Synthesis and Characterization of ZnO Thin Films Using Advance SILAR Method

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ABSTRACT

ZnO thin films were prepared by advance SILAR method using 0.1 M Ammonium Zincate bath. The coated films were annealed 2hr at 400 °C. The structural and optical properties were studied by X-ray diffraction and UV– vis spectroscopy respectively. The hexagonal Wurtzite structured ZnO thin films were confirmed by X-ray diffraction (XRD) and preferential orientation along the (101) plane was confirmed from structural analysis. The crystallite size is found to be in range 29-31 nm and which is increases with no. of dipping cycles. The optical properties of the ZnO thin films were estimated using the absorption spectrum in the range of 400 –700 nm.

Keywords: Ammonium Zincate bath, Structural property, Optical property, Advance SILAR.

I. INTRODUCTION

In recent research field, nanoscience and nanotechnology is become an essential subject due to its application in various field and researcher shows their interest in nano scale nanomaterials are the set of substances where at least one dimension is less than 100 nanometers. Nanomaterials occurred naturally and also engineered artificially. The property of nanomaterials is different from large scale material. In recent day many methods are available to form nano powder and nano thin films. Thin film may be two dimensional depositions of nanomaterials having thickness in range few nanometer to 100 μm typically used in different applications. The different properties of thin film are changes with thickness, temperature and composition of material. Thin film of oxide like TiO_2, PbO, CuO, CdO are studied which were prepared by different methods like evaporation and sputtering processes, LASER assisted techniques, chemical vapour deposition, spray pyrolysis, sol-gel, spin coating, SILAR etc .

Zinc oxide (ZnO) has attracted recent interest for a range of applications and has been prepared and investigated in various physical forms such as single crystals, ceramic pellets, thick films, thin films and nanostructures etc. The typical hexagonal wurtzite structure of ZnO thin films is inferred from the XRD pattern [1-4]. Pure zinc oxide thin films have certain limitations in their application. They are not stable against corrosive environments and in humid ambient and lack stability in terms of thermal edging in air [5-6]. To stabilize the ZnO system against such changes, dopant ions have to be incorporated into them to obtain certain desired properties like wider or narrower band gap, higher optical absorbance, lower or higher melting point, ferromagnetism, etc. Therefore polycrystalline ZnO films have been doped with metals of group I, group II, group III and group

V. Thus the thin films of pure and polycrystalline ZnO have been widely studied during the last few decades because of their high optical transparency (80%) in the visible region, high conductivity and technological applications particularly in the field of semiconductor electronics and optoelectronic devices includes integrated circuit chips, micro-fabricated mechanisms, micro-electromechanical systems (MEMS), micro-electronic optical systems, as well as gas sensing, light-emitting diodes (LEDs), optical coatings, photovoltaic solar cells, and thin film batteries [7-9,10].

Khadher AL-Rasheedi et al. [11] was prepared the ZnO thin films by sol-gel method on glass. They were reported that crystal structure and orientation of the ZnO thin films investigated by X-ray diffractometer has peaks at $2\theta = 31.80°, 34.40°, 36.20°, 47.50°, 56.60°, 62.90°, 66.28°, 68°$, were assigned to (100), (002), (101), (102), (110), (103), (112), (201) of ZnO indicating that the samples were polycrystalline wurtzite structure. The grain size of the crystallites and band gap energy were found to be 14.7nm and 3.27 eV. ZnO thin films have been successfully deposited on silica glass substrate using chemical bath deposition technique. There was a red shift in the band gap energy as the annealing temperature was increased and band gap energy was found to be 2.66 eV [12]. ZnO thin films were deposited on a glass substrate by dip coating technique. The films were found to exhibit high transmittance, low absorbance and low reflectance in the visible regions. The thickness of the films was evaluated in the range of 173 to 323 nm [13]. O.A. Fouad et al. [14] were Prepared ZnO thin film by Thermal Evaporation Deposition method and studied the structural properties and showed the photocatalytic activity. ZnO Thin Films Deposited by RF magnetron sputtering [15].

The aim of the present work is to use a relatively simplest SILAR technique to prepare ZnO thin films from Zinc complex solutions and studied their structural, optical properties with choice of precursors, concentration and pH of the reacting precursors, temperature of deposition.

