Characterization Of Aluminum Doped Zinc Oxide Thin Films For Photovoltaic Applications

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CHARACTERIZATION OF ALUMINUM DOPED
ZINC OXIDE THIN FILMS FOR PHOTOVOLTAIC
APPLICATIONS

by

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B.E.E.E. Visvesvaraya Technological University (2006)

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science
in the School of Electrical Engineering and Computer Science
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2010
ABSTRACT

Growing demand for clean source of energy in the recent years has increased the manufacture of solar cells for converting sun energy directly into electricity. Research has been carried out around the world to make a cheaper and more efficient solar cell technology by employing new architectural designs and developing new materials to serve as light absorbers and charge carriers. Aluminum doped Zinc Oxide thin film, a Transparent conductive Oxides (TCO) is used as a window material in the solar cell these days. Its increased stability in the reduced ambient, less expensive and more abundance make it popular among the other TCO’s. It is the aim of this work to obtain a significantly low resistive ZnO:Al thin film with good transparency. Detailed electrical and materials studies is carried out on the film in order to expand knowledge and understanding.

RF magnetron sputtering has been carried out at various substrate temperatures using argon, oxygen and hydrogen gases with various ratios to deposit this polycrystalline films on thermally grown SiO₂ and glass wafer. The composition of the films has been determined by X-ray Photoelectron Spectroscopy and the identification of phases present have been made using X-ray diffraction experiment. Surface imaging of the film and roughness calculations are carried out using Scanning Electron Microscopy and Atomic Force Microscopy respectively. Determination of resistivity using 4-Probe technique and transparency using UV spectrophotometer were carried out as a part of electrical and optical characterization on the obtained thin film. The deposited thin films were later annealed in vacuum at various high temperatures and the change in material and electrical properties were analyzed.
Dedicated to my parents
ACKNOWLEDGMENTS

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<th>Definition of Acronym</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>AMD</td>
<td>Acetone, Methanol and Distilled water</td>
</tr>
<tr>
<td>AZO</td>
<td>Aluminum doped zinc oxide</td>
</tr>
<tr>
<td>CBD</td>
<td>Chemical beam deposition</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DI</td>
<td>De-Ionized</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width half maxima</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>I-V</td>
<td>Current-Voltage</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal organic chemical vapor deposition</td>
</tr>
<tr>
<td>MSP</td>
<td>magnetron sputter deposition</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conductive oxide</td>
</tr>
<tr>
<td>UV/Vis</td>
<td>Ultraviolet/Visible</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
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</table>
CHAPTER 1 INTRODUCTION

Solar radiation is one of the most available renewable energy on the Earth, along with wind power, wave, hydroelectricity and biomass. It has been approximated that the amount of solar radiation that reaches the earth every year is about twice the energy obtained from all the non renewable resources of the earth, among which, only a minuscule fraction of the available solar energy is used. Growing demand for clean source of energy in the recent years has increased the manufacture of solar cells for converting solar energy directly into electricity.

Research has been carried out around the world to make a cheaper and more efficient solar cell technology by employing new architectural designs and developing new materials to serve as light absorbers and charge carriers. Transparent conductive oxide (TCO) thin films are used as a transparent front electrode in the solar cells and in most of the optoelectronic devices such as flat panel displays. These thin films with wide band gap, low resistivity and high transparency are used as a window material and front electrode in most of the photovoltaic heterojunction solar cell to be suitable for solar energy conversion. Although tin doped indium oxide (ITO) have been in practical use for most transparent electrode applications, a regular supply of them towards the growing application of TCO’s has been difficult due to higher cost and scarce availability of indium.

Binary compound such as CdO, ZnO, In\textsubscript{2}O\textsubscript{3} and SnO\textsubscript{2} can also be used as transparent conductive films. But, its instability at higher temperatures keeps it away from being used as an transparent electrode for practical applications [1]. These compounds are easily doped and its chemical composition in the thin film can be easily controlled for a better transparent electrode.
The property of Zinc oxide (ZnO) such as good stability in hydrogen plasma ambient, good thermal stability when doped with III group elements, non-toxicity, wide band gap (~3.3), high conductivity, easy doping and its abundant availability has increased attentions as a TCO[2][3]. Obtaining TCO thin films with better electrical properties always depends on the preparation techniques and conditions adopted, whereas, lower resistive films can only be obtained using impurity doped binary compounds. Aluminum doped ZnO thin films has been studied a lot these days due to its continuous drop in resistivity on the other hand, films obtained using other binary compounds remained unchanged for past few decades.

Investigation of RF sputtered ZnO:Al thin film deposited at various power and substrate heating with argon, oxygen and hydrogen gas flow in the deposition chamber by studying their electrical, material and optical properties is the major focus of this work. Change in properties of these thin films when annealed in vacuum at various higher temperatures has also been reported in the later chapters.

Chapter 2 is intended to provides the reader with a comprehensive background on current state of the art in the literature pertaining to study of ZnO:Al thin films as a transparent electrode. An overview of the recent accomplishment, opportunities and challenges of ZnO:Al as a transparent conductive oxide for modern day applications has been systematically studied.

Chapter 3 provides a detailed description of the actual experimental process carried out in the deposition of the ZnO:Al thin films. Equipments used and the techniques carried out for all electrical, material and optical characterization of the deposited thin films has also been discussed.
Chapter 4 provides the result obtained during the study for electrical, material and optical studies on the deposited thin film. Characterization techniques such as XPS and XRD which was done to study the composition of the deposited film have been reported. Later, films are studied for their surface characteristics using SEM and AFM. Resistivity of the films is measured and their optical characteristic is studied to obtain a better transparent electrode.

Chapter 5 summarizes the present work and provides a future outlook for continued research in this direction.
CHAPTER 2 LITERATURE REVIEW

This chapter provides a detailed review of the background of ZnO:Al thin films as a transparent electrode. Its recent research accomplishment, opportunities and challenges has also been discussed thoroughly.

2.1 TCO as transparent electrode

Transparent conductive oxide which is used as transparent electrode in most of the optoelectronic devices are polycrystalline or amorphous with lower resistivity and high transparency. In general, these thin films have resistivity in the order of $10^{-4}\Omega \text{cm}$ or less, transparency above 80%, band-gap energy above 3eV and carrier concentration of the order of $10^{20}\text{cm}^{-3}$. Epitaxial growth can also be carried out to obtain a single crystal structure of the thin film.

A thin film for transparent electrode applications with resistivity, transparency and atomic concentration of the required magnitude can be obtained using binary compounds such as CdO, ZnO, In$_2$O$_3$ and SnO$_2$[4] but, their instability towards high temperatures provides a need for impurity doping to obtain a thin film with better property[1]. These binary compounds can be easily doped with an impurity and its chemical composition in the thin film can be easily controlled for a better transparent electrode. Table1 lists the binary compound and the dopants which can be used to obtain a thin film transparent electrode.
Table 1: List of binary compound for transparent electrode and impurity dopant.

<table>
<thead>
<tr>
<th>Binary compound</th>
<th>Dopants</th>
</tr>
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<tbody>
<tr>
<td>In$_2$O$_3$</td>
<td>Sn, Ge, Zr, Hf, Nb, Mo, F, Ti, Ta, W, Te</td>
</tr>
<tr>
<td>ZnO</td>
<td>Al, B, Ga, In, Y, F, V, Si, Sc, Ge, Ti, Zr, Hf</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>Sb, F, As, Nb, Ta</td>
</tr>
<tr>
<td>CdO</td>
<td>In, Sn</td>
</tr>
</tbody>
</table>

2.2 Aluminum doped zinc oxide as a TCO

Indium tin oxide (ITO) thin film has been used increasingly as a transparent electrode for optoelectronic application. Their good electrical and optical properties have made it popular for practical application. But, due to the limited availability of indium in nature, the production cost of these ITO’s has increased. To resolve this problem impurity doped binary compound such as Al-doped zinc oxide and In-doped cadmium oxide as alternative materials was proposed. Though low resistivity was obtained in both of these alternative material, usage of cadmium oxide thin films is being limited due to its toxicity. Zinc oxide being inexpensive, non-toxic, abundant and its ability to exhibit similar properties as that of ITO makes it a suitable alternative material [1].

