CHAPTER - 3
CHAPTER (3)

EXPERIMENTAL
DEPOSITION AND CHARACTERIZATION TECHNIQUES

3.1: INTRODUCTION

The present study has been done with intention of investigating the feasibility of the Chemical Spray Pyrolysis (CSP) technique to deposit best quality undoped and Al, Cu and Cd doped ZnO films for TCC applications. This technique was preferred over the other techniques like sputtering, CVD, etc. because it offers the following features:-

1. simple, inexpensive and ease of operation,
2. feasibility of commercialization,
3. moderate operating temperatures (200–500°C),
4. versatility for large area depositions,
5. offers easy way for dopant incorporation and
6. easy control on film thickness and deposition rate.

3.2: CHEMICAL SPRAY PYROLYSIS (CSP) PROCESS

Spray pyrolysis is based on the pyrolytic decomposition of a metal organic compound dissolved in a liquid mixture when it is sprayed onto a preheated substrate. The method depends on the surface hydrolysis of metal chloride or acetate on a heated substrate surface. Spray pyrolysis process consists of a thermally stimulated chemical reaction between clusters of spraying solution and/or vapor of different chemical species. Every sprayed droplet reaching the surface of the hot substrate undergoes pyrolytic (endothermic) decomposition and forms single crystalline or polycrystallites film as a product. Other volatile byproducts and solvent escape in the vapor phase and are exhausted out of the system. The film deposition occurs due to pyrolytic reaction of jet of fine droplets of precursor solution driven by the carrier gas on the surface of the hot substrate. The substrate provides necessary thermal energy to constituent species for decomposition and subsequent recombination, resulting in uniform, pinhole free coherent film. The structural and optoelectronic properties of deposited films depend on various process parameters [1].

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3.3: PROCESS PARAMETERS INVOLVED IN CSP TECHNIQUE

Though CSP technique appears very simple, the optimization of process parameters to deposit good TCC is quite a laborious activity. This is because of the large number of interrelated process parameters involved, some of which are difficult to assess. The main process parameters which affect the structural and optoelectronic properties of the deposited film are as given below,

1. Substrate Temperature ($T_S$),
2. Precursor solution Composition and Concentration ($S_C$),
3. Solution flow rate ($S_f$),
4. Spray nozzle diameter,
5. Spray nozzle to substrate distance,
6. Air flow rate ($A_f$),
7. Volume of solution sprayed ($V$) and
8. Dopant concentration.

3.3.1: Substrate Temperature ($T_S$): The substrate temperature $T_S$ decides the state of oxidation of a film. The lower limit of the substrate temperature is imposed by the reaction itself. On the other hand the upper limit must be selected on the basis of quality of film. The nonstoichiometry, unintentional and intentional doping are also governed by the substrate temperature [2] which in turn affect electro-optical properties. Further the structural properties of a film also get affected by substrate temperature [3,4]. Low temperature deposition yields amorphous films and high temperature deposition results in polycrystalline films.

3.3.2: Precursor Solution Composition: An aqueous/alcoholic solution of inorganic or organometallic compound is preferred for spray pyrolysis. The compound should satisfy following necessary requirements [5],

a) Decomposition temperature of compound should not be very high,

b) Decomposition reaction should be thermodynamically favored so as to obtain deposition of desired coating without any residual contamination, and

c) Products of decomposition other than desired one (ZnO) should be volatile so that they can easily exhaust out.

Based on these conditions Zinc acetate based precursor is preferable over Zinc chloride or Zinc nitride. Alcohol (methanol/ethanol) is used for the dilution of aqueous solution. The high vapor pressure and low surface tension of alcohol enables
the formation of fine droplets which are essential for growing nanocrystalline thin films. Dilution by alcohol governs the uniformity of thin film. Alcohol also acts as a reducing agent which controls the oxygen deficiency [6]. The upper limit of dilution is decided by the growth rate and quality of thin film.