II. METHODS AND MATERIAL

2.1 Preparation of Zinc Oxide (ZnO) thin film by SILAR Method

The preparation of Zinc oxide thin film was prepared by SILAR method. This method has two beaker one is cationic and other is anionic bath. The cationic bath contain ammonium zincate solution $[(NH_4)_2ZnO_2]$ kept at room temperature and anionic bath contain hot water at near 85-90 °C. The ammonium Zincate bath was prepared by low addition of ammonium hydroxide (NH_4OH, Fischer Scientific India Pvt. Ltd. approx. 25% ammonia solution, mol. wt. 17.03 g/mol) to an aqueous solution of 0.1 M Zinc sulphate heptahydrate [$ZnSO_4.7H_2O$, Fischer Scientific India Pvt. Ltd mol wt. 281.53 g/mol]. Ammonia solution was introduced slowly under continuous stirring until the solution becomes clear and homogenous. The pH of the solution was maintained between 9.5-10 to obtain better quality films. The substrates were cleaned prior to deposition by first boiling them in hot water and subsequently cleaning them with acetone. They were further kept dipped in double ionized distilled water for some time to remove the contaminants. This pre-cleaned glass substrate was alternatively dipped in the cationic precursor ammonium zincate bath for 10s and then in the hot water bath kept at temperature between 85°-90°C. To obtain variation in thickness Zinc oxide thin films were deposited at 25, 35 and 45 dipping cycles. After the growth process thin films were washed with distilled water and dried in air at room temperature. The films were then annealed at 400°C for about 1 hour for better quality film. The thickness of Zinc oxide thin film was determined by weight difference-density consideration method or also known as the gravimetry method using an electronic high-precision balance.The structural analysis of annealed Zinc oxide thin film was was carried out with X-ray Diffraction

technique using a diffractometer Seimens D5000. This diffractograms were taken within range of diffraction angle (2θ) between 10 to 80 degree, employing a step of 2 deg/min at room temperature with CuKα radiation (λ = 1.5406 A⁰). The optical absorption was measured with a UV-Vis spectrophotometer (Perkin Elmer) within wavelength range between 400 and 700.

2.2 Film Thickness Measurement

The film thickness was determined by weight difference-density consideration method or also known as the gravimetry method using an electronic high-precision balance.

$$t = \frac{(W2-W1)}{A\rho} \times 10^{-4} \; \mu m \; \text{.....................} \; (1)$$

Where 't' thickness of film,'W$_1$' and 'W$_2$' be the weights of the substrate before and after film deposition in gm., and 'A' be the area of the deposited film in cm³ and 'ρ' be the theoretical density(5.6 gm/cm³) of ZnO.

Table 1 and Fig.1 shows Variation of film thickness with increase in dipping cycles.

Dipping cycles	Thickness of the film (nm)
25	573
35	700.2
45	881.8
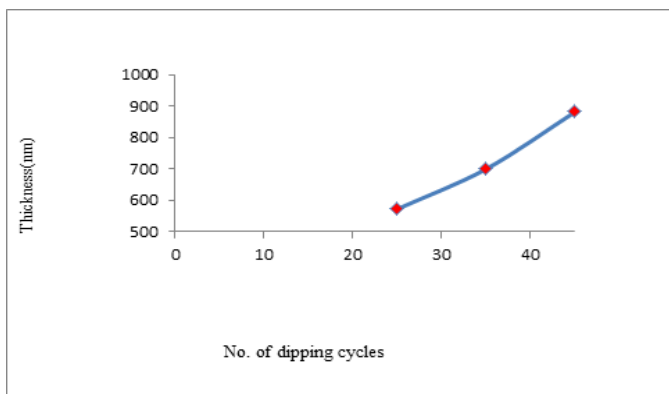
III. RESULTS AND DISCUSSION

3.1 Structural Property

The X-ray diffraction (XRD) is well known technique for characterization of bulk and thin film samples. The structural identification and determination of lattice parameters are based on the interpretation of XRD patterns. The value of interplaner spacing'd' was measured using Bragg's equation,

$$2 \, d \sin\theta = n\lambda \; \text{................................(2)}$$

Where, d = interplaner spacing, θ = glancing diffraction angle, n = order of diffraction (n =1), λ = wavelength of monochromatic X-ray. The observed "d" values are compared with standard "d" values using (JCPDS) American Society for Testing Materials (ASTM) data card.

The crystallite size or particle size (D) can be determined using the Scherrer's formula,

$$D = \frac{K.\lambda}{\beta.\cos\theta} \; \text{.............................(3)}$$

Where D is a average crystallite size, k is a constant determined by the geometry of the crystallites and it is approximately 0.95 for spherical particles, β is the full width at half maximum (FWHM) intensity of the observed diffraction peak and λ is a wavelength of monochromatic X-ray (1.5406 A⁰).

