INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN CHEMISTRY AND PHARMACEUTICAL SCIENCES

(p-ISSN: 2348-5213: e-ISSN: 2348-5221)
www.ijcrcps.com

Research Article

PREPARATION AND CHARACTERIZATION OF ZINC OXIDE THIN FILMS USING SPRAY PYROLYSIS

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Abstract

The paper reports the synthesis of ZnO thin film deposition by Chemical Spray Pyrolysis technique, and Characterization Studies done by Powdered XRD method. The fundamental properties and importance of thin films have been discussed. The interesting properties of thin film and their applications have also been discussed. The thin film techniques, Basic concepts of Chemical Spray Pyrolysis (CSP), and also the preparation methods of zinc oxide thin films have been discussed. The structural properties of the zinc oxide thin film were characterized by X-Ray Diffraction (XRD) method.

Keywords: synthesis of ZnO, Spray Pyrolysis technique, X-Ray Diffraction.

Introduction

Thin film science and technology plays an important role in the high-tech industries. Thin film technology has been developed primarily for the need of the integrated circuit industry. The demand for development of smaller and smaller devices with higher speed especially in new generation of integrated circuits requires advanced materials and new processing techniques suitable for future giga scale integration (GSI) technology. In this regard, physics and technology of thin films can play an important role to achieve this goal. The production of thin films for device purposes has been developed over the past 40 years. Thin films as a two dimensional system are of great importance to many real-world problems. Their material costs are very small as compared to the corresponding bulk material and they perform the same function when it comes to surface processes. Thus, knowledge and determination of the nature, functions and new properties of thin films can be used for the development of new technologies for future applications.

Materials and Methods

Cadmium sulphate was purchased from Sigma Aldrich, India. The host metal such as Zn, Cd, were purchased from S.D. All the chemicals used in the present study were of Analytical grade. Hydrochloric acid, Zing acetate was purchased from Chemical Drug House Ltd., India.

Chemical spray pyrolysis (CSP) Techniques

Chemical Spray Pyrolysis technique has been developed in 1966 by *Chamberlain* and Sharman for the deposition of CdS and CdSe films. Nowadays chemical spray pyrolysis technique has been found to be useful for the preparation of metal oxides, semi conducting oxides, binary and ternary chalcogenides and super conducting thin films of various materials. Materials obtained by CSP find a wide range of applications in solar cells, optoelectronic devices, antireflective coatings, sensors, etc. [19, 20].

Kinetics involved in Spray Pyrolysis

The basic principle involved in chemical spray pyrolysis is that when a droplet of the spray solution reaches the hot substrate, owing to the pyrolytic decomposition of the solution, well adherent films are deposited. In this process the solution is pulverized by means of air and arrives on the substrate placed inside the furnace in the form of fine drops known as aerosols which form a thin layer at the substrates. The phenomenon for the preparation of a metal oxide thin film depends on surface hydrolysis of metal chloride on a heated substrate surface in accordance with the equation,

$$MCl_x + yH_2O \rightarrow MO_y + xHCl$$

where M is the host metal such as Zn, Cd, In etc of the oxide films. The spray nozzle with the help of the carrier gases accomplishes the atomization of the chemical solution into aerosols. The temperature of the substrate is maintained at a constant value by using a temperature controlled furnace or hot plate. In general, the films grown at a substrate temperature less than 300^0C are amorphous in nature. To get polycrystalline films, one needs to employ higher substrate temperatures or post annealing treatment. The film formation depends upon the droplet lending, reaction and solvent evaporation, which relates to the droplet size. When the droplet approaches the substrate just before the solvent is completely removed, that is the ideal condition for the preparation of the film. [20]

Atomization Techniques

The critical operations for the spray pyrolysis technique are

(I) preparation of uniform and fine droplets and

(II) the controlled thermal decomposition of these droplets in terms of environment, location and time.