Fast etching rate of Zinc oxide thin films in acid and alkaline solutions can both be advantage and disadvantage in different circumstances. ITO can have an improved etching rate by doping it with Zn[5], but controlling their etching during photolithography process would be difficult. Etching rate also depends on the crystallinity of the thin film deposited, their composition and the technique used to deposit them. Doping of the ZnO thin film with different dopants decreases the etching rate[6], for example, Al-doped zinc oxide has less etch rate
compared to undoped zinc oxide. Some of the commonly used etchant for ZnO etching are HCl and KOH solutions.

2.3 Methods used for the deposition of ZnO:Al thin films

Many different methods are adopted in the deposition of ZnO:Al thin films for good electrical and optical properties. The properties of these thin film vary with the deposition methods and conditions adopted for it formation. A survey of the methods of deposition used in recent times has been discussed briefly.

Sato H et al was successful in preparing a Al-doped thin film with resistivity \(3.4 \times 10^{-4}\) ohms cm and a transmittance above 85% in the visible region using Chemical beam deposition (CBD) at low substrate temperature. Diethylzinc (DEZ), water (H\(_2\)O) and triethylaluminium (TEA) of trimethylaluminium (TMA) source gases was fed intermittently and alternately to prepare ZnO:Al thin films.[7].

Metal organic chemical vapor deposition (MOCVD) has been used in the preparation of AZO thin films extensively. B. P. Zhang et al studied the growth characteristics, optical characteristics and surface morphology of the ZnO thin film deposited using MOCVD on Al\(_2\)O\(_3\) substrate at different substrate heating temperatures. It has been reported that the crystalline and optical quality of the thin film deposited became better at higher growth temperatures [8].

Pulsed laser deposition (PLD) technique to deposit AZO thin films was carried out by Suzuki A et al, employing an ArF laser (\(\lambda=193\) nm). Al-doped thin film with 90% transparency and resistivity of about \(5.62 \times 10^{-4}\) \(\Omega\cdot\)cm were obtained at different substrate temperatures [9]. T Minami at el has successfully deposited a highly conductive and transparent aluminum doped zinc oxide thin films by RF magnetron sputter deposition (MSP) technique. A ZnO target with
Al$_2$O$_3$ dopant of 1–2 wt% was used to obtain a low resistive and highly transparent film. It has been reported that the film with stable resistivity for use in various ambient at high temperature can be obtained[1]. Transparent and conductive multicomponent oxide films with different chemical composition was also prepared using RF magnetron sputter deposition (MSP) technique. Additionally, a target consisting of a mixture of various combinations of In$_2$O$_3$, ZnO, MgO, Ga$_2$O$_3$, and SnO$_2$ powders were used to yield better results. The metal elements the film contained can be determined by analyzing for the chemical properties of the deposited thin film. Physical properties such as band gap and work function can be varied with the change in chemical composition of the thin film deposited [10].

2.4 Magnetron sputtering of AZO thin films

Magnetron sputter deposition, a physical vapor deposition (PVD) method of depositing thin films is employed widely in the preparation of Al-doped zinc oxide. Zinc oxide targets doped with aluminum (1-4%) wt is sputtered with different RF or DC powers, argon flow and substrate heating at very high pressure. The incorporation of oxygen in the deposited AZO thin films hugely effects the conductivity and transparency. Zinc being more chemically active in an oxidizing atmosphere than Sn and In, controlling its oxidation is much more difficult compared to other binary compounds such as SnO$_2$ and In$_2$O$_3$[11]. Therefore, the amount of oxygen in the AZO thin film should be precisely controlled during sputter deposition. In other words, AZO thin films must be deposited in less oxidizing atmosphere compared to In$_2$O$_3$ and SnO$_2$ thin films. Generally, In$_2$O$_3$ and SnO$_2$ thin films are deposited with very less flow of oxygen into the sputtering chamber in order to obtain a TCO with better properties. Minimal flow of oxygen while deposition may effect the transparency of the obtained AZO thin film. Resistivity and
transparency of the obtained ZnO:Al thin film during MSP always depends on oxygen content in the ZnO:Al target, substrate heating employed while deposition the amount of oxygen generated from the target reaching the substrate surface and amount of oxygen flow in the deposition chamber [7].

DC magnetron sputtering technique to prepare a ZnO:Al thin film using an oxide target is largely difficult because of random distribution of resistivity in the different part of the deposited film. This is due to target erosion pattern which is created on the target while deposition which therefore effects the activity and quantity of oxygen that reaches the substrate surface [12]. Research has been carried out to improve this behavior of DC magnetron sputtering by placing target perpendicular to the substrate [13,1] and applying magnetic field while deposition[13,14], but complete solution for the whole problem is yet to be found out.

2.4.1 Comparison between DC and RF magnetron sputtering

A brief study comparing DC and RF magnetron sputtering is carried out in this section. Oliver Kluth et al stated that RF magnetron sputtering showed a weak dependence on film thickness and substrate temperature while a strong dependence on sputter pressure and oxygen addition to the process gas. In DC sputtering at lower substrate temperatures, the supply of small amounts of oxygen was required to maintain high transparency and achieve significant roughness for light scattering after wet chemical etching. It has also been noted that the heat stability of the thin film deposited increases with the decrease in sputtering pressures.

Figure 2.1 shows dependence of resistivity of the film deposited with different sputter pressure at different gas ratios for both RF and DC magnetron sputtering. It shows that the film deposited using both DC and RF sputtering has a decrease in resistivity with the decrease in sputtering
pressure. Addition of oxygen flow in the system increased the resistivity at higher pressures for RF sputter deposition technique. Though there was slight increase in the resistivity of the thin film deposited with argon at higher pressures, its resistivity is far lesser than film deposited with the oxygen flow at higher sputter pressures. DC magnetron sputtering showed a constant resistivity with the increase in sputter power. It can be observed that resistivity decreased with substrate heating[15].

Figure 2.1Pressure dependence of the resistivity of ZnO:Al films RF and DC sputtered in different gas atmospheres (pure Ar, $p_{Ar}/p_{O2}=$const., oxygen partial pressure $p_{O2}=$const.)[15].
Figure 2.2 shows the variation of resistivity with increase in sputter pressure for the thin film deposited by RF sputter deposition technique. A low resistivity was achieved for all films deposited at low sputter pressures. It has also been observed that resistivity decreases with the increase substrate temperature and increase in thickness. When small amount of oxygen is added, there is increase in resistivity at higher sputter pressure but there is remarkable decrease in resistivity when sputter pressure is decreased [15].

ZnO:Al thin films are highly oriented with their c-axis perpendicular to the surface of the substrate which is independent of sputtering gas pressure. The crystalline size in the deposited thin film is found to be decreasing with the increase sputtering pressure[16].
Figure 2.3  Variation of AZO (002) peak intensity and FWHM as a function of substrate temperature at rf power=150 W, Pressure=5 mtorr [17]

Figure 2.3 shows the intensity of the peak and the full width half maxima of the deposited ZnO:Al thin film with the increase in substrate temperature at a particular pressure and deposition power. Due continuous increase and decrease of peak intensity and FWHM with the increase of substrate temperature, it can be said that the crystallinity and crystal size increases at higher substrate temperature. Ki Cheol Park et al has also reported the peak intensity decreases with the increase in sputtering pressure, indicating decrease in crystallinity of the deposited thin film[17]. On an extra note, the growth rate increases with increasing RF power, but decreases with increasing substrate temperature and sputtering pressure [16]. With the Ar pressure increase, surface roughness of the deposited AZO thin film increases [16].
Percentage of transmission for the ZnO:Al thin film decreases with the increase in thickness of the film deposited. Transparency of the film in the visible region does not change with the increase of deposition power but there is a decrease in transmission in the IR region [18]. There is a small drop in percentage transmittance with the decrease in sputter pressure [16] As the Al$_2$O$_3$ content increases, the absorption edge shifts monotonically to the shorter wavelength region [17]
CHAPTER 3 EXPERIMENTS AND DESIGN

In this chapter the experimental procedures and techniques used in characterization and fabrication of the Aluminum doped zinc oxide has been discussed. Electrical, material and optical characterization techniques used in the study of these deposited films has been outlined. This chapter has been divided depending on the number of methods used in the preparation of ZnO:Al thin films.

3.1 Deposition with oxygen flow in the chamber

Silicon substrates (p-type) were used for the experiments. These silicon wafers were cleaned thoroughly using Acetone, Methanol and DI water (AMD) to remove contaminants present on the surface of the wafer. Later, the wafer was oxidized using the wet oxidation process. This process was carried out at 1100°C for 20 minutes with 3 minutes of push in and pullout time each.