The dislocation density was calculated using the equation,

$$\delta = \frac{1}{D^2} \; \text{...............................(4)}$$

The average strain in the film can be calculated using Williamson-Hall equation,

$$\beta \cos\theta = \frac{k\lambda}{D} + 4\varepsilon \sin\theta \; \text{...............................(5)}$$

Where β is the full-width half maxima, θ is the angle at which a particular peak is obtained in the XRD data, k is a constant, D is average particle size, and λ is the wavelength.

The lattice constants a and c are calculated using the formula,

$$a = \frac{\lambda}{\sqrt{3}\sin\theta} \quad \& \quad c = \frac{\lambda}{\sin\theta} \; \text{.............(6)}$$

The numbers of crystalline per unit are (Nc) was evaluated using the relation,

$$N_c = \frac{t}{D^3} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

and the lattice distortion (LD) developed in thin films can be evaluated from the relation,

$$LD = \frac{\beta}{4\tan\theta} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

The structural analysis of annealed Zinc oxide thin film was carried out with X-ray Diffraction technique using a diffractometer Seimens (D5000, CuKα radiation λ = 1.5406 A⁰).
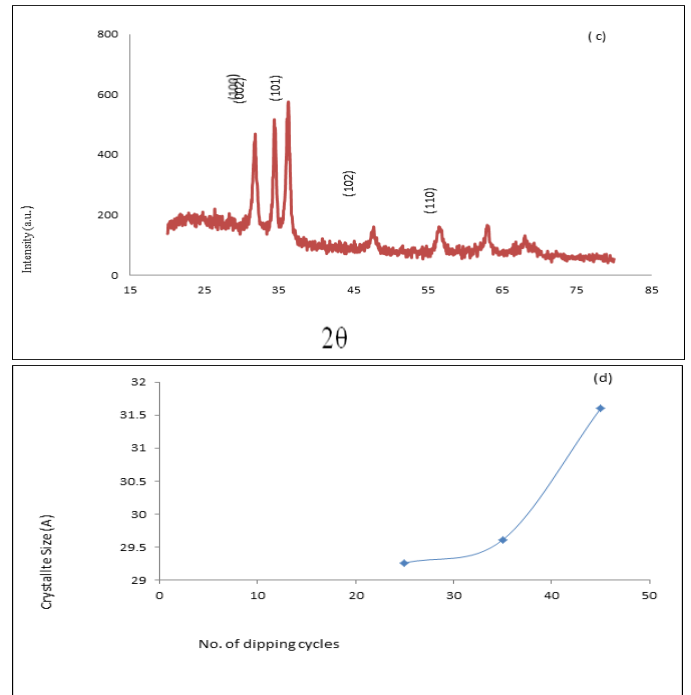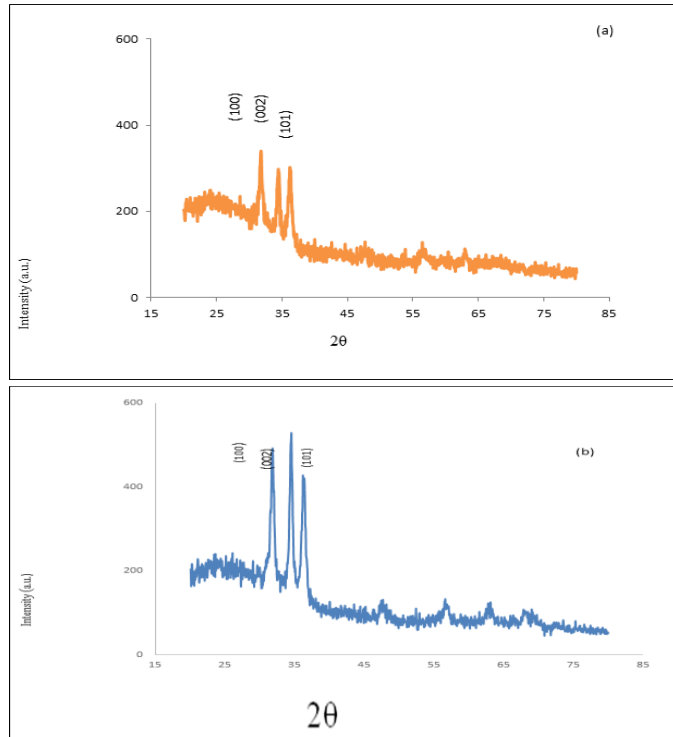

Fig.2 XRD spectra of ZnO thin films at (a) 25 cycle, (b) 35 cycle, (c) 45 cycle and (d) variation of crystallite size with dipping cycles at 101 plane.