Generally commercialized nozzle atomizers are used to spray solutions for thin film preparation. However, such nozzle atomizers are neither sufficient to obtain reproducibly micrometer or submicron size droplet nor to control their size distribution. Consequently, some new or modified spray atomization techniques have been developed recently and used effectively for thin film preparations [21]. The modified spray atomization techniques are given below:

- *Ultrasonic nebulized atomization*
- *Improved spray pyrohydrolysis*
- *Corona spray pyrolysis*
- *Electrostatic spray pyrolysis*
- *Microprocessor based spray pyrolysis*

Kinetics of growth

Thin-film deposition, using the spray pyrolysis technique, involves spraying a metal salt solution onto a heated substrate (Fig 3.4). Droplets impact on the substrate surface, spread into a disk shaped structure, and undergo thermal decomposition. The shape and size of the disk depends on the momentum and volume of the droplet, as well as the substrate temperature. Consequently, the film is usually composed of overlapping disks of metal salt being converted into oxides on the heated substrate.

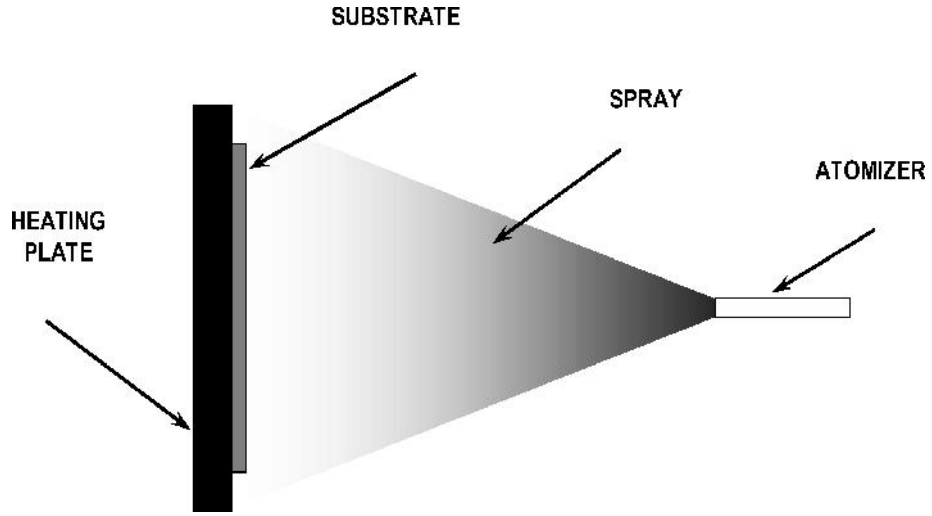

Fig 1: Schematic diagram of Chemical Spray Pyrolysis

Reparation of zno thin film by CSP Method

Preliminary Steps for Preparing ZnO Thin Film

Choose a suitable substrate, spraying nozzle and burette which are clean. Take suitable amount of solution of the constituent atoms and its concentration. The carrier gas pressure, volume of the solution, nozzle substrate distance, rate of flow of solution and the substrate temperature should be kept constant throughout the spray process.

Parameters of chemical spray pyrolysis method

The properties of the thin films deposited, mainly depend upon the following properties:

- Substrate temperature
- Carrier gas pressure
- Volume of the solution
- Solution and its concentration
- Rate of flow
- Nozzle-substrate distance

Experimental procedure for chemical spray pyrolysis zinc oxide (ZnO) thin film

a) Physical Properties of Zinc acetate dihydrate [23]

Table 1: summarizes some important physical parameters of Zinc acetate dihydrate

Zinc acetate – Properties	
IUPAC Name	Zinc acetate
Other Names	Zinc salt, Zinc(II) salt, Zinc diacetate
Molecular formula	$C_4H_{10}O_6Zn$ (dihydrate)
Molar mass	219.50 g/mol (dihydrate)
Appearance	White solid (all forms)
Density	1.735 g/cm^3 (dihydrate)
Melting point	Decomposes 237 °C (dihydrate loses water at 100 °C)
Boiling point	Decomposes
Solubility in water	43 g/100 mL (20 °C, dihydrate)
Solubility	soluble in alcohol
Structure	
Coordination geometry	octahedral (dihydrate)
Molecular shape	Tetrahedral

b) Preparation of ZnO Thin Films

Zinc Oxide thin films were prepared with Zinc acetate (dihydrate) as precursor solutions using Chemical Spray Pyrolysis method.