The thickness of the oxide on the silicon wafer can be found out using Deal-Grove Model.

\[
Z = \frac{A}{2} \left[ \left( 1 + \frac{4B(t + \tau)}{A^2} \right)^{\frac{1}{2}} - 1 \right]
\]

Where,

\( Z \) = oxide thickness in microns

Linear rate constant, \( B/A \), where \( A = 2D/k_s \) (\( \mu m \))

\( D \) = Diffusion coefficient

\( k_s \) = rate constant

Parabolic rate constant, \( B = 2DN_0/M \) (\( \mu m^2/hr \))

\( N_0 \) = surface concentration
M = no of molecules of oxidizing species per unit volume of oxide.

Therefore, using the rate constant Table 3.1 below,

*Table 3.1 Rate constants for wet oxidation*

<table>
<thead>
<tr>
<th>Oxidation T(°C)</th>
<th>A(μm)</th>
<th>B(μm²/hr)</th>
<th>B/A(μm/hr)</th>
<th>t(hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>0.05</td>
<td>0.720</td>
<td>14.40</td>
<td>0</td>
</tr>
<tr>
<td>1100</td>
<td>0.11</td>
<td>0.510</td>
<td>4.64</td>
<td>0</td>
</tr>
<tr>
<td>1000</td>
<td>0.226</td>
<td>0.287</td>
<td>1.27</td>
<td>0</td>
</tr>
<tr>
<td>920</td>
<td>0.50</td>
<td>0.203</td>
<td>0.406</td>
<td>0</td>
</tr>
</tbody>
</table>

With, Temperature (T) = 1100°C; t = 15 minutes; Z = Final oxide thickness on the silicon wafer, we obtain thickness, \( Z = 3062 \text{ Å} \) approximately.

*Figure 3.1 Wet oxidation growth chart*
The thickness can also be found using the wet oxidation growth chart shown in Figure 3.1.

ZnO:Al films were deposited on Si/SiO₂ substrate and glass(corning) substrates by RF magnetron sputtering at various RF power levels using target consisting of Zinc oxide with 3%wt Al₂O₃ in presence argon and oxygen in the chamber. The deposition process is schematically represented in Figure 3.2. The parameters used in the deposition of ZnO:Al thin films using oxygen in the chamber is listed in Table 3.2.

Figure 3.2 Model of the deposition process with oxygen and argon flow including substrate heating
Table 3.2 Parameters used in the deposition of ZnO:Al thin films using oxygen in the chamber

<table>
<thead>
<tr>
<th>RF Power supplied</th>
<th>Pressure in mtorr</th>
<th>Argon flow rate in sccm</th>
<th>Oxygen flow rate in sccm</th>
<th>Time of deposition in minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>F in watt</td>
<td>V in Volts</td>
<td>R in watt</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>113</td>
<td>0</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>100</td>
<td>126</td>
<td>0</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>100</td>
<td>120</td>
<td>0</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>100</td>
<td>125</td>
<td>0</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>120</td>
<td>138</td>
<td>0</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>140</td>
<td>147</td>
<td>0</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>150</td>
<td>167</td>
<td>0</td>
<td>10</td>
<td>56</td>
</tr>
<tr>
<td>150</td>
<td>166</td>
<td>0</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>150</td>
<td>150</td>
<td>0</td>
<td>2</td>
<td>10</td>
</tr>
</tbody>
</table>

Base pressure = 6.8×10⁻⁸ mtorr  
Distance between the target and the substrate = 20 cm  
Speed of rotation of the substrate = 21 rpm

3.1.1 Electrical characterization
The deposited ZnO:Al thin films as described above is measured for the sheet resistance using 4-probe measurement instrument. Later, the resistivity of the material is calculated using the thickness data measured using Alpha-Step 500 Surface Profilometer.

3.2 Deposition with substrate heating and without oxygen flow in the chamber

ZnO:Al thin films is deposited on oxidized silicon wafer and glass(corning) wafer with only argon flow in the chamber. The substrate is cleaned thoroughly using Acetone, Methanol and DI water (AMD) to remove contaminants present at their surface. The substrate is heated to 200°C and 250°C during RF sputtering process which is carried out at different RF powers. The parameters used in the deposition of ZnO:Al thin films with substrate heating and with only argon gas in the chamber is listed in Table 3.3 and Table 3.4.
Table 3.3 Parameters used in the deposition of ZnO:Al thin films at 200°C and without oxygen.

<table>
<thead>
<tr>
<th>RF Power supplied</th>
<th>Pressure in mtorr</th>
<th>Argon flow rate in sccm</th>
<th>Time of deposition in minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>F in watt</td>
<td>V in Volts</td>
<td>R in watt</td>
<td></td>
</tr>
<tr>
<td>125</td>
<td>92</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>150</td>
<td>102</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>175</td>
<td>111</td>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>

Base pressure = 3.1×10⁻⁷ mtorr
Distance between the target and the substrate = 20 cm
Speed of rotation of the substrate = 21 rpm

Table 3.4 Parameters used in the deposition of ZnO:Al thin films at 250°C and without oxygen.

<table>
<thead>
<tr>
<th>RF Power supplied</th>
<th>Pressure in mtorr</th>
<th>Argon flow rate in sccm</th>
<th>Time of deposition in minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>F in watt</td>
<td>V in Volts</td>
<td>R in watt</td>
<td></td>
</tr>
<tr>
<td>125</td>
<td>91</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>150</td>
<td>102</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>175</td>
<td>111</td>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>

Base pressure = 2×10⁻⁷ mtorr
Distance between the target and the substrate = 20 cm speed of rotation of the substrate = 21 rpm

3.2.1 Electrical characterization

The obtained ZnO:Al thin film using technique and the parameters described above, is measured for the sheet resistance using the 4-probe measurement. Thickness of the deposited film is found out using Alpha-Step 500 Surface Profilometer and thus the deposition rate and the resistivity of the film is calculated.
3.2.2 Material characterization

The sputtered film is characterized for its surface morphology and its chemical composition using various techniques. Scanning Electron Microscopy (SEM) is carried out using Hitachi S3500N to find the surface morphology of the deposited ZnO:Al thin film. Roughness of the deposited film is measured using Atomic force microscopy (AFM) measurements. Later, X-ray diffraction (XRD) measurements were used to investigate the crystal structure and preferred crystal orientation. The chemical composition in the film and atomic concentration of various elements in the film is studied using the X-ray Photoelectron Spectroscopy (XPS).

3.2.3 Optical characterization

Transparency of the ZnO:Al thin film is one of the important factor which needs to be taken into consideration for a better TCO. The percentage of transmission is measured using UV/Vis Spectrophotometer and later, the optical band gap of the material is found out through Tauc Plot which is represented by the Tauc equation given below [19]

\[
(\alpha h \nu)^{1/2} = B(h \nu - E_{opt})
\]

The refractive index for the samples deposited at various deposition power and substrate heating is calculated using H.Demiryont’s method[20].

\[
n(\lambda) = \frac{1}{2}\left[8n_s c(\lambda) + (n_s + 1)^2\right]^{1/2} + \left[8n_s c(\lambda) + (n_s - 1)^2\right]^{1/2},
\]

\[
c(\lambda) = \frac{T_{(\lambda)} - T_{(\lambda)}^\infty}{2T_{(\lambda)}^* - T_{(\lambda)}^\infty}.
\]

Where,

\(n(\lambda)\) = Refractive index of the thin film material

\(n_s\) = Refractive index of the substrate
$T^+=\text{Maximum value transmission at a particular wavelength}$

$T^-=\text{Minimum value transmission at a particular wavelength}$

### 3.3 Annealing at vacuum for the film deposited at different deposition power and substrate heating

In this experiment the ZnO:Al thin films obtained using the procedure described in section 3.2 is further annealed in vacuum at different temperatures. Table 3.6 shows the process condition used while annealing of the deposited thin film. The film deposited with deposition power 175 watt at both $200^\circ C$ and $250^\circ C$ are considered during this experiment as these films recorded the least resistivity.

*Table 3.5 The process condition used while annealing of the deposited AZO thin film.*

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Original sample used</th>
<th>Annealing temperature in $^\circ C$</th>
<th>Time in minutes</th>
<th>Pressure in the chamber in mtorr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Power=175watt</td>
<td>250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Substrate temp=200$^\circ C$</td>
<td>300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>350</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Power=175watt</td>
<td>300</td>
<td>15</td>
<td>$4.1 \times 10^{-7}$</td>
</tr>
<tr>
<td>6</td>
<td>Substrate temp=250$^\circ C$</td>
<td>350</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>400</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.3.1 Electrical characterization

The annealed samples are measured for the sheet resistance using the 4-probe measurement. The values of the resistivity of the thin films deposited with deposition power 175 watt at different substrate heating is compared with that of the annealed samples.
3.3.2 Material characterization

X-ray Photoelectron Spectroscopy (XPS) is done on the annealed thin films to study the chemical composition and the change in atomic concentration of different element in the film.