3.3.3: Solution Flow Rate ($S_f$): Solution flow rate $S_f$ along with air flow rate $A_f$, decides the size of the impinging spray droplet. $S_f$ control achieved with peristaltic pump can provide sufficient time for nucleation and recrystallization to occur to produce better quality TCO films.

3.3.4: Spray Nozzle Diameter: Spray nozzle diameter along with $S_f$, $A_f$, and air pressure governs the droplet size and hence the uniformity of a film. As a result the optoelectronic properties of deposited film are influenced. Thermal shocks due to bigger droplets from nozzle (diameter $> 1$mm) lead to cracking of the substrate, whereas, powdery and non adherent films are due to smaller droplets from nozzle diameter $< 0.2$ mm. The spray nozzle diameter (0.3 to 0.5 mm) was optimized for depositing high quality ZnO films with good repeatability.

3.3.5: Spray Nozzle to Substrate Distance: The time of transit for spray droplet to reach the substrate surface is decided by nozzle to substrate distance. Due to fast piling up of layers, strenuous, incompletely oxidized and highly resistive thin films are formed for small distances [7]. However, for larger distances, droplets evaporate before reaching the substrate and result in formation of powdery films.

3.3.6: Air Flow Rate ($A_f$): Air flow rate $A_f$ determines the size, velocity distribution and force of the impinging droplet [8]. Films deposited at lower flow rates are non uniform while high flow rate results in powdery films.

3.3.7: Volume of the Solution Sprayed: The film thickness increases with increase in volume of solution sprayed [9]. Though increase in film thickness increases the electrical conductivity of the film but subsequently causes transmittance to decrease. Hence an optimum thickness is a compromise between the transparency and the conductivity of the film.

3.3.8: Dopant Concentration: The presence of impurity atoms at interstitial sites enhances the electrical conductivity. Each addition of a dopant impurity atom in a host lattice creates one extra charge carrier and thus increases the conductivity of
deposited layer. For the n-type doping [10] lower valent anion or higher valent cation having size closer to the host ion should be used. Dopant incorporation also modifies the growth mechanism which may lead to an increase in grain growth [11].

3.4: EXPERIMENTAL SET UP

The schematic of spray pyrolysis system is shown in figure 3.1. The system consists of following components,

1. Spray nozzle,
2. Peristaltic pump,
3. Heater with thermal shield,
4. Temperature controller unit,
5. Air compressor,
6. Exhaust system.

Details of these components are discussed below.

Figure 3.1: Schematic of Chemical Spray Pyrolysis (CSP) set-up used for synthesis of ZnO thin films.
3.4.1: Spray Nozzle: Glass spray guns are non-corrosive and preferred over the metal spray guns. In the present case glass spray nozzle (Optimized diameter: 0.3 mm) was used for spraying the solution on hot substrate. In conventional spray gun (Nozzle with precursor solution reservoir), solution flow rate ($S_f$) depends on the air flow rate ($A_f$). $S_f$ increases with increase in $A_f$ which causes the large solution quantities to be sprayed in a short time. This hampers the nucleation process because of incomplete pyrolysis and a drop down of substrate temperature, due to which nonuniform and powdery films are obtained. Higher $A_f$ is essential for formation of fine droplets which is the prime requirement for synthesis of nanocrystalline films.

The success of most spray coating applications will depend on evenly distributing the spray’s volume flux over the target area. The volume flux distribution can be described as the variation of spray density over a spray area. The volume flux distribution for conventional atomizer nozzle generally consists of high concentration of volume at the center of the spray and lower concentration towards the edge. Figure 3.2 shows the photograph of conventional spray gun and its plausible swirling spray distribution. The bell cup atomizer in conventional spray gun causes the development of swirling flow in the spray jet due to which volume flux distribution over spray area becomes uneven and nonuniform. This Gaussian volume flux distribution (with the peak of volume flux directly under the nozzles centerline) limits the uniformity of the films deposited using the conventional nozzle. It is critical to minimize the swirling rate to obtain the uniform film deposition over a large area. High air flow rates can make volume flux distribution even and uniform up to certain extent but causes the large solution quantities to be sprayed in a short time which results in formation of powdery films.