The deposition system consists of five sections which include:

- Electric oven
- Digital temperature controller
- Burette
- Nozzle and
- Air compressor.

An electric oven had been prepared already in our laboratory for the purpose of preparing thin films by spray pyrolysis method. This is a versatile and easy method for preparing thin films. Also this method provides a cheaper ways and means of choosing the substrate and the precursor compounds. Hence this method of chemical spray pyrolysis is chosen to prepare ZnO thin films for the present study. Also thin films were prepared for various precursor concentrations. The nozzle was specially designed to provide a fine spray and a facility as mentioned earlier to regulate the rate of spray. The quantity of chemicals is taken in the burette, which acts as a solution reservoir. The most probable reaction occurred during the spray may be given by:

$$Zn(CH_3COO)_2.2H_2O+(CH_3)_2CHOH+H_2O \rightarrow ZnO+\text{Gaseous Products} \uparrow$$

The molarity can be calculated by using the given formula

$$\text{Molarity} = \frac{\text{Molecular weight}}{\text{Litre}} \quad \text{---------- (3.1)}$$

Molecular weight of $Zn(CH_3COO)_2.2H_2O$: 219.50 g/m

Experimental Conditions

Volume of solution ‘	**40 ml**
Molarity of Zinc acetate dihydrate	0.05 M,0.1M,0.15M, 0.2M,0.25M,0.3M
Flow rate	4 ± 0.2 ml/min
Substrate Temperature	380˚C
Pressure	0.7 kg/cm^2
Distance between nozzle and the substrate	24cm

Powder diffraction method

Powder XRD (X-ray Diffraction) is perhaps the most widely used X-ray diffraction technique for characterizing materials. The sample is usually in a powdery form, consisting of fine grains of single crystalline material to be studied.

Experimental procedure

The x-ray diffraction spectrum of the prepared film is recorded using the XPERT-PRO diffactometer system. Copper $K_{\alpha 1}$ line with wavelength of 1.5406 Å generated with a setting of 30 mA and 40 kV with the electrodes is used for diffraction. The slit width setting is 91 mm. The diffracting angle (2θ) is scanned from 10.0881^o to 79.9381^o continuously with a rate of 2^o per minute. The whole process takes place at a temperature of 25˚C. The diffracted intensity is detected and recorded with the counter and computer facility attached with the instrument. Finally the x-ray diffraction pattern is drawn by the computer with the diffracting angle 2θ in degrees along the x-axis and the intensity in counts along the y-axis. Then from the obtained spectrum the corresponding values of 2θ and their intensities for the peaks obtained are noted and tabulated. In the obtained spectrum, the Bragg peak position and their intensities are compared with the standard JCPDS files to identify the crystal structure. The interplanar spacing (d-values) of the respective miller planes responsible for the peaks obtained are also determined and compared.

Results and Discussion

Thin films are formed on the glass substrates by the chemical spray pyrolysis method at various precursor concentrations of 0.05 M, 0.1 M, 0.15 M, 0.2 M, 0.25 M, and 0.3 M. The films formed are almost uniform at 0.05 M and 0.25 M concentrations, but the thin film obtained on the glass substrate is very powdery in this concentrations. This shows that the 0.05 M and 0.25 M concentrations are not sufficient for the chemical reaction to takes place to form the desired compound ZnO thin film, which did not adhere to the glass substrate and it may peel off when stress or strain is applied. A very good thin film is obtained at 0.1 M, 0.15 M, 0.2 M, and 0.3 M concentrations. The thin film formed at these concentration is adherent on to the substrate and is very reflective and uniform. The surface of the film looked with multi color due to multiple internal reflection of light.