3.3.3 Optical characterization

Transparency of the annealed ZnO:Al thin film is measured in terms of percentage transmission using UV/Vis Spectrophotometer. Later, the optical band gap of the material is found out through Tauc Plot. The refractive index of these thin films after annealing is calculated using H.Demiryont’s method[20].

3.4 Deposition with substrate heating, DC bias and no oxygen flow

This experiment involves the deposition ZnO:Al thin film with substrate heating and DC biasing. Oxidized silicon wafer and glass wafer that are used as the substrates in this deposition are cleaned thoroughly using Acetone, Methanol and DI water (AMD) to remove contaminants present at their surface.

The substrate is heated to 200°C and 250°C during RF sputtering process which is carried out at different RF powers. The deposition is carried out at Argon ambiance only. This deposition process is schematically represented in Figure 3.3. The parameters used in the deposition of ZnO:Al thin films with substrate heating and DC biasing is listed in Table 3.6.
Figure 3.3 Model of the deposition process with substrate heating and DC biasing.

Table 3.6 Parameters used in the deposition of ZnO:Al thin films with substrate heating and DC biasing.

<table>
<thead>
<tr>
<th>RF Power supplied</th>
<th>DC bias</th>
<th>Substrate temp in °C</th>
<th>Pressure in mtorr</th>
<th>Argon flow rate in sccm</th>
<th>Time of deposition in minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>F in watt</td>
<td>V in Volts</td>
<td>R in watt</td>
<td>FW in watt</td>
<td>Voltage in Volts</td>
<td>R in watt</td>
</tr>
<tr>
<td>125</td>
<td>98</td>
<td>0</td>
<td>10</td>
<td>94</td>
<td>2</td>
</tr>
<tr>
<td>150</td>
<td>106</td>
<td>0</td>
<td>5</td>
<td>72</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>104</td>
<td>0</td>
<td>5</td>
<td>62</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>102</td>
<td>0</td>
<td>9</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

Base pressure = 3.2×10⁻⁷ mtorr

Distance between the target and the substrate = 20 cm

speed of rotation of the substrate = 21 rpm
3.4.1 Electrical characterization

Sheet resistance of the ZnO:Al thin film which was deposited using the technique and parameters described in the section above is measured using 4-probe measurement technique and later resistivity was found out.

3.5 Deposition with substrate heating and with hydrogen flow in the chamber

ZnO:Al thin films is deposited on oxidized silicon wafer and glass(corning) wafer with flow of 2.8% hydrogen and argon gas mixture in the chamber. The substrate is cleaned thoroughly using Acetone, Methanol and DI water (AMD) to remove contaminants present at their surface. The substrate is heated to until 250°C during RF sputtering process which is carried out at different RF powers. The parameters used in the deposition of ZnO:Al thin films with substrate heating and with argon and hydrogen gas in the chamber is listed in Table 3.6.

Table 3.7 Parameters used in the deposition of ZnO:Al thin films with the mixture of hydrogen and argon.

<table>
<thead>
<tr>
<th>RF Power supplied</th>
<th>Substrate heating temperature in °C</th>
<th>Pressure in mtorr</th>
<th>Hydrogen/Argon flow rate in sccm</th>
<th>Time of deposition in minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>F in watt</td>
<td>V in Volts</td>
<td>R in watt</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>119</td>
<td>0</td>
<td>Room temp</td>
<td>5</td>
</tr>
<tr>
<td>150</td>
<td>119</td>
<td>0</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>150</td>
<td>117</td>
<td>0</td>
<td>150</td>
<td>5</td>
</tr>
<tr>
<td>150</td>
<td>114</td>
<td>0</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>150</td>
<td>113</td>
<td>0</td>
<td>250</td>
<td>5</td>
</tr>
<tr>
<td>125</td>
<td>103</td>
<td>0</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>175</td>
<td>124</td>
<td>0</td>
<td>200</td>
<td>5</td>
</tr>
</tbody>
</table>

*Base pressure = 7x10^-7 mtorr
Distance between the target and the substrate = 20 cm
Speed of rotation of the substrate = 21 rpm*
3.5.1 Electrical characterization

The samples are measured for the sheet resistance using the 4-probe measurement. The values of the resistivity of the thin films deposited with hydrogen flow in the chamber are found out after measuring the thickness of the thin film.

3.5.2 Material characterization

X-ray Photoelectron Spectroscopy (XPS) is done on the annealed thin films to study the chemical composition and the change in atomic concentration of different element in the film. Later, X-ray diffraction (XRD) measurements were used to investigate the crystal structure and preferred crystal orientation.

3.5.3 Optical characterization

Transparency of the annealed ZnO:Al thin film is measured in terms of percentage transmission using UV/Vis Spectrophotometer. Later, the optical band gap of the material is found out through Tauc Plot. The refractive index of these thin films after annealing is calculated using H.Demiryont’s method [20].

Table 3.7 lists the names of all the instruments used in electrical, material and optical characterization of the deposited ZnO:Al thin films.
<table>
<thead>
<tr>
<th>Characterization technique</th>
<th>Instrument used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Profilometer(Thickness)</td>
<td>Alpha-Step 500 Surface Profilometer</td>
</tr>
<tr>
<td>Scanning Electron Microscopy(SEM)</td>
<td>Hitachi S3500N</td>
</tr>
<tr>
<td>Atomic force microscopy (AFM)</td>
<td>Molecular Imaging PicoSPM</td>
</tr>
<tr>
<td>X-ray diffraction (XRD)</td>
<td>Rigaku D-MaxB</td>
</tr>
<tr>
<td>X-ray Photoelectron Spectroscopy (XPS)</td>
<td>5400 PHI ESCA system.</td>
</tr>
<tr>
<td>Spectrophotometer UV/Vis (Optical measurements)</td>
<td>CAREY 100CONC.</td>
</tr>
</tbody>
</table>
CHAPTER 4 RESULT AND DISCUSSION

In this chapter the results and discussion from the electrical, material and optical characterization done on the ZnO:Al thin films deposited as mentioned in the previous chapter is systematically reported. The sections in this chapter is divided depending on the number of methods used in the preparation of ZnO:Al thin films as discussed in chapter 3.

4.1 Deposition with oxygen flow in the chamber

4.1.1 Electrical characterization

The aluminum doped zinc oxide was deposited using RF sputtering with different power and different ratios of oxygen and argon flow in the chamber as reported in section 3.1. Good transparency and low resistivity being the prime properties, the obtained thin film was measured for conductivity and transparency initially. Though the films deposited on the glass wafer had high transparency of about 95%, it showed no electrical conductivity.

Transparent and non conductive ZnO:Al thin films obtained using the flow of oxygen in the deposition chamber can be attributed to more incorporation of oxygen in the deposited film. Variation of the power of deposition and oxygen-argon ratio in the chamber during deposition showed no great improvement in the conductivity of the film.

4.2 Deposition with substrate heating and without oxygen flow in the chamber

Deposition of aluminum doped thin films was carried out using RF sputtering with different power, substrate heating and argon gas flow in the chamber. Using the parameters provided in the section 3.2, a good conducting and transparent ZnO:Al thin films was successfully obtained. Later, electrical, material and optical characterization was carried out to
understand the change in properties of the deposited thin film with change in deposition parameters.

Figure 4.1 shows the deposition rate of aluminum doped thin films as a function of power of deposition and substrate heating temperature. It is observed that the deposition rate continuously increased from ~21.3 A/min at 125 W to ~34.9 A/min at 175 W for 250°C substrate temperature and similarly, there is an increase in deposition rate from ~22.4 A/min at 125 W to ~41.2 A/min at 175 W for 200°C substrate temperature. This increase in deposition rate indicates that the number of atoms sputtered from the target is proportional to the increase in the RF power. It is observed that the deposition rate decreased for the film deposited at higher substrate heating temperatures. This is attributed to the increase in the number of atoms bolting out from the substrate surface due to thermal desorption [21]. Limited surface mobility of the adatom at low substrate temperatures also leads to higher growth rate[21].