Figure 3.2: A) Photograph of Conventional Spray Gun and B) its plausible swirling spray distribution/pattening.
To avoid this problem we replaced conventional spray gun with just a spray nozzle to which precursor solution was fed using peristaltic pump. The nozzle enables to try several principals that may improve the atomization of precursor jet. This is an external-mix two fluid atomizer. This nozzle features coaxial liquid and air inlets. The liquid is directed through to a nozzle externally by peristaltic pump. The liquid exits the nozzle and makes contact with the atomizing air initiating primary breakup. The use of this nozzle has enabled us to obtain a solid conical spray pattern of small droplet size. The swirling effects were minimal and volume flux distribution though Gaussian, was more evenly distributed when the spray pattern was analyzed. The analysis of spray pattern for conventional nozzle and new nozzle was done by spraying water on cardboard sheet. A few preliminary experiments with new nozzle have indicated that good control of droplet size may be obtained through design of the nozzle. The figure 3.3 A, B, C and D shows photographs of new spray gun, its spray distribution and its plausible volume flux distribution.

Figure 3.3 A) Photograph of new spray gun, B) its spray distribution, C) nozzle schematic and D) plausible Gaussian distribution of volume flux ($V_{flux}$)
3.4.2: **Peristaltic Pump:** Peristaltic pump (Make: Remi) with fine adjustment was used to control solution flow rate to spray nozzle at desired flow rate. This was done to have no control of air flow rate ($A_f$) on solution flow rate ($S_f$). Both $A_f$ and $S_f$ were optimized independently to synthesize nanocrystalline ZnO films with best optoelectronic properties. This also helped in maintaining the substrate temperature and provided sufficient time for nucleation to occur on substrate resulting in deposition of uniform non powdery films.

3.4.3: **Heater with Thermal Shield:** A 3 kW imported coil (Make: Baker UK) was used to heat the circular stainless steel block (Radius: 20 cm, thickness: 1.5cm) (substrate holder). Properly insulated housing was used around the substrate heater to avoid heat loss. This was done to avoid drop in substrate temperature due to spraying of solution and dissipation. Insulated housing of asbestos sheet (Thickness: 3mm) wrapped in glass wool (Thickness: 2.5cm) and stainless steel was used as thermal shield to avoid dissipation of heat.

3.4.4: **Temperature Controlling Unit:** A temperature controller (Make: Gaurav Engineers) having an accuracy of ±2 °C with a contactor relay coil was used to control the temperature of the substrate holder. Chromel-Alumel thermocouple was used to measure the temperature. Biasing to heater was given using dimmer stat (0-280V).

3.4.5: **Compressor:** Ultra filtered compressed air (8 kg/cm$^2$) (Compressor: make Ingersoll Rand, UP 5-5) was used as a carrier gas for all depositions. The ultra filtering of air was achieved using three stage moisture and dust filters set of (make: Ingersoll Rand, Kushako 1µm) before passing air to the spray nozzle. The air flow controller (Eureka make: 0-25 lit/min) with fine needle valve was used to control the air flow rate.

3.4.6: **Exhaust System:** An exhaust system becomes a necessary part of the spray unit to exhaust out hazardous gases and fumes generated due to spraying of precursor solution. Exhaust fan and blower arrangement was used at the top of fuming chamber as a very efficient exhaust system.

3.5: **OPTIMIZATION OF PROCESS PARAMETERS**

The demand for superior structural and optoelectronic properties for smart TCO based coatings led to the development of various deposition techniques. Synthesis of
good TCO films requires optimizing process parameters in CSP techniques. In the present work we have optimized process parameters for depositing better quality ZnO thin films by varying only one process parameter at a time and keeping all other parameters constant. The sheet resistance and figure of merit of the films was a criterion for optimization of a particular process parameter [12-13]. More the figure of merit and less the sheet resistance better is the transparent conducting coating.