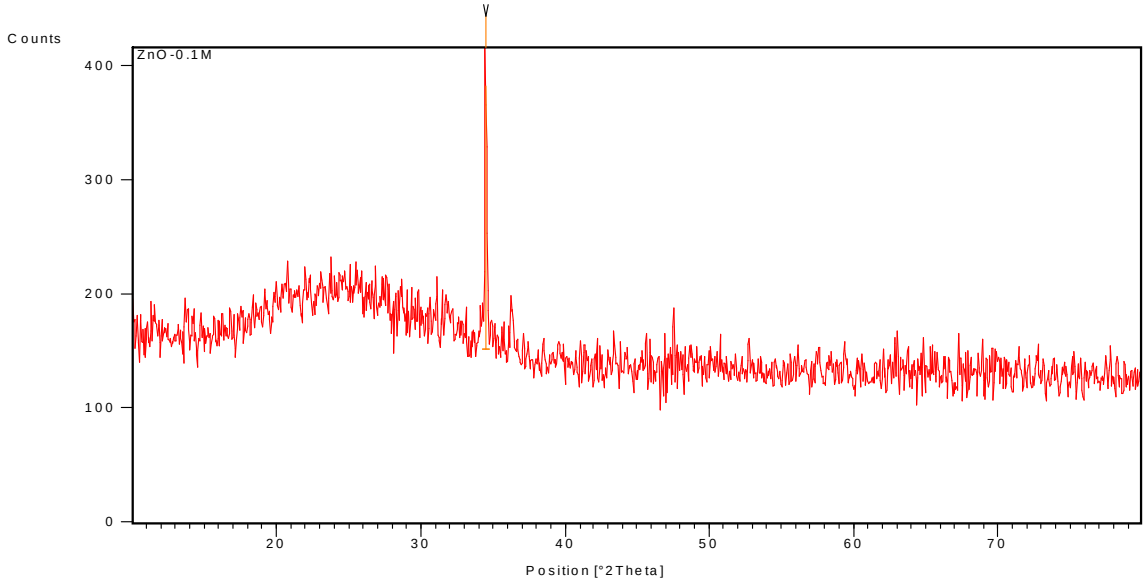

Fig 2: XRD pattern of ZnO thin film prepared at 0.1 M Concentration

The X-Ray diffraction patterns recorded with the thin films deposited at a various precursor concentrations at 0.1 M, 0.15 M,0.2 M, 0.3 M, are shown in figures 4.5- 4.8. The structures, grain size formed in those films are calculated from the XRD data taken from these spectra
.

Table 2: XRD pattern of ZnO thin film prepared at 0.1 M Concentration

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
34.4582	231.46	0.1187	2.60067	100.00