![Deposition rate vs. power at different substrate temperatures](image)

*Figure 4.1 Deposition rate with respect to power of deposition at different substrate temperatures*
4.2.1 Material characterization

Material characterization for the AZO thin films obtained for the deposition condition discussed in the section 3.2 is presented here.

**Scanning Electron Microscopy (SEM)**

A side view image of the ZnO:Al thin film deposited at various deposition conditions taken through SEM is shown in the figure 4.3.

Figure 4.2 shows SEM images of ZnO:Al thin film obtained using (a)125 W at 200°C (b) 175 W at 200°C  (c)125 Watts at 250°C . The image clearly shows the columnar grain growth that starts from the substrate surface as discussed previously by Sundaram[22] and Dinescu[23]. The columnar growth is more prominent at the lower power. The width of these columnar grains increases with the increase in the deposition power, irrespective of substrate temperature applied. The width of these columnar structures are larger for the ZnO:Al thin film deposited at 250°C substrate heating temperatures compared to that of film deposited at 200°C substrate heating temperature and this film microstructure agrees with the trend explained by Thornton’s structure zone model[24]. Figure 4.3 Structure zone model for sputtered films of metals. This structure zone model identifies four zones in the surface structure as a function of T/T_m and argon pressure, where both T and T_m are substrate temperature and coating.
Figure 4.2 Surface morphology of the deposited ZnO:Al films (a) 125 W at 200°C (b) 175 W at 200°C (c) 125 Watts at 250°C
Figure 4.3 Structure zone model for sputtered films of metals [24]

Atomic force microscopy (AFM)

The average roughness of all the ZnO:Al thin films deposited at various deposition conditions described in section 3.2 is calculated and the surface imagining is taken using the atomic force microscopy (AFM). Figure 4.4 shows the AFM images of ZnO:Al thin films deposited using (a) 125 W (b) 150 W (c) 175 W at 250°C substrate heating temperature. The plot for average roughness with respect to deposition powers at different substrate temperature is shown in Figure 4.5. The average roughness of the deposited thin films varied from 22.1 Å to 5.21 Å. The average roughness of the ZnO:Al thin films decreases with the increase in deposition power irrespective of substrate heating temperature. It has also been observed that average roughness has a slight increase with the increase in substrate heating temperature. Least roughness of 5.21 Å was obtained for thin film deposited at 175 watt and 200°C and highest roughness of 22.1 Å was obtained for the film deposited.
Figure 4.4 AFM images of ZnO:Al thin films deposited using (a) 125 W (b) 150 W (c) 175 W at 250°C substrate heating temperature
X-ray diffraction (XRD)

The ZnO:Al thin film deposited at conditions described in the section 3.2 is studied for the crystal orientation, crystallinity and crystalline size using x-ray diffraction measurement.

Figure 4.6 (a) and (b) shows the diffraction pattern for various deposition powers at 200°C and 250°C substrate heating respectively. The diffraction pattern obtained for the AZO thin films indicated that these films have polycrystalline hexagonal wurtzite structure with the orientation perpendicular (002) to the substrate surface (c-axis orientation) at 34.4(2-theta). Large peaks were observed at 34.4(2-theta) which determines the presence of (002) crystal orientation in the deposited film. Some of these films showed peaks at 36.25(2-theta) and at 38.35(2-theta) indicating (101) and (202) texture growth respectively.

Figure 4.7 shows the plot of intensity and FWHM of the XRD peak for different deposition power and substrate heating temperatures. The peak becomes more intense at lower
powers for films deposited at both 200\(^0\)C and 250\(^0\)C substrate heating temperatures. Therefore, it can be stated that films deposited at lower powers will have improved crystallinity. FWHM of the peaks of these films decrease with the increase in deposition power for the films deposited at both 200\(^0\)C and 250\(^0\)C substrate heating indicating increase in grain size of the thin film deposited. When a film deposited at a particular power and two different substrate temperature is considered, it has been observed that diffraction peaks become more intense and sharp at 200\(^0\)C substrate heating temperature, indicating increase in crystallinity and crystalline size.

Table 4.1 provides the values of FWHM, intensity of the peak and \(2\theta\) for the films deposited at various deposition powers and substrate temperatures. Though there is very small changes in the location of the measured diffraction peaks, it is attributed to the error in loading of sample while measurement. The change in the location of the measured diffraction peaks also depend on the amount of aluminum incorporation in the film [25]. As the incorporation of aluminum in the film is minimal, the reason for the change in the position of the diffraction peaks due to amount of aluminum incorporation in the film can be eliminated. The grain size of the films was found to be in the order of 15-20 nm.
Figure 4.6 The diffraction pattern for various deposition powers at (a)200°C and (b)250°C
### Table 4.1 FWHM, intensity of the peak and $2\theta$ for the films at various powers and substrate temperatures

<table>
<thead>
<tr>
<th>Substrate Temperature ($^\circ$C)</th>
<th>Deposition Power (watt)</th>
<th>$2\theta$</th>
<th>Height of the peak</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>200$^\circ$C</td>
<td>125</td>
<td>34.598</td>
<td>80</td>
<td>0.685</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>34.551</td>
<td>33.4</td>
<td>0.659</td>
</tr>
<tr>
<td></td>
<td>175</td>
<td>34.548</td>
<td>25.1</td>
<td>0.637</td>
</tr>
<tr>
<td>250$^\circ$C</td>
<td>125</td>
<td>34.598</td>
<td>184.3</td>
<td>0.616</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>34.602</td>
<td>56.3</td>
<td>0.592</td>
</tr>
<tr>
<td></td>
<td>175</td>
<td>34.601</td>
<td>51.6</td>
<td>0.585</td>
</tr>
</tbody>
</table>

![Figure 4.7 Plot of intensity and FWHM of the XRD peak for different deposition power and substrate heating.](image-url)
**X-ray Photoelectron Spectroscopy (XPS).**

The chemical composition and atomic concentration in the deposited aluminum doped zinc oxide is studied using the X-ray Photoelectron Spectroscopy (XPS).

Figure 4.8 shows the relative atomic concentration of zinc, oxygen and aluminum obtained using XPS surface scan. Zinc and aluminum content in the film increases with the increase in the power of deposition for both 200°C and 250°C substrate heating temperature. It is also observed that the atomic concentration of zinc and aluminum is further increased with the increase in substrate heating temperature from 200°C to 250°C. Whereas, atomic concentration of oxygen in the film decreases with the increase in deposition power and it further reduces for the ZnO:Al thin film deposited at 250°C substrate heating temperature.

The bonding conditions of oxygen on the surface of ZnO:Al films were investigated using high resolution XPS scans. Figure 4.9 shows the O1s photoelectron peaks in the XPS spectra of ZnO:Al films prepared at 125 watts and 200°C substrate heating temperature. The O1s was composed of four peaks (OI, OII, OIII and OIV). The peak OI at at 530.4±0.1eV is attributed to the O²⁻ ions on the wurtzite structure of hexagonal Zn⁺ ion array. In other words these include O²⁻ ion surrounded by Zn atom with their full compliment [26, 27, 28]. O²⁻ ions in the oxygen deficient regions of the ZnO matrix is located at 531.4±0.10eV (OII)[29]. The binding energy component located at 530.1±0.15eV (OIII) is attributed to loosely bonded oxygen in the surface of the ZnO:Al thin films[30,31]. These chemisorbed oxygen impurity could be due to O²⁻ , O⁻ , O²⁻ O²⁻ , O²⁻ ions [32].The lower binding energy peak at 529.4±0.15eV (OIV) is probably due to oxygen in ZnO structure[30].
Figure 4.10 shows the relative strength of O1s peaks for the ZnO:Al thin film prepared at various deposition powers with 200°C and 250°C substrate heating temperature. The relative strength was obtained by dividing the area of the particular peak area by total peak area. From the figure it is evident that most of the oxygen atom was prone to form O^{2-} ions on the wurtzite structure of hexagonal Zn^{+} ion array for all the ZnO:Al thin film deposited at various deposition powers and substrate temperatures 200°C and 250°C. The relative strength of the O1s peaks remains almost constant for most of the deposited at different powers. Figure 4.10b shows increase in peak O1V at 175watts indicating that oxygen atoms in films were favorable to form ZnAl_2O_4 and ZnO structures at higher powers.
Figure 4.8 The relative atomic concentration of (a) Zinc and oxygen and (b) Aluminum
Figure 4.9 shows the O1s photoelectron peaks in the XPS spectra of ZnO:Al films prepared at 125 watts and 200°C substrate heating temperature