3.6: CHARACTERIZATION OF THIN FILMS

Undoped and Al, Cu and Cd doped ZnO films were deposited using spray pyrolysis. The effect of each process parameter on the structural and optoelectronic properties was studied. The structure, morphology, electrical and optical properties of undoped and Al, Cu and Cd films were investigated using following characterization techniques:

Structural Properties and Morphology:
1. Low angle X-ray Diffraction
2. Scanning Electron Microscopy
3. Atomic Force Microscopy

Optical Properties:
1. UV-VS-NIR Spectroscopy

Electrical Properties:
1. Resistivity by four point probe technique
2. Hall effect measurement at room temperature (Van der Pauw Geometry)

3.6.1: Low angle X-ray Diffraction: The Bruker (Model D8 – Advanced) X-ray diffraction (XRD) system was used to study the structural properties of the ZnO thin films. The analysis was made with Cu Kα radiation (λ= 1.542 Å) in the range 20°-80° with slow scanning speed 2°/min and step width of 0.02°. The X-ray analysis can be used to determine the orientation of grains [4], lattice constants [14], micro-structural properties [15], grains size [16] and texture coefficient [17].

X-ray diffraction measurements for doped and undoped ZnO thin films revealed that the films are of polycrystalline in nature with a hexagonal Wurtzite structure with most preferred orientation along c-axis [002] plane. The relative intensities of various planes were different than the corresponding intensities registered in the ASTM data
sheet, indicating that the films are preferentially oriented. The contribution of other orientations though less was also detected. The structural properties have been studied by using Texture Coefficients, Standard Deviation [18] and grain size. Texture coefficients represent the extent of preferred orientation of a particular plane taking into account other planes observed in the X-ray diffractionogram. Texture Coefficient of any plane \((h k l)\) determined using a powder pattern (ASTM data) always equals to unity. In thin film form it differs from unity, which is mainly due to the existence of preferred orientation in the film. The texture coefficients (TC) of preferred orientation were determined by Barret–Massalski formula [17]. The texture coefficient TC \([h k l]\) is given by

\[
TC[hkl] = \frac{I(hkl)}{I_0(hkl)} = \frac{1}{N} \sum_1^N \frac{I(hkl)}{I_0(hkl)}
\]

where TC\([h k l]\) is the texture coefficient of \((h k l)\) plane, \(I(h k l)\) is the relative intensity of \((h k l)\) plane, \(I_0(h k l)\) is the relative intensity of the corresponding plane given in ASTM data and \(N\) is number of reflections.

Standard deviation represents the deviation of structure of thin film from the regular powder pattern. The nucleation and reorientation effects can also be studied using standard deviation. The standard deviation \((\sigma_g)\) of the texture coefficient of various planes from their respective ASTM values was used to analyze the growth mechanism [18]. In comparison with regular ASTM data the standard deviation is given by,

\[
\sigma_g = \frac{1}{N} \left[ \sum_1^N TC[hkl]^2 - 1 \right]^{1/2}
\]

Grain size of the crystallites in the film co-relates the dependence of structural and electrical properties. The grain size of the film was estimated from the Full Width at Half Maximum (FWHM) of the peak with highest intensity for all films. Slow scan XRD having step size \(0.02^\circ\) was used to calculate the average crystallite size \((D)\) of the ZnO film from the classical Scherrer formula [16]:

\[
D = \frac{k \lambda}{\beta_{1/2} \cos \theta_b}
\]
where the constant k is the shape factor usually equal to 1, B is Full Width at Half Maximum (FWHM) of the diffraction peak expressed in radian, \( \lambda \) is the wavelength of X-ray used and \( \theta \) is Bragg's angle. For this purpose, full width at half maxima of only high intensity reflection was considered. It is well known that the XRD peak can be widened by internal stress and defects, so the mean grain size estimated by this method is normally smaller than the actual value.