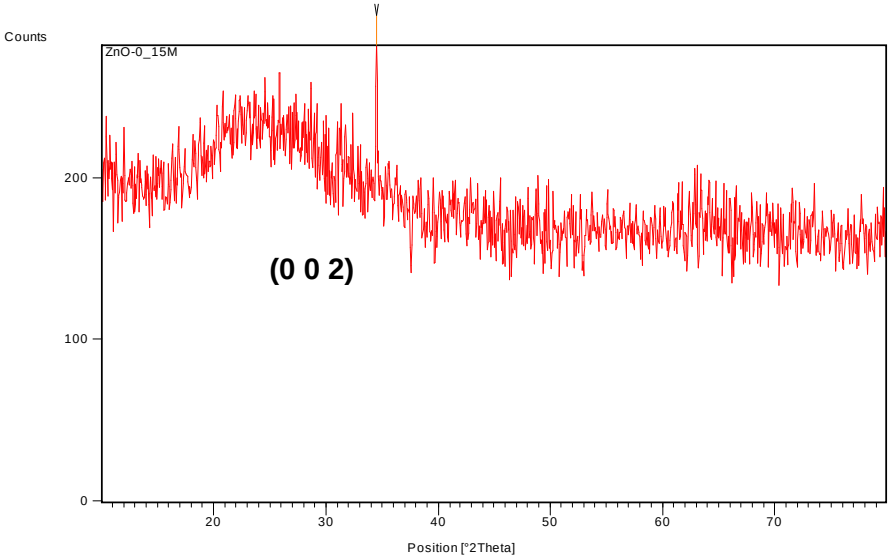

Fig 3: XRD pattern of ZnO thin film prepared at 0.15 M Concentration

Table 3:XRD pattern of ZnO thin film prepared at 0.15 M Concentration

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
34.4779	105.76	0.1800	2.59923	100.00

For concentration 0.1 M, the XRD pattern is given as above the graph 4.5. The Bragg peak position (2θ) values and their corresponding d-values are noted and tabulated in table 4.2. The d-spacing and 2θ values are compared with the JCPDS file No. 75-1526 and the structure of the ZnO (Zincite) thin film is ***Hexagonal***. The miller indices of the obtained are (0 0 2). The (0 0 2) film is only c-axis oriented crystals.

For concentration 0.15 M, the XRD pattern is given as above the graph 4.6. The Bragg peak position (2θ) values and their corresponding d-values are noted and tabulated in table 4.3. The d-spacing and 2θ values are compared with the JCPDS file No. 75-1526 and the structure of the ZnO (Zincite) thin film is ***Hexagonal***. The miller indices of the obtained film are (0 0 2). The (0 0 2) film is only c-axis oriented crystals.

From all the data given above, the structure of the compound is determined. By comparing the XRD data with the JCPDS file the lattice constants (c) and the miller indices (h k l) are determined. The XRD 2θ and d-spacing data for the predominant peak is compared with the JCPDS file and is tabulated below.

Table 4: Comparison of observed values with JCPDS values [28]

Precursor Concentration	JCPDS File No.	(h k l)	Observed Values			JCPDS Values			System
			2θ (deg)	d-spacing (Å)	Lattice constant c (Å)	2θ (deg)	d-spacing (Å)	Lattice constant c (Å)	
0.1 M	**75-1526**	**(0 0 2)**	**34.4582**	**2.6007**	**5.2013**	**34.467**	**2.6000**	**5.2**	**Hexagonal**
0.15 M	**75-1526**	**(0 0 2)**	**34.4779**	**2.5992**	**5.1986**	**34.467**	**2.6000**	**5.2**	**Hexagonal**
0.2 M	**80-0075**	**(0 0 2)**	**34.4005**	**2.6049**	**5.2098**	**34.400**	**2.6049**	**5.209**	**Hexagonal**
0.3 M	**80-0074**	**(0 0 2)**	**34.3203**	**2.6108**	**5.2216**	**34.3640**	**2.6075**	**5.215**	**Hexagonal**

(* JCPDS files have been enclosed in Appendix A,B,C)

The graph is drawn between observed d-spacing and lattice parameter (c-axis) with various precursor concentrations along x-axis, the observed d-spacing in primary y-axis and the c-axis value along the secondary y-axis.

