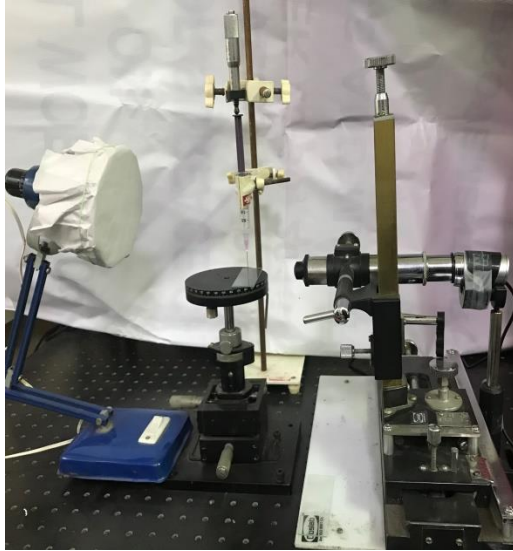
A turbomolecular pump supported by a rotary pump was used to evacuate the chamber to a base pressure lower than  $5 \times 10^{-6}$  mbar. The Ar gas is introduced into the chamber through mass flow controller, fixed at 15 standard cubic centimetre SCCM, to retain the working pressure of  $1.5 \times 10^{-3}$  mbar. **Figure 2.3** shows the image of the RF magnetron sputtering system used for the fabrication of ZnO:Al films. All the measurements and characterizations were done for the films which were cut from the B side of the thin film due to its low sheet resistance.



**Figure 2.3:** RF magnetron sputtering system used for the fabrication of ZnO:Al films.

### 2.3 Characterization Techniques

The crystal structure of the films was investigated by X-ray diffraction (XRD) measurements using Cu  $K\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ). The Scherrer's formula was used to calculate the crystallite size ( $D$ ) of the films. The electrical properties such as resistivity ( $\rho$ ), carrier concentration ( $n$ ) and hall mobility ( $\mu$ ) were determined using a standard Hall measurement system in Vander Pauw configuration, at room temperature. The surface morphology and cross section of the thin films was studied using field emission scanning electron microscope (FESEM). The optical properties, namely transmittance and band gap were measured using UV- Visible spectrophotometer in the wavelength range of 300 to 1400 nm. Contact Angle measurements to determine the hydrophobicity were carried out using an in-house designed setup, as shown in **Figure 2.4**. It consists of a webcam attached to the eyepiece of the travelling microscope, a vernier calliper for controlled movement of syringe to dispense a water droplet, a stand to place the thin film, and a diffused light. The image was taken through the webcam attached to the computer system and the contact angle was measured using imagej software.



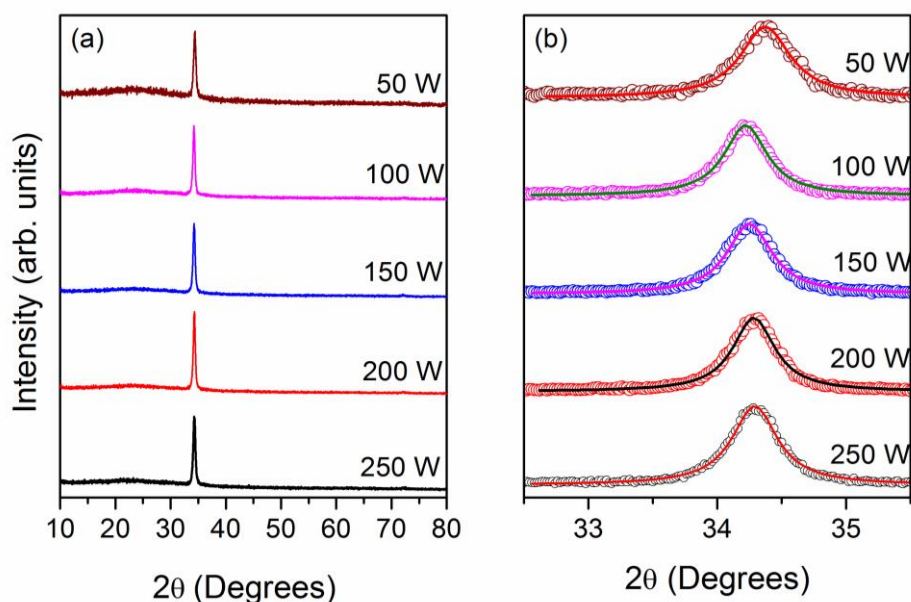
**Figure 2.4:** Photograph of the contact angle measurement setup.