For undoped and Al, Cu and Cd doped ZnO films lattice parameters were calculated using a method of successive iterations [16]. High angle reflections with \( 2\theta > 50^\circ \) were considered in order to improve the accuracy. In this method, first step is to calculate the approximate values of the lattice parameters ‘a’ and ‘c’ viz. \( a_1 \) and \( c_1 \) from the positions of the two reflections occurring at highest \( 2\theta \) values. The values of ‘a’ and ‘c’ from all other (h k l) reflections above 50° were then calculated using following formulae for ZnO structure with the trial values of \( a_1 \) and \( c_1 \).

\[
a = \frac{\lambda}{2\sin \theta} \left[ (h^2 + k^2) + \frac{l^2}{(a_1)^2} \right]^{1/2}
\]
and
\[
c = \frac{\lambda}{2\sin \theta} \left[ (c_1)^2 (h^2 + k^2) + \frac{l^2}{(a_1)^2} \right]^{1/2}
\]

The values of ‘a’ and ‘c’ thus obtained were plotted against \( \cos^2 \theta \). The more accurate values of ‘a’ and ‘c’ i.e. \( a_2 \) and \( c_2 \) were obtained by the extrapolation of these curves to \( \cos^2 \theta = 0 \). This process was repeated with the new value of axial ratio \( c_2/a_2 \) to yield still more accurate values of the parameters namely \( a_3 \) and \( c_3 \). It was found that generally two or three iterations are sufficient to obtain lattice parameters with highest accuracy.

3.6.2: Scanning Electron Microscopy: The scanning electron microscope (SEM) is electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography. SEM can produce very high-resolution images of a sample surface. SEM micrographs have a very large depth of field yielding
characteristic three-dimensional structural information useful for understanding the surface morphology of a sample. A wide range of magnifications is possible, ranging from about x 25 (about equivalent to that of a powerful hand-lens) to about x 250,000, about 250 times the magnification limit of the best light microscopes. A Field Emission Scanning Electron Microscope (FE-SEM: Make: JEOL JSM 6700F) and Scanning Electron Microscope (SEM: Make: JEOL JSM 6360A ) was used with maximum magnification (up to x 100,000) to investigate the surface morphology and topographical changes in undoped and doped ZnO films deposited at optimized process parameters. The FE - SEM was operated at an accelerating voltage 10 kV, and the samples were not coated with any conductive layers before imaging.

3.6.3: Atomic Force Microscopy (AFM): It provides non-destructive three-dimensional high-spatial resolution real-space images of surfaces by measuring attractive or repulsive forces between a tip and the samples. The AFM employs an optical detection system in which the tip is attached to the underside of a reflective cantilever. A diode laser is focused onto the back of a reflective cantilever. As the tip scans the surface of the measured sample, moving up and down with the contour of the surface, the laser beam is deflected off the attached cantilever into a position-sensitive detector. The detector measures the vertical deflection of the cantilever, which indicates the local sample height. The resulting image resembles an image on a television screen. The AFM has several advantages over the Scanning Electron Microscope (SEM). Unlike the electron microscope which provides a two-dimensional projection or a two-dimensional image of a sample, the AFM provides a true three-dimensional surface profile. Additionally, samples viewed by AFM do not require any special treatments (such as metal/carbon coatings) that would irreversibly change or damage the sample. While an electron microscope needs an expensive vacuum environment for proper operation, most AFM modes can work perfectly well in ambient air or even a liquid environment. In principle, AFM can provide higher resolution than SEM.

AFM images can also be affected by hysteresis of the piezoelectric material and cross-talk between the (x,y,z) axes that may require software enhancement and filtering. Such filtering could "flatten" out real topographical features. However, newer AFM use real-time correction software or closed-loop scanners which
practically eliminates these problems. Once images are captured during real-time operation, a wide variety of analysis functions are available in the analyzing menu of equipment. Apart from 2D images of the surface of samples obtained with up to atomic resolution, AFM can provide real 3D images and quantitative measurements, such as detailed characteristic surface roughness parameters, which are important features of thin-films used in photovoltaic devices.