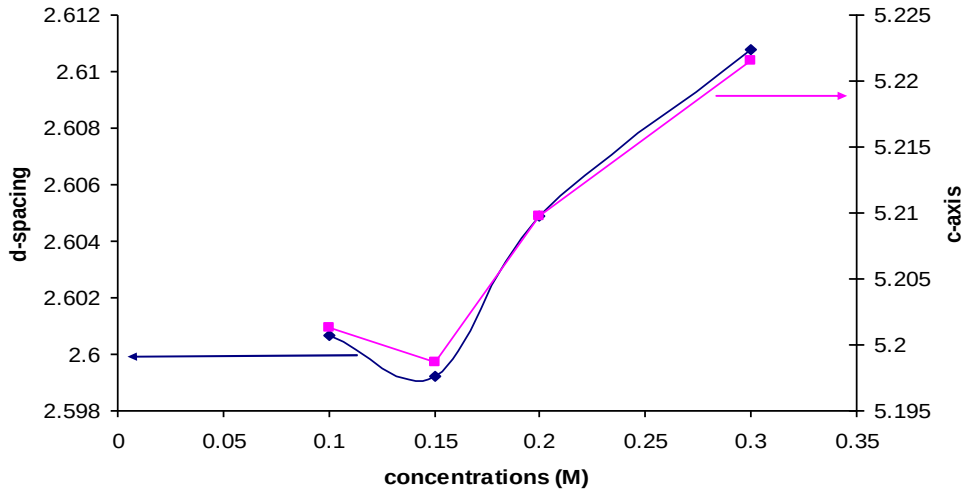

Fig 4: variation of d-spacing and c-axis with concentrations

From the above graph, we can understand that, when concentration increases the observed d-spacing and c-axis also decreasing and then maximum point.

Calculation of Grain size (D)

From the XRD data, the grain size of the ZnO thin film prepared by the Chemical Spray Pyrolysis method can be calculated. If the wavelength of X-ray (λ), full width half maximum (β) and θ values are known, then it is easy to calculate the grain size of the ZnO thin film. The average grain size of the spray pyrolysed ZnO thin film for the various precursor concentrations can be calculated using Debye-Scherrer formula. [29]

$$Grain\ size\ D = \frac{0.94^{a}}{\cos} \text{ (nm)} \quad \text{----------} \quad (4.1)$$

Where,
λ = Wavelength of X-ray (1.54060 Å)
β = Full width half maximum (radian)
θ = Diffraction angle (degree)

Table 5: Calculation of grain size for various precursor concentrations

Precursor Concentration	FWHM β	θ (deg)	Height (cts)	Grain size (nm)	Thickness (t)(nm)
0.1 M	0.00207	17.2291	231.46	73.24	103
0.15 M	0.00314	17.2389	105.76	48.28	110
0.2 M	0.00172	17.2003	393.10	88.13	158
0.3 M	0.01256	17.1602	131.30	12.06	145

The graph 4.10 is drawn between the various precursor concentrations along x-axis, the observed grain size in y-axis and drawn a graph 4.11 is between the various precursor concentrations with observed thickness and also drawn a graph 4.12 is between the various precursor concentration with height (cts)