Figure 4.11 shows the Zn2p\(_{3/2}\) photoelectron peaks in the XPS spectra of ZnO:Al films prepared at 125 watts and 200°C substrate heating temperature. From the data obtained for Zn2p\(_{3/2}\) in ZAO thin films, a peak was found at 1022.4±0.20eV (ZnI) which is attributed to the presence of Zn2p\(_{3/2}\) in ZnO or ZnAl\(_2\)O\(_4\) [33] A vacancy state of Zn\(^{2+}\) is formed by all the maximum number of Zn atoms in the oxygen deficient ZnO\(_{1-x}\) matrix [34] The peak at the binding energy 1021.4±0.20eV (ZnII) is attributed to the presence of metallic Zn atom in the thin film [33,35]. These metallic zinc exists as an interstitial atom in ZnO crystalline lattice[36]. From the figure 4.12(a) and (b) we can see that the relative strength of peak ZnI is always more than peak ZnII at all deposition power and substrate heating. There has been a very little decrease in the relative strength of peak ZnI with the increase in power at both 200°C and 250°C whereas, ZnII followed opposite trend. It can be noted that most of the zinc in the deposited thin film is in the form of ZnO or ZnAl\(_2\)O\(_4\) and the presence metallic zinc in the deposited thin film is
relatively less. The metallic zinc may exist as interstitial atoms or at grain boundaries. The study of zinc oxide aluminum doped thin film by Islam et al [35] has reported that formation of metallic zinc in the deposited AZO thin film is very less.

Figure 4.10 The relative strengths of O 1s peaks (OI, OII, OIII and OIV) for the ZnO:Al thin film deposited at (a)200°C (b)250°C substrate heating temperatures and various deposition powers.
Figure 4.11 Zn2p\(_{3/2}\) photoelectron peaks in the XPS spectra of ZnO:Al films prepared at 125 watts and 200°C substrate heating temperature.
Figure 4.12 The relative strength of Zn2p3/2 peaks (ZnI, ZnII) in the AZO thin films deposited with different powers at (a) 200°C (b) 250°C

4.2.2 Optical characterization

Aluminum doped zinc oxide thin films which is deposited with various deposition power and substrate heating is characterized for the optical properties. Achieving a ZnO:Al thin film for transparent electrode with low resistivity and high transparency has always been the goal of the process. Figure 4.13 (a) and (b) shows the percentage transmission of the films deposited with different power at 200°C and 250°C respectively. Average percentage transmission of most of the films is between 90-95%. It can also be observed that films deposited at the higher power shows that its transparency does not have much effect in the visible region, whereas, the film has become more opaque in the IR region with the increase in the deposition power. This means that the film obtained using higher deposition powers is better heat absorbers. A slight drop in the transparency is attribute to the increase in incorporation of Zn with the increase in deposition
power. No noticeable changes in transparency were observed with the films deposited at higher substrate temperatures.

Optical Band gap was obtained through Tauc Plot which is represented by the Tauc equation[19]. Figure 4.14 shows the optical band gap obtained from Tauc Plots for different ZnO:Al films deposited with different powers and substrate temperatures. Optical Band gap of the films deposited is measured to be around 3.23eV, which does not change much with the change in deposition conditions.

Figure 4.15 shows the variation of refractive index n as a function of wavelength for ZnO:Al thin films deposited on glass corning substrate with different deposition power at (a)200°C and (b)250°C substrate heating temperatures. The measurement of the transmittance enables us to determine the optical refractive index. The refractive index was calculated using the relation proposed by H. Demiryont et al[20]. It is seen that the refractive index increases with the increase in deposition power for thin films deposited at 200°C and 250°C substrate heating temperatures.
Figure 4.13 Transmission (%T) curves of as deposited ZnO:Al films at (a) Various RF Power at 200°C

(b) Various RF Power at 200°C
4.2.3 Electrical characterization

Figure 4.16 shows the plot of resistivity with respect to the deposition powers at various substrate heating temperatures. Resistivity decreases continuously as the deposition power increases for both the thin films deposited at 200°C and 250°C substrate heating temperature. A AZO thin film showed lower resistivity for the film deposited at higher substrate heating temperature. Least resistivity of a ZnO:Al thin film obtained was 1.15×10⁻³Ωcm for the film deposited at 175 watts deposition power and 250°C substrate temperature. Increase incorporation of zinc and aluminum in the thin film and decrease in the amount of oxygen with the increase in deposition power and increase in substrate heating temperature is the major reason for the drop in resistivity.
Figure 4.15 The variation of refractive index $n$ as a function of wavelength for ZnO:AL thin films deposited on glass corning substrate with different deposition power at (a)200°C and (b)250°C.
4.3 Annealing at vacuum for the film deposited at different deposition power and substrate heating

The study to investigate electrical, material and optical properties of the annealed thin films using the parameters listed in table 3.6 is carried out.

4.3.1 Material characterization

Figure 4.17 shows the O1s photoelectron peaks in the XPS spectra of ZnO:Al films prepared at (a) 175 watts and 250°C substrate heating temperature (b) annealed in vacuum at 300°C (c) annealed in vacuum at 400°C. It can be seen that the peak OI drops at higher annealing temperatures, whereas, peak OII raises at higher annealing temperatures. This indicates a clear increase in oxygen deficiency with the increase in annealing temperatures. Figure 4.18 The relative strengths of O 1s peaks (OI, OII, OIII and OIV) after annealing for the ZnO:Al thin film deposited at 175 watts (a)200°C(b)250°C substrate heating temperatures. It can be seen that there
is a clear change in the chemical states of oxygen with the increase in annealing temperature which is evident from the continuous decrease in relative intensity of peak OI and continuous increase of peak OII and OIII with the increase in annealing temperature. The decrease in relative intensity of peak OI is not the only reason for increase relative intensity of peak OII and OIII but it is evident that there is a clear change in chemical states of oxygen as there is a faster increase in the relative intensity of OII peak compared to that of OIII peak with the increase in annealing temperature. Hence, more oxygen deficient ZnO:Al thin film is obtained on annealing the obtained film in vacuum at higher temperatures.
Figure 4.17 shows the O1s photoelectron peaks in the XPS spectra of ZnO:Al films prepared at (a) 175 watts and 250°C substrate heating temperature (b) annealed in vacuum at 300°C (c) annealed in vacuum at 400°C.
Figure 4.18. The relative strengths of O 1s peaks (OI, OII, OIII and OIV) after annealing for the ZnO:Al thin film deposited at 175 watts (a) 200°C (b) 250°C substrate heating temperatures

Figure 4.19 compares the relative strength of the Zn2p3 peaks after and before annealing for the AZO thin films deposited with 175 watts deposition power and at different substrate
heating. It is clearly seen that the relative strength of all the peaks remained that same even after annealing. This infers that amount of Zn content in the film remains the same after annealing.

Figure 4.19 Comparing the relative strength of Zn2p3s peaks after annealing at 400\(^{\circ}\)C for film deposited with 175 W and substrate heating 200\(^{\circ}\)C, 250\(^{\circ}\)C.

### 4.3.2 Optical characterization

Figure 4.20 shows the percentage transmission of the ZnO:Al thin films after annealing at higher temperatures for film deposited at 175 watts (a)2000C and (b)2500C substrate heating *temperatures*. It can be seen that percentage transmission of the AZO thin film decreases with the increase in annealing temperature. This decrease in transparency with the increase in
annealing temperature can be attributed to the increase in oxygen deficiency in the deposited thin film.

Optical Band gap was obtained through Tauc Plot which is represented by the Tauc equation [19]. Figure 4.21 shows the optical band gap obtained from Tauc Plots for different ZnO:Al films deposited with different powers and substrate temperatures. Optical Band gap of the films deposited is measured to be around 3.20eV, which does change much with the change with the increase in the annealing temperature.