Some AFM use separated orthogonal scanners (as opposed to a single tube) which also serve to eliminate cross-talk problems. Due to the nature of AFM probes, they cannot normally measure steep walls or overhangs. Specially made cantilevers can be modulated sideways as well as up and down (as with dynamic contact and non-contact modes) to measure sidewalls, at the cost of more expensive cantilevers and additional artifacts. Surface morphology and topographical changes in undoped and Al, Cu and Cd doped ZnO films deposited with optimized parameters were analyzed by AFM technique.

3.6.4: UV-Visible-Near-Infra-Red (UV-VIS-NIR) Spectroscopy: The sources of loss of light in transparent conductor films are absorption, reflection and scattering. Absorption is primarily due to free carriers. Bound charges and molecular scattering are related to the film material. The spectral selectivity of transparent conducting films [19] makes them extremely useful as heat mirror [20], energy efficient windows, cooling and heating devices. Hence it is necessary to know how transmittance and reflectance of the film varies with incident wavelength (\(\lambda\)) viz. absorption-(Ultraviolet region \(\lambda<0.35\mu m\)), transmittance-(visible region \(0.35\mu m<\lambda<0.8\mu m\)) and reflectance-(infrared region \(\lambda>0.8\mu m\)). The film response to incident wavelength can be enhanced by the doping of desired impurities.

The optical transmittance and absorptance at normal incidence for ZnO: X (X = Al, Cu and Cd) films was measured with double beam Shimadzu Spectrophotometer (model: UV-1650PC, wavelength accuracy: \(\pm0.5\)nm, reproducibility \(\pm0.1\)nm) in the spectral region 200 nm to 1100 nm using a glass substrate as reference. The powerful, flexible and easy to use UV Probe software with very good processing capabilities was used to analyze the data from spectrometer. From this data and using analytic technique developed by Manifacier et al. [21] thickness of the films was calculated.
The Energy Band Gap ($E_g$) is the minimum energy required for exciting a charge carrier from the valence band to the conducting band. In general, in pure ZnO film, $E_g$ is energy separation between the band edges. In doped semiconductors, the donor electrons occupy states at the bottom of conduction band. Thus, $E_g$ is the energy difference between the states with Fermi momentum in conduction and valence bands. The blocking of low energy transition is known as the Burstein-Moss shift and increases the optical gap by the energy $\Delta E_{BM}$ which depends on effective masses of electron and hole in conduction and valence bands. The energy band gap ($E_g$), of the films was calculated from the dependence of the absorption coefficient ($\alpha$) on the photon energy ($h\nu$) considering that ZnO is a direct band gap semiconductor [11,22]. For the direct allowed transition, absorption coefficient $\alpha$ [22,23] is given as,

$$\alpha \propto (h\nu - E_g)^{1/2}$$

$$\alpha^2 = A (h\nu - E_g)$$

Thus the energy gap can be calculated by plotting $\alpha^2$ versus photon energy ($h\nu$) and then extrapolating linear portion of the curve to energy axis. The visible and near IR regions are the high transparent regions for the transparent conducting films due to wide band gap ($E_g \sim 3.3$ eV). The transmission in this region is limited by,

1. Reflection losses that include both spectral and scattered components
2. Absorption in the film which is primarily due to the free carriers [19,20]
3. Variation in transmission that may occur due to interference phenomenon related to the thickness of film.

The visible and near infrared region is the transparent region of the transparent and conductive films. The variation in transmission is due to interference phenomena. The average transmission is about 90% up to a region where free carrier absorption begins. The refractive index of glass substrate is about 1.5 and since film has relatively high indices, reflection is then the main source of loss of light. At a minimum of transmission and for normal incidence of the impinging light, we have

$$T_{\text{min}} = \frac{4n_f^2n_s}{n_f^2 + n_s^2}$$

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$n_f$ and $n_s$ being the film material refractive index and substrate refractive index respectively. The value of film material refractive index ($n_f$) can be deduced for the wavelength at the minimum of transmission, $\lambda_{\text{min}}$.