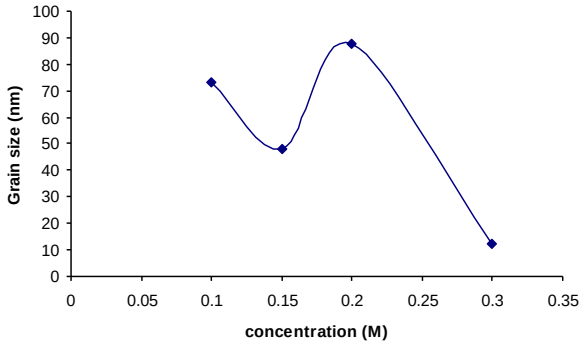

Fig 5: Variation of grain size with concentration

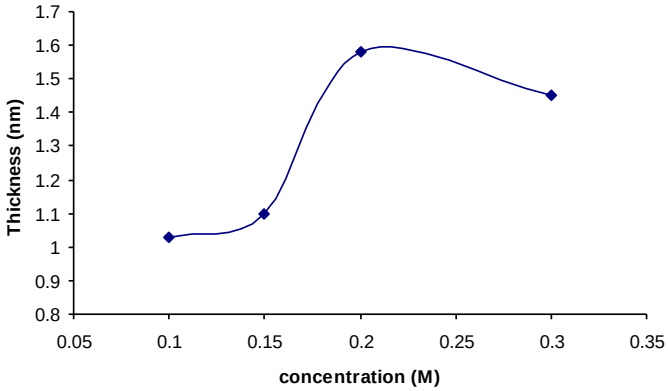

Fig 6: variation of thickness with concentration

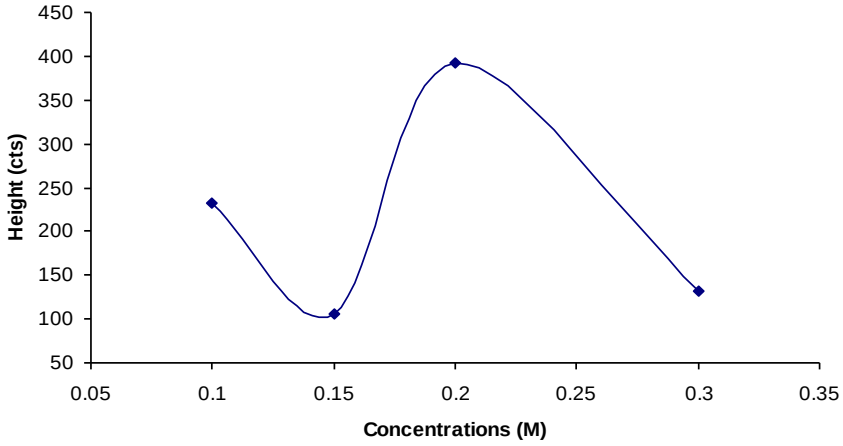

Fig 7: Variation of Height with concentration

From the above graphs (4.10, 4.11, 4.12) it was understood that as the concentration increase's the grain size and height of the thin film crystals first decreasing and then to increasing the maximum and also the thickness, with concentration first increasing and then decreasing.

It is clear that the ZnO thin film exihibit hexagonal structure with lattice parameter along c-axis [5.2013A^o, 5.1986A^o, 5.2098A^o, 5.2216 A^o,]. The c-axis orientation is due to a self-texturing mechanism as discussed by V.B.Patil et. al [8] .The miller indices of the (h k l) is (0 0 2) orientation.

Conclusion

Using Chemical Spray Pyrolysis method, the ZnO thin films were deposited on the glass substrates for the various precursor concentrations of 0.05 M, 0.1M, 0.15 M, 0.2M, 0.25 M, and 0.3 M with substrate temperature 380^{0}C. The thin films thus formed at concentrations 0.1 M, 0.15 M, 0.2 M and 0.3 M are reflective and uniform. The thin films are transparent and colorless. The thin films formed at 0.05 M and 0.25 M is not reflective, and they are white in color.

Compound formation (ZnO) was confirmed by the XRD method. By comparing the JCPDS diffraction patterns, the film which corresponds to the 0.1 M and 0.15 M concentrations contain ZnO (Zincite mineral) with Hexagonal crystal structure and the lattice parameter 'c' values are 5.2013 Å and 5.1986 Å. The 0.2 M and 0.3 M has Zinc oxide with Hexagonal crystal structure with the lattice parameter c values are 5.2098 Å and 5.2216 Å. On increasing the concentration the natural abundance of the thin film formed is changed to artificial abundance.

In all ZnO films, the Hexagonal crystal structure is built around the one preferred orientations (0 0 2). As the concentration increases the grain size and height of the thin film crystals is decreasing with increases. The thickness of the film increases as the concentration increases from 0.1 M to 0.2 M. Suddenly at the concentration 0.2 M the thickness of the film increases and start decreases from 0.3 M.

The conductivity of the Zinc Oxide thin films prepared at the various precursor concentrations 0.05 M, 0.1M, 0.15 M, 0.2M, 0.25 M, and 0.3 M were determined to be n-type using the hot probe technique.

In this study the undoped Zinc oxide thin films were found to be highly resistive. So further it is planned to study its electrical properties for any photovoltaic (or) optoelectronic devices fabrication. Doping this ZnO thin film with Al, In, Li, (or) Cu and hence a study of its variations towards all of its properties.

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