## Chapter 3

### Results and Discussion

#### 3.1 Structural Properties

**Figure 3.1** shows the typical XRD patterns of the ZnO:Al films deposited at various deposition powers. All patterns irrespective of the RF power showed a strong reflection peak at  $\sim 34.3^\circ$  corresponding to the (0002) peak of wurtzite structure. Since there is no peak corresponding to  $\text{Al}_2\text{O}_3$ , it implies that Zn is partially replaced by Al in the lattice [21]. To find out the lattice strain, typical of the sputter deposition technique and the lattice parameters, the exact peak position was determined from the Lorentzian peak fitting, as shown in Fig. 3.1(b).



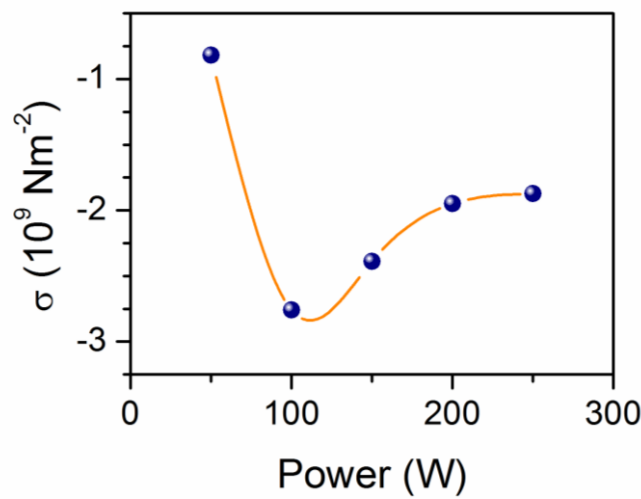
**Figure 3.1:** (a) XRD patterns of the ZnO:Al films, (b) Zoomed-up XRD patterns in the region of (0002) peak position. The symbols denote the experimental data, while solid line shows the Lorentzian peak fitting in (b)

The crystallite size ( $D$ ) was deduced from the FWHM ( $\beta$ ) of the (0002) peak using the Debye Scherrer's formula,  $D = 0.9\lambda/\beta\cos\theta$ ,  $\lambda$  is wavelength of the X-rays used,  $\theta$  is the Bragg angle. The crystallite size was found to be about 180 Å.

Analysis of the peak positions revealed that for all samples the peaks are shifted to the lower  $2\theta$  values, suggesting the presence of compressive stress in the films. The compressive stress was calculated using the formula [11]:

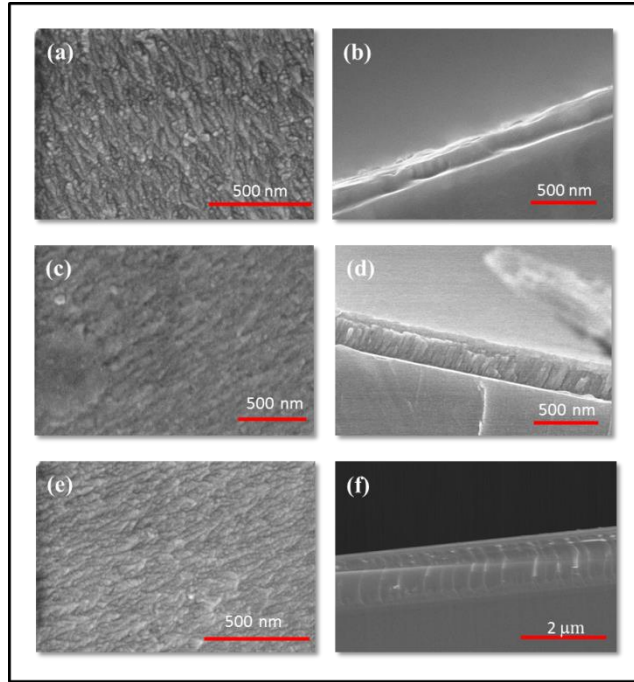
$$\sigma = [2C_{13} - C_{33} ((C_{11}+C_{12})/C_{13})] (c-c_0)/c_0, \quad (1)$$