\[
\begin{align*}
    n_{f1} &= \left( \frac{n_s(2-T_{\text{min}})+2n_s(1-T_{\text{min}})}{T_{\text{max}}} \right)^{1/2} \\
    n_{f2} &= \left( \frac{n_s(2-T_{\text{max}})+2n_s(1-T_{\text{max}})}{T_{\text{min}}} \right)^{1/2}
\end{align*}
\]

Knowing refractive indices $n_f$, we can use the pattern of transmission with successive minima and maxima to evaluate the thickness ($t$) of the film. In general, when the film thickness increases, grain size becomes larger. A thicker film provides lower resistivity although it implies less transparency. By taking into account the oscillations observed in the transmission spectrum due to interference phenomenon (two maxima or minima) in the visible region ($\lambda < 0.8 \mu m$). The thickness of the films were deduced using formula proposed by Manifacier et al. [21] as

\[
t = \frac{m \lambda_1 \lambda_2}{2 [n_{f1} \lambda_2 - n_{f2} \lambda_1]}
\]

where $n_{f1}$ and $n_{f2}$ are the refractive indices of the film at wavelengths $\lambda_1$ and $\lambda_2$ respectively (usually in this region, $n_f$ is nearly constant: $n_f \sim n_{f1} \sim n_{f2}$) and $m$ is the number of oscillations between two successive minima at wavelengths $\lambda_1$ and $\lambda_2$. Equation 3.9 works equally well for reflection measurements and it can be used when the film is so thin that there is only one minimum and one maximum. The value of $m$ is then $1/2$. The equation is strictly valid for self-supporting film. If at the second interface, we have a transparent substrate instead of air, there is phase shift difference between the two interfaces, which should be considered. However, this relation will compensate for any phase shift between the two interfaces as long as they are independent of the wavelength. This is a valid approximation in our case.

3.6.5: Resistivity by Four Probe Method: Many conventional methods for measuring resistivity are unsatisfactory for thin films because metal-semiconductor thin film contacts are usually rectifying in nature. Also, there is generally minority
carrier injected in film by current carrying probes. An injected carrier will affect the potential of other points and modulate the resistance of the thin film. The four-point probe method overcomes these drawbacks and offers several other advantages. The resistivity of the film deposited on glass substrate was measured using equally spaced collinear four-point probe technique [24]. The resistivity of the thin film prepared on glass substrate was measured using four-point probe technique. The constant current (dc) was supplied through the two outer electrodes and the floating potential developed across the inner pair electrodes was measured. The four probe resistivity setup arrangement (Make: VHS Electronics, Model: VHS FP – 28) was used with standard constant current source and voltmeter (Make: Scientific Equipments, Model: DEP-Q2). The resistivity for a thin film \((t \ll S/2)\) backed by non-conducting base were calculated using equation

\[
\rho = \frac{4.235V}{I} \times t, \quad \text{and the conductivity of the film}, \quad \sigma = \frac{I}{\rho}
\]

Where \(V\) is the potential developed due to applied current \(I\), and \(t\) is the thickness of the film.

Furthermore, \(R_s = \frac{\rho}{t} = \frac{4.235V}{I}\) gives the sheet resistance \((R_s)\) of the film.

Where, 4.235 is the correction factor as derived by Smits [25].

3.6.6: Figure of Merit for Transparent Conducting Applications: The evaluation of thin film, as a transparent conductive coating is necessary because under optimum deposition conditions visible transmittance and electrical resistivity depend significantly on film thickness. The electrical resistivity decreases with increasing film thickness and adversely affects on its transparency. Ideally, both parameters should be as large as possible. However, the simultaneous accomplishment of maximum transmission and conduction is not possible in most cases. The practical consequence is a trade-off between electrical resistivity and optical transmittance. To minimize this trade-off, a simple definition of figure of merit is used i.e. ratio of average visible transmission to the sheet resistance. This figure of merit, proposed by Haacke [26], is widely used to compare the performance of various transparent conductors over a wide thickness range. This leads to the optimization of process
parameters. Excellent quality TCO film is associated with maximum value of figure of merit. The figure of merit of the films was calculated using the relation [26],

$$\Phi_{TC} = \frac{T^{10}}{R_s}.$$

Where T is the transmittance and Rs is the sheet resistance.