Figure 4.22 shows the variation of refractive index n as a function of wavelength for ZnO:Al thin films annealed at various high temperatures for a film deposited on glass corning substrate with 175 watts (a)200\degree C and (b)250\degree C substrate heating temperature. It has been observed that the refractive index increases with the increase in annealing temperatures. This change in refractive index is in perfect agreement with the result obtained by the study of x-ray spectroscopy where the thin film becomes oxygen deficient when it is subjected to higher annealing temperatures.
Figure 4.20 The percentage transmission of the ZnO:Al thin films after annealing at higher temperatures for film deposited at 175 watts (a)200°C and (b)250°C substrate heating temperature
4.3.3 Electrical characterization

Figure 4.22 shows the plot of resistivity with respect to annealing temperatures for ZnO:Al thin films deposited with 175 watt at 200°C and 250°C substrate heating temperature. Though film deposited with 175 watt and 250°C substrate heating temperature had less resistivity compared to that of the film obtained at 175 watt and 200°C substrate heating temperature, the resistivity of the film deposited with 200°C substrate heating temperature dropped more drastically with the increase in annealing temperature compared to the other. Lowest recorded resistivity was $6.67 \times 10^{-4} \Omega\text{-cm}$ for the thin film deposited with 175 watt, 200°C substrate heating and annealed at 400°C. Drop in resistivity is attributed to formation of more oxygen deficiency caused in the thin film when annealed at higher temperatures.
Figure 4.22 The variation of refractive index \( n \) as a function of wavelength for ZnO:Al thin films annealed at various high temperatures for a film deposited on glass corning substrate with 175 watts (a)200°C and (b)250°C substrate heating temperature.
4.4 Deposition with substrate heating, DC bias and no oxygen flow

In this section the thin film deposited with the parameters listed in the section 3.4 is studied. All the film obtained by this method showed the pealing off from the substrate. The peel off increased with the increase in DC bias voltage. The pealing off of the thin film which was deposited can be attributed to the stress while deposition. The film could not be deposited with DC biasing below 60V using the sputter system because of the instability of the voltage controller at lower DC bias voltages. Some part of the deposited thin film which showed no peel off measured low resistivity. Therefore, thin film obtained using DC biasing at very low voltages may yield AZO thin film with low resistivity.
4.5 Deposition with substrate heating and with hydrogen flow in the chamber

Deposition of aluminum doped thin films was carried out using RF sputtering with different power, substrate heating and hydrogen/argon gas flow in the chamber. Using the parameters provided in the section 3.5, a good conducting and transparent ZnO:Al thin films was successfully obtained. Later, electrical, material and optical characterization was carried out to understand the change in properties of the deposited thin film with change in deposition parameters.

Figure 4.24 shows the deposition rate of aluminum doped thin films as a function of (a) power of deposition and (b) substrate heating temperature. In the figure, 4.24a it is observed that the deposition rate continuously increased from ~18.73Å/min at 125 W to ~32.1 Å/min at 175 W for 200°C substrate temperature and hydrogen/argon gas flow in the chamber. It can be observed that the deposition rate samples deposited with hydrogen/argon flow in the chamber is lesser compared to samples deposited with only argon flow in the chamber, keeping all the other deposition parameter similar. This increase in deposition rate with the increase in deposition power indicates that the number of atoms sputtered from the target is proportional to the increase in the RF power. In figure 4.24b it is observed that the deposition rate increases till the 150°C substrate heating temperature and then there is a continuous decrease in deposition rate. The decrease in deposition rate after 150°C substrate heating temperature is attributed to the increase in the number of atoms bolting out from the substrate surface due to thermal desorption [21]. Limited surface mobility of the adatom at low substrate temperatures also leads to higher growth rate [21].
Figure 4.24. Deposition rate with respect to (a) power of deposition (b) different substrate temperature.

4.5.1 Material characterization

Material characterization for the AZO thin films obtained for the deposition condition discussed in the section 3.5 is presented here.

X-ray diffraction (XRD)
The ZnO:Al thin film deposited at conditions described in the section 3.2 is studied for the crystal orientation, crystallinity and crystallinitie size using x-ray diffraction measurement.

Figure 4.25 shows the diffraction pattern for the sample deposited at various (a) substrate heating temperature and (b) deposition powers. The diffraction pattern obtained for the AZO thin films indicated that these films have polycrystalline hexagonal wurtzite structure with the orientation perpendicular (002) to the substrate surface (c-axis orientation) at 34.4(2-theta). Large peaks were observed at 34.4(2-theta) which determines the presence of (002) crystal orientation in the deposited film. Film deposited at $200^\circ$C and 125 watts showed peaks at 36.25(2-theta) indicating (101) and texture growth. From the figure it can be observed that the peaks becomes more intense at lower substrate heating temperature and lower deposition powers. Therefore it can be stated that the films deposited at lower substrate heating and lower power of deposition has higher cristallinity. FWHM of these films on the contrary increases with the decrease in substrate heating and power of deposition. Though there is very small changes in the location of the measured diffraction peaks, it is attributed to the error in loading of sample while measurement. The change in the location of the measured diffraction peaks also depend on the amount of aluminum incorporation in the film [25]. As the incorporation of aluminum in the film is minimal, the reason for the change in the position of the diffraction peaks due to amount of aluminum incorporation in the film can be eliminated. The grain size of the films was found to be in the order of 15-20 nm.
Figure 4.25 shows the diffraction pattern for the sample deposited at various (a) substrate heating temperature and (b) deposition powers.
**X-ray Photoelectron Spectroscopy (XPS).**

The chemical composition and atomic concentration in the deposited aluminum doped zinc oxide is studied using the X-ray Photoelectron Spectroscopy (XPS).

Figure 4.26 (a) and (b) shows the relative atomic concentration of zinc and oxygen obtained using XPS surface scan for the samples deposited at different substrate heating and deposition power respectively. Zinc content in the film increases with the increase in the substrate heating temperature until 200\(^{0}\)C for the thin film deposited at 150watt. There is a slight decrease and increase in the zinc and oxygen content respectively, in the film deposited at 250\(^{0}\)C. There constant increase in atomic concentration of zinc with the increase in deposition power with 200\(^{0}\)C substrate heating temperature. Power of deposition for both 200\(^{0}\)C and 250\(^{0}\)C substrate heating temperature. Whereas, the atomic concentration of oxygen decreases with the increase in deposition power.

Figure 4.27 shows the relative atomic concentration of zinc and oxygen obtained using XPS surface scan for the samples deposited at different deposition power and 200\(^{0}\)C substrate heating temperature with H\(_2\)/Ar or Ar gas flowing in the chamber. This graph clearly indicates that the samples prepared with addition of hydrogen gas in the chamber had more atomic concentration of zinc and lesser oxygen content when other conditions are kept unchanged.
Figure 4.26 The relative atomic concentration of zinc and oxygen obtained using XPS surface scan for the samples deposited at different (a) substrate heating and (b) deposition power
Figure 4.27 The relative atomic concentration of zinc and oxygen obtained using XPS surface scan for the samples deposited at different deposition power and 200°C substrate heating temperature with H2/Ar or Ar gas flowing in the chamber.

The bonding conditions of oxygen on the surface of ZnO:Al films were investigated using high resolution XPS scans. Figure 4.28 shows the O1s photoelectron peaks in the XPS spectra of ZnO:Al films prepared at 150 watts and 200°C substrate heating temperature with H2/Ar gas flowing in the chamber. The O1s was composed of four peaks (OI, OII, OIII and OIV). The peak OI at at 530.4±0.1eV is attributed to the $\text{O}^{2-}$ ions on the wurtzite structure of hexagonal Zn$^+$ ion array. In other words these include O$^{2-}$ ion surrounded by Zn atom with their full compliment [26, 27, 28]. O$^{2-}$ ions in the oxygen deficient regions of the ZnO matrix is located at 531.4±0.10eV (OII)[29]. The binding energy component located at 532.1±0.15eV (OIII) is attributed to loosely bonded oxygen in the surface of the ZnO:Al thin films[30,31]. These chemisorbed oxygen impurity could be due to O$^{2-}$, O$^-$, O$^{2-}$ O$^{2-}_2$, O$^2_2$ ions [32].
lower binding energy peak at 529.4±0.15eV (OIV) is probably due to oxygen in ZnO structure[30].

Figure 4.28 shows the O1s photoelectron peaks in the XPS spectra of ZnO:Al films prepared at 150 watts and 200°C substrate heating temperature with H2/Ar gas flowing in the chamber.