where  $C_{ij}$  are the elastic stiffness constants,  $c$  is the lattice constant corresponding to (0002) Bragg reflection, and value for corresponding stress-free system,  $c_0$ , is 5.205 Å. The values of stiffness constants are,  $C_{13} = 1.05 \times 10^{11}$  N/m<sup>2</sup>,  $C_{12} = 1.2 \times 10^{11}$  N/m<sup>2</sup>,  $C_{44} = 0.42 \times 10^{11}$  N/m<sup>2</sup>,  $C_{11} = C_{33} = 2.1 \times 10^{11}$  N/m<sup>2</sup> [22]. Compressive stress is indicated by the negative sign of  $\sigma$ . Plot of stress ( $\sigma$ ) as a function of power for all the AZO films are as shown in **Fig. 3.2**.



**Figure 3.2:** Plot of stress ( $\sigma$ ) as a function of deposition power.

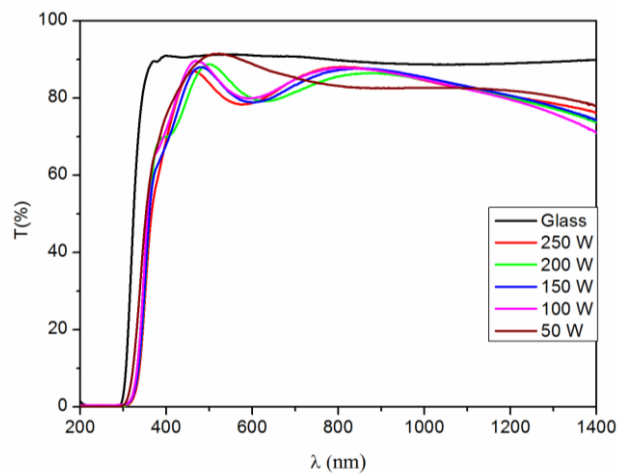
**Figure 3.3.** shows representative FESEM images of surface and cross-sectional features of various films. All samples were found to be conformally coated with fine grains without any pin-holes or anomalies.



**Figure 3.3:** Surface and cross-sectional FESEM images of the ZnO:Al films grown at different powers: (a, b) 250 W, (c, d) 150 W, (e, f) 50 W.

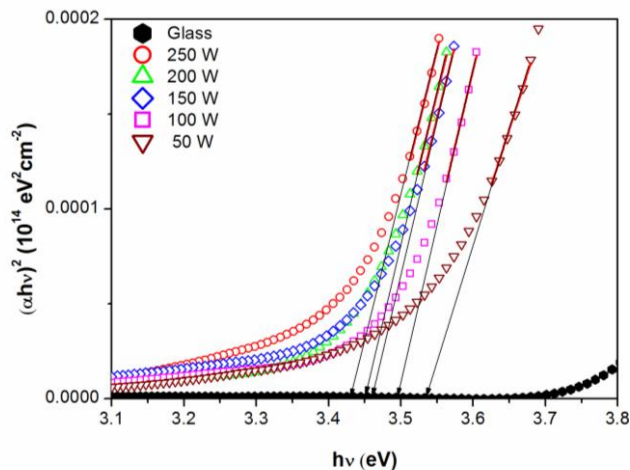
### 3.2 Optical Properties

**Figure 3.4** shows the optical transmittance of ZnO:Al films deposited at various RF powers ranging from 50 to 250 W over the visible range of 190 nm to 1400 nm. The figure also shows the transmittance curve for the glass substrates. High visible transmittance (> 80%) is observed for all samples.