3.6.7: Room Temperature Hall Measurements: The Van der Pauw geometry is a commonly used to measure the sheet resistance of semiconductor thin films [27-28]. In order to reduce errors in the measurements, it requires a symmetrical sample of very small film thickness than the width and length of the film. Also four ohmic contacts require for measurement should be placed on the sample following the conditions that, they must be on the boundary of the film and infinitely small so that any errors will be of the order of D/L, where D and L are the average contact diameter and distance between the contacts. In addition to this, all four contacts should be of the same material (conductive silver paste) to minimize thermoelectric effects. The clover leaf geometry of film is recommended for the measurement but geometry shown in the adjacent figure is also acceptable. The measurements lead to determination of

1. The sheet resistance and the resistivity for a sample of a given thickness.
2. The type of doping (i.e. if it is a p or n-type material).
3. The carrier concentration of the majority carrier (doping level)
4. The mobility of the majority carriers.

Sheet resistance Rs is given by

$$R_s = \frac{\pi}{2ln2} \times (R'+R'') \times f\left(\frac{R'}{R''}\right)$$

where $R'$ is the potential difference between the contacts C and D per unit current through A and B ; $R''$ is the potential difference between the contacts A and D per unit current through contacts B and C.

$f\left(\frac{R'}{R''}\right)$ is the van der Pauw function defined as
The resistivity $\rho$ of the film was calculated as a product of sheet resistance ‘$R_s$’ and film thickness ‘$t$’. To isolate the contribution of carrier concentration and carrier mobility to the resistivity of the films, Hall measurements were carried out at room temperature. For this purpose sample was kept in the magnetic field with 8 - 7 k Gauss. Current $I$ of the order of 1-10 mA was passed through probes A and C. Probes B and D were used to measure the Hall voltage $V_H$. There are a number of voltages [29] which get included in the true value of Hall Voltage. These voltages are due to Nernst effect ($V_N$), Righi-Leduc effect ($V_{RL}$), misalignment in Hall probes ($V_M$), Ettinghaussen’s voltage ($V_E$) and Seebeck or thermoelectric effect ($V_T$). These errors can be eliminated by reversing the current and magnetic field. In the actual measurements one measures the perturbed Hall voltages in the following way.

$$
\begin{align*}
\text{B} + I: & \quad V_{\text{meas}, 1} = V_H + V_E + V_N + V_{RL} + V_M + V_T \\
\text{B} - I: & \quad V_{\text{meas}, 2} = -V_H - V_E - V_N - V_{RL} + V_M + V_T \\
\text{B} + I: & \quad V_{\text{meas}, 3} = -V_H - V_E + V_N + V_{RL} - V_M + V_T \\
\text{B} - I: & \quad V_{\text{meas}, 4} = V_H + V_E - V_N - V_{RL} - V_M + V_T
\end{align*}
$$

Thus one can deduce the true Hall voltage $V_H$ as

$$
\frac{V_1 + V_4 - V_2 - V_3}{4} = V_H + V_E = V_H \quad \text{(Since $V_E$ is very small)}
$$

Knowing the Hall voltage, Hall coefficient $R_H$ and carrier concentration $n$ can be calculated using the formulae

$$
R_H = \frac{V_H \times t}{B \times I}
$$

Knowing the electrical resistivity $\rho$, and Hall coefficient $R_H$, carrier concentration $n$, carrier mobility $\mu$ was calculated.

$$
\eta = \frac{1}{R_H \times e}
$$

$$
\mu = \frac{1}{\eta \times e \times \rho}
$$

In the present work, the effect of doping on the electrical transport phenomenon in ZnO and ZnO:Al, ZnO:Cu and ZnO:Cd films was investigated.
REFERENCES:
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