Figure 4.29 shows the relative strength of O1s peaks for the ZnO:Al thin film prepared with various substrate heating temperature at 150 watt and H2/Ar flowing in the chamber. The relative strength was obtained by dividing the area of the particular peak area by total peak area. From the figure it is evident that most of the oxygen atom was prone to form O²⁻ ions on the wurtzite structure of hexagonal Zn⁺ ion array for all the ZnO:Al thin film deposited with various substrate heating temperature at 150 watt and H2/Ar flowing in the chamber. The relative strength of the O1s peaks remains almost constant for most of the deposited at different substrate temperature. This figure shows that least amount of oxygen is in the form of loosely bonded oxygen in the surface of the ZnO:Al thin films. When Figure.4.29 is compared with
Figure 4.12(a) it can be observed that OIII peak has drastically reduced with the introduction of hydrogen in the chamber. Figure 4.30 shows the relative strength of O1s peaks for the ZnO:Al thin film prepared with deposition power at $200^\circ$C and H$_2$/Ar flowing in the chamber. In this graph it is evident that most of the oxygen atom was prone to form O$^{2-}$ ions on the wurtzite structure of hexagonal Zn$^+$ ion array and least oxygen content is in the form of loosely bonded oxygen in the surface of the ZnO:Al thin films deposited. When Figure 4.30 is compared with Figure 4.12(B) it can be clearly observed that OIII peak has drastically reduced with the introduction of hydrogen in the chamber. The amount of absorbed oxygen species on the surface of the thin film grain boundaries decreased with the introduction of hydrogen gas. These weekly oxygen species were reduced due to desorption on the grain boundaries due to hydrogen [37]. Deposition with hydrogen ambience will make the thin film surface passive from adsorption of further oxygen species [38].
Figure 4.29 shows the relative strength of O1s peaks for the ZnO:Al thin film prepared with various substrate heating temperature at 150 watt and H₂/Ar flowing in the chamber.

Figure 4.30 shows the relative strength of O1s peaks for the ZnO:Al thin film prepared with deposition power at 200°C and H₂/Ar flowing in the chamber.
Figure 4.31 shows the Zn2p$_{3/2}$ photoelectron peaks in the XPS spectra of ZnO:Al films prepared at 150watts, 200°C substrate heating temperature and H$_2$/Ar gas flow in the deposition chamber. From the data obtained for Zn2p$_{3/2}$ in ZAO thin films, a peak was found at 1022.4±0.20eV (ZnI) which is attributed to the presence of Zn2p$_{3/2}$ in ZnO or ZnAl$_2$O$_4$ [33] A vacancy state of Zn$^{2+}$ is formed by all the maximum number of Zn atoms in the oxygen deficient ZnO$_{1-x}$ matrix[34] The peak at the binding energy 1021.4±0.20eV (ZnII) is attributed to the presence of metallic Zn atom in the thin film [33,35]. These metallic zinc exists as an interstitial atom in ZnO crystalline lattice [36]. the relative strength of peak ZnI is always more than peak ZnII at all deposition power and substrate heating. There has been no major change in the relative strength of peak ZnI with the change in deposition conditions. It can be noted that most of the zinc in the deposited thin film is in the form of ZnO or ZnAl$_2$O$_4$ and the presence metallic zinc in the deposited thin film is relatively less. These metallic zinc may exist as interstitial atoms or at grain boundaries.
Figure 4.31 shows the Zn2p\(3/2\) photoelectron peaks in the XPS spectra of ZnO:Al films prepared at 150 watts, 200°C substrate heating temperature and \(H_2/Ar\) gas flow in the deposition chamber.

4.5.2 Optical characterization

Aluminum doped a zinc oxide thin film which is deposited with various deposition powers and substrate heating with \(H_2/Ar\) flow in the chamber is characterized for the optical properties. Figure 4.32 shows the percentage transmission of the films deposited with different (a) substrate heating at 150 watts and (b) deposition power at 200°C with \(H_2/Ar\) gas flow in the chamber. Average percentage transmission of most of the films is between 92-95%. It can also been observed that films deposited at the higher power and higher substrate temperature shows that its transparency does not have much effect in the visible region, whereas, the film has become more opaque in the IR region with the increase in the deposition power and substrate heating temperature.
Figure 4.32 shows the percentage transmission of the films deposited with different (a) substrate heating at 150 watts and (b) deposition power at 200°C with H2/Ar flow in the chamber.
Figure 4.33 shows the optical band gap obtained from Tauc Plots for different ZnO:Al films deposited with different (a) substrate heating temperature at 150 watt and (b) Powers at 200°C with H2/Ar gas flow in the chamber
Optical Band gap was obtained through Tauc Plot which is represented by the Tauc equation [19]. Figure 4.33 shows the optical band gap obtained from Tauc Plots for different ZnO:Al films deposited with different (a)substrate heating temperature at 150 watt and (b) powers at 200°C with H₂/Ar gas flow in the chamber. Optical Band gap of the films deposited is measured to be around 3.15eV, which has little changes with the change in deposition conditions.

4.5.3 Electrical characterization

Figure 4.34 shows the plot of resistivity for the deposition carried out at various substrate heating temperatures and 150 watt deposition power with H₂/Ar gas flow in the chamber. Resistivity decreases continuously as the substrate heating temperature increases. A AZO thin film showed lower resistivity for the film deposited at higher substrate heating temperature. There is an increase in the resistivity for the film deposited at 250°C and 150 watts deposition power. Increase incorporation of zinc in the thin film and decrease in the amount of oxygen with the increase in deposition power and increase in substrate heating temperature is the major reason for the drop in resistivity.

Figure 4.35 shows the comparison of resistivity of the film with and without hydrogen flow in the chamber for the thin film deposited at 200°C substrate heating temperature and various deposition powers. This figure clearly shows that the resistivity has dropped with the introduction of hydrogen gas in the chamber. Least resistivity of a ZnO:Al thin film obtained was $1.83 \times 10^{-4} \Omega \text{cm}$ for the film deposited at 125 watts deposition power and 200°C substrate temperature. The decrease in resistivity with the introduction of hydrogen gas is due to the adsorption of oxygen species in film grain boundary.
Figure 4.34 shows the plot of resistivity for the deposition carried out at various substrate heating temperatures and 150 watt deposition power with H$_2$/Ar gas flow in the chamber.

Figure 4.35 shows the comparison of resistivity of the film with and without hydrogen flow in the chamber for the thin film deposited at 200°C substrate heating temperature and various deposition powers.
CHAPTER 5 CONCLUSION

Aluminum doped zinc oxide thin film was deposited using different deposition powers, different substrate heating and with and without oxygen flow into the sputtering chamber. RF sputtering using oxygen flow did not yield a low resistive AZO thin film though the film was transparent. Low resistive and highly transparent AZO thin film was successfully obtained with only argon flow in the system along with substrate heating. The AZO thin film obtained using deposition at higher powers does not affect the transparency of the thin film in visible region but percentage transmission decreases in the infrared region. The Band gap of these thin films deposited does not change much with the change in deposition conditions. The roughness of the deposited AZO thin film decreases at higher power. The film obtained were found to be polycrystalline with the prominent orientation (002) perpendicular to the substrate surface where crystallinity increases with the increase in substrate heating and decreased with the increase in deposition power. Increase in power of deposition increases the incorporation of zinc and aluminum in the film. It also causes increase in oxygen deficiency at higher substrate temperatures which is the main reason for the decrease in resistivity of the ZnO:Al thin film deposited.

Annealing of the thin film deposited at 175 W and at both 200°C and 250°C where carried out. This caused the further decrease resistivity of the AZO thin film. XPS result showed that this decrease in resistivity is due to increase in oxygen deficiency in the thin film after annealing at high temperatures. Transparency of the annealed thin film deposited decrease with the increase in annealing temperature. There was a increase in refractive index of the annealed...
film with the increase of annealing temperature which agrees with the XPS results indicating the increase of oxygen deficiency in the deposited thin film.

Aluminum doped zinc oxide was deposited by applying DC bias voltage. Peeling off the deposited film was observed that increased with the increase in DC bias voltage. The peel off of the deposited film may be attributed to the increase in stress on the film during deposition. The unpeeled part of the film measured low resistivity. Hence, a film deposited at very low DC bias may yield a AZO thin film with low resistivity.

Later, ZnO:Al doped thin film were deposited at different substrate heating temperature and deposition powers with constant H₂/Ar gas flow in the chamber. It is found out that the resistivity dropped immediately with the introduction of hydrogen which is due to adsorption of oxygen species in thin film grain boundaries. 1.83×10⁻⁴ Ωcm resistivity was measured for the sample deposited at 200°C and 150 watts deposition power. XRD results revealed that the crystallinity of the thin film increased with the decrease in both substrate heating temperature and deposition power. The ZnO:Al thin film obtained with the H₂/Ar gas flow in the chamber yielded a transparent and very good conducting film.
LIST OF REFERENCES