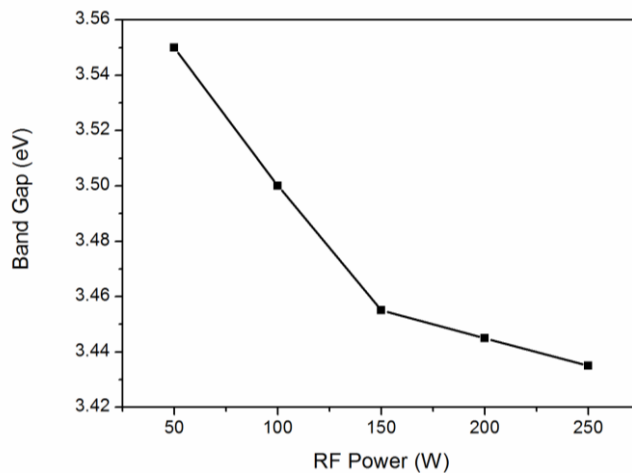
**Figure 3.4:** Optical transmittance spectra of the ZnO:Al thin films grown with different RF power.

The optical bandgap  $E_g$  was estimated from the Tauc plots, i.e., by extrapolating linear portions of  $(\alpha h\nu)^2$  against photon energy ( $h\nu$ ), as shown in **Fig. 3.5**, where  $\alpha$  is the absorption coefficient.



**Figure 3.5:** Plot of  $(\alpha h\nu)^2$  against photon energy ( $h\nu$ ) of ZnO:Al thin films deposited at various powers.

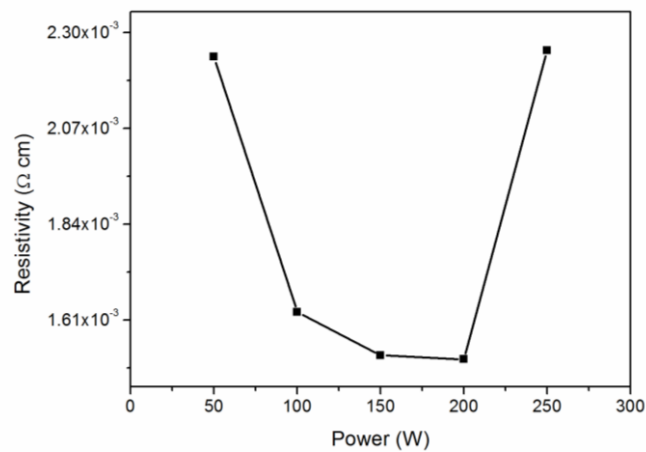
**Figure 3.6** shows the dependence of optical bandgap  $E_g$  on the sputtering power. As seen from the figure, the bandgap decreased from 3.61 eV to 3.48 eV as the power increased from 50 W to 250 W [5].



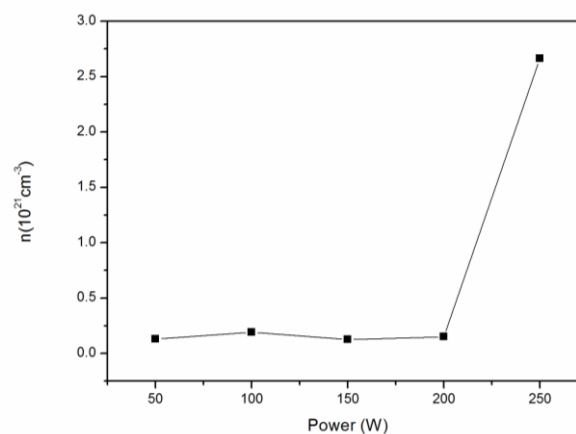
**Figure 3.6:** Plot of band gap as a function of deposition power.