Table 2 XRD parameters of ZnO thin films at 25, 35 and 45 dipping cycles

2θ	Plane (hkl)	No. of cycles	d (Å)	FWHM (β) (10^{-3} radian)	Crystallite Size (D) (nm)	($\delta \times 10^{14}$) (lines/m²)	Strain(ϵ) (lines⁻² m⁻⁴)	Lattice constants (Å)		Nc (10^{16})	Lattice Distortion (LD) ($\times 10^{-3}$)
								a	c		
36.4	101	25	2.46	5.21	29.26	11.68	0.0040	2.80	4.9	3.40	1.72
		35	2.46	5.14	29.61	11.65	0.0039	2.84	4.93	3.42	1.75
		45	2.52	4.82	31.6	10.01	0.0037	2.86	4.98	3.43	1.77

Fig.2 (a), (b), (c) are the diffraction patterns for ZnO thin film at 25, 35 and 45 cycle respectively. Peaks for pure ZnO appear at 31.79°, 34.6°, 36.35°, 47.85°, 56.85° corresponding to (100), (002), (101), (102) and (110) reflecting planes which indicate towards the hexagonal wurtzite structure of ZnO. No diffraction peaks of the impurities were detected in three cases indicating the high purity and single phase nature of the films. From the figure it is clear that ZnO film is oriented at (101) plane .Other orientation

corresponding to (100) ,(002),(102) and (110) are present with low relative intensities as compared to (101) plane. XRD pattern revealed the formation of hexagonal phase ZnO and the intensity of the film were found to increase with increasing dipping cycle. . It is found that pure ZnO films prepared from ammonium zincate baths have a polycrystalline structure with strong preferred orientation in the (101) plane. Fig.2 (d) shows the plot of relative crystallite size for (101) plane vs. increase in dipping cycle, we were found that the overall crystallite size increase with increase in dipping cycle. The crystallite size increases from 41.94nm for ZnO thin film at 25 cycle to 42.33 nm for ZnO thin film at 45 cycle corresponding to (101) plane.

3.2 Optical Property

The optical absorption spectrum of the ZnO thin films were determined at room temperature in a UV-VIS spectrophotometer ((Perkin Elmer) in the wavelength range 400-700 nm. The absorbance of ZnO thin film increases with dipping cycle due to increase in thickness. The absorbance edge not seen in graph, it was already reported that it occurred before 400 nm wavelength.
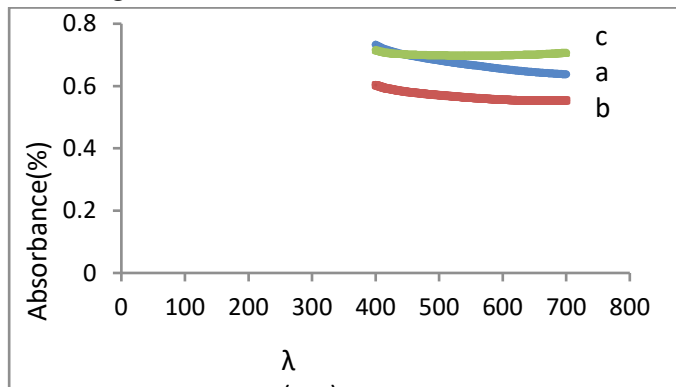

 Fig.3 Spectra of absorbance vs wavelength λ (nm) of ZnO thin films at 25, 35 and 45 cycles.

The average extinction coefficient (K) calculated using the formula given by equation

$$K = \alpha\lambda/4\pi \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(9)$$

It was\ found to be 0.393, 0.868 and 0.993 at 25, 35 and 45 cycles of ZnO thin films.

IV.CONCLUSION

ZnO thin film was prepared by advance SILAR method using Ammonium Zincate bath. The structural properties were characterised by using a diffractometer Seimens (D5000, CuKα radiation λ = 1.5406 A⁰) and it is found that pure ZnO thin film has polycrystalline hexagonal wurtzite structure oriented along 101 plane.The crystallite size is increase with dipping cycle. The optical properties were characterised by using a UV-VIS spectrophotometer ((Perkin Elmer) in the wavelength range 400-700 nm. The average extinction coefficient was calculated from absorbance graph and its increased with increasing dipping cycles.

V. REFERENCES

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