### 3.3 Electrical Properties

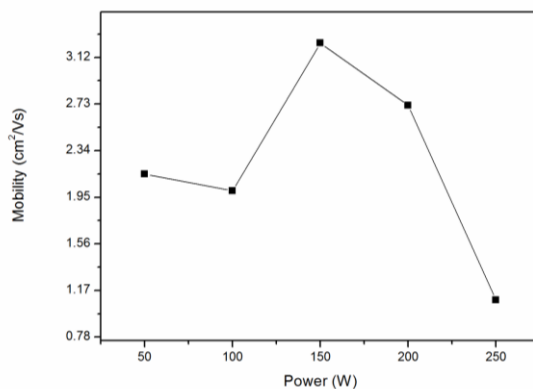
**Figure 3.7** shows the resistivity, calculated by vander pauw method as a function of power of ZnO:Al films deposited for different deposition times. It is to be noted that the deposition time was decreased from 75 minutes to 20 minutes as the power was increased from 50 to 250 W in order to prepare films of similar thicknesses and to isolate the contributions of thickness to the observed values. The minimum resistivity of  $1.52 \times 10^{-3} \Omega \text{ cm}$  is found for the film deposited at 200 W for 30 minutes. This phenomenon is directly related to the change of carrier concentration and hall mobility according to the formula of resistivity  $\rho = 1/(ne\mu)$ . The carrier concentration ( $n$ ) and the mobility ( $\mu$ ) were determined directly from the Hall measurement. The variation in  $n$  and  $\mu$  with RF power is shown in **Figure 3.8** and **3.9**, respectively.



**Figure 3.7:** Resistivity of ZnO:Al films as a function of power.



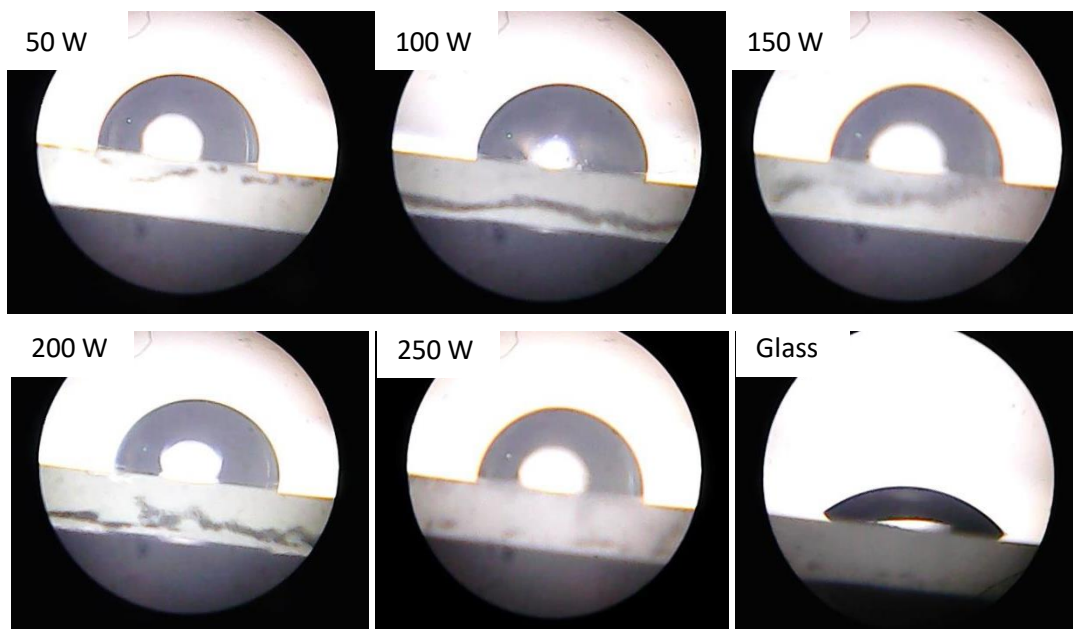
**Figure 3.8:** Plot of carrier concentration of ZnO:Al films as a function of power.



**Figure 3.9:** Plot of mobility as a function of power.

### 3.4 Wettability Studies

The surface wetting properties were studied using an in-house assembled contact angle measurement setup. **Figure 3.10** shows the images of contact angle measurements for different films and a bare glass. As the power was varied from 50 to 250 W, the contact angle exhibited a variation from 89.15° to 94.48°, indicating the hydrophobic nature of the ZnO:Al films.



**Figure 3.10:** Images of contact angle measurements of different ZnO:Al films and glass.

## Chapter 4

### Conclusion

ZnO:Al thin films were deposited on the glass substrates by RF magnetron sputtering technique. The deposition was done under different process parameters in order to study the influence of deposition power on the film properties. The structural, optical, electrical and surface properties were studied using XRD, UV-Visible spectrophotometer, Hall Effect and Contact angle measurements. Irrespective of the deposition power, all films crystallized in the wurtzite structure and showed a very strong c-axis orientation. The results indicate that all the films were highly transparent ~ 80 %. The resistivity was found to decrease as the power was increased from 50 to 200 W but showed a large increase in its value at 250 W. The minimum resistivity was found to  $1.52 \times 10^{-3} \Omega \text{ cm}$  for the film deposited at 200 W for 30 minutes. Films were hydrophobic in nature with average contact angle ~ 91.96°.

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Chapter 1 Introduction 1.1 Zinc Oxide Thin Films Zinc Oxide (ZnO) is an n-type semiconductor oxide, which crystallizes in the hexagonal wurtzite structure. It has a wide optical band gap ( $\sim 3.37$  eV) which provides it high transparency over the visible range. However, ZnO is found to have very high electrical resistivity, which can be reduced to the order of  $\sim 10^{-4} \Omega \text{ cm}$  by doping it with group III elements like aluminium (Al), boron (B) or gallium (Ga) [1]. Among all these impurity doped ZnO films, aluminium doped zinc oxide (ZnO:Al) films have been widely studied for various applications due to its low resistivity and high visible transmittance [2]. Furthermore, due to its low cost, non-toxicity, high chemical stability, abundance in nature, it has emerged as a promising transparent conducting oxide (TCO) material [2-4]. The TCO thin films have acquired considerable interest because they are the key element in a number of optoelectronic applications. Earlier indium tin oxide (ITO) was most commonly used TCO, but there were issues related to its toxicity, availability and cost [2, 5]. Due to a unique blend of optical and electrical properties, ZnO:Al thin films finds applications in numerous optoelectronic devices such as window layers of solar cells, organic light emitting diodes (OLED's), and flat panel displays [2, 3].

1.2 ZnO:Al thin films as window layer for solar cells Solar cells are the photovoltaic devices that convert the solar energy into the electrical energy. A typical inorganic thin film based solar cell is made up of several layers such as topmost window layer, buffer layer, and the absorber layer. The efficiency of the solar cell is affected by number of parameters such as amount of incident light, dust or other impurities on cell surface, etc., besides the inherent cell design and properties of the absorber layer. For high efficient solar energy harvesting, the amount of light entering the absorber layer should be maximum. This suggests that there should be minimum absorption of incident light by the window layer. Therefore, the window layer of solar cells is often made from transparent metal oxides allowing large amount of light to enter the absorber layer, and thus increasing its efficiency. Self-cleaning surfaces of the window layers are another important factor which helps in increasing the efficiency of the solar cell. Wettability is a property that depends on the surface energy and roughness, and helps in the cleaning of the surface [6]. It is determined by the water contact angle (?) which is defined as the angle between solid-liquid interface and liquid-vapour interface. A surface that provides non-wetting characteristics with water contact angle higher than  $90^\circ$  is called hydrophobic surface, for example: lotus leaf, as shown in Figure 1.1(a). A surface that attracts water and has contact angle less than  $90^\circ$  is called hydrophilic surface, for example: glass, as shown in Figure 1.1(b). (a) (b) Figure 1.1: (a) Lotus leaf (hydrophobic surface), (b) Glass (hydrophilic surface) [7]. Both of these surfaces exhibit self-cleaning