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Optical and Structural Properties of ZnO Thin Films Fabricated by SILAR Method

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ABSTRACT: A novel and simple chemical route was used for the deposition of ZnO thin film from aqueous solution of zinc–ammonia complex, integrating the merits of successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition methods. ZnO thin films on glass substrates were deposited with the precursor of zinc–ammonia complex. Characterization techniques of XRD, SEM, EDAX and DRS are used to characterize ZnO thin films. X-ray diffraction study show that the film prepared in this work exhibits good crystallinity with the hexagonal wurtzite crystalline structure and the preferential orientation along (0 0 2) plane, with a texture coefficient value of ~2.56, average crystallite size of 28.92 nm and with lattice constants a = b = 3.257 Å, c = 5.215 Å. EDAX spectrum indicates that the film consists of zinc and oxygen elements. The optical band gap energy of the thin films is calculated from optical absorption spectrometry using DRS data and the value was found to be direct allowed transition ~3.22 eV.

KEYWORDS: ZnO, Thin films, XRD, SEM, EDAX

I. INTRODUCTION

Zinc oxide (ZnO) is an interesting wide band gap (~3.3 eV) II-VI semiconductor because exhibits numerous characteristics suited for various technological applications such as antireflection coatings, transparent electrodes in solar cells [1], piezoelectric devices [2],gas sensors [3], varistors [4], UV and blue light emitters [5] and even thin film transistors [6]. It is also being considered as a potential candidate in the new frontiers of research like spintronics[7]. Various chemical and physical processes have been employed for thin film deposition, such as conventional sputter deposition technique [8], chemical vapor deposition (CVD) [9,10], thermal evaporation [11,12], spray pyrolysis [13,14], and electro deposition [15]. Like chemical bath deposition technique, the Successive Ionic Layer Adsorption and Reaction (SILAR) technique for the preparation of thin films from aqueous solution is a promising technique because of its simplicity and economics. The facts affecting the process are the quality of the precursor solutions, their concentrations, pH values, complexing agents and individual rinsing and immersion time periods [16].

II. BACKGROUND

Advantages of SILAR are effectiveness and simplicity of the deposition equipment, controlled deposition rates, wide spectrum of deposition parameters for the control and the optimization of film properties, and film thickness. SILAR is a wet chemical route for the synthesis of thin films in which the basic building blocks are ions instead of atoms and therefore the preparative parameters are easily controllable. The SILAR method, also known as modified version of chemical bath deposition, has a number of advantages apart from it being inexpensive, simple and convenient for large scale deposition: i) the process can be carried out on any kind of substrate, ii) unlike closed vapor deposition method, SILAR does not require high quality target and/or substrates. Also it does not require vacuum at any stage, iii) the deposition rate and the thickness of the film can be easily controlled by changing the deposition cycles, iv) it is a low temperature chemical solution method and does not cause local over heating that can be detrimental for materials to be deposited.

The SILAR method is basically a two-step chemical bath deposition technique in which a substrate is dipped in cationic and anionic precursors. The technique is thus based on the adsorption and reaction of the ions from the solutions.

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Sequential reaction on the substrate surface under optimized conditions of concentration and pH of the reacting solutions results in the formation of the film. In this study synthesis of ZnO film was made from ammonium zinc complex prepared from zinc nitrate hexahydrate as the starting reagent. The coated films have been characterized by different techniques such as X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), energy dispersive x-rays (EDX) and diffuse reflectance spectroscopy (DRS).

III. MATERIALS AND METHODS

(a) Cleaning of the substrate:

The microscope glass substrate was cleaned with following steps (1) washed with mild detergent, (2) rinsed with distilled water, (3) dipped in dilute chromic acid for three hours (4) rinsed thoroughly with distilled water and (5) heated at 20^0C for 10 minutes by keeping the substrate vertically.

(b) Deposition of thin film:

Thin films of ZnO were deposited on glass by successive immersion of the substrate into a $(NH_4)_2ZnO_2$ bath kept at room temperature and into hot water at nearly boiling point. The bath was prepared by adding 25% ammonia solution to 100ml of aqueous $Zn(NO_3)_2.6H_2O$ (0.25M) solution. The addition of ammonia solution was stopped when pH of the solution becomes 9.0. The cleaned glass substrate was immersed in the zinc complex (at room temperature) for a known standardized time (20 sec) followed by immersion in hot water (near boiling point) for the same time for hydrogenation. This cycle was repeated fifty times in order to increase the overall film thickness.

In this paper, we have made use of the thermal decomposition of $[Zn(NH_3)_4]^{2+}$ in neutral aqueous solution (hot water), which will release ions of Zn^{2+} and OH^- into solution and result in the formation of $Zn(OH)_2$ or ZnO particles. Following equations (1)-(3) illustrate the chemical reaction related to this process. A dynamic equilibrium exists in the precursor under the presence of excessive ammonia:

$$Zn(OH)_2 + 4NH_3.H_2O = [Zn(NH_3)_4]^{2+} + 2OH^- + 4H_2O \quad (1)$$

During the reaction process in hot water, complex $[Zn(NH_3)_4]^{2+}$ decomposes with the final formation of $Zn(OH)_2$ precipitation:

$$[Zn(NH_3)_4]^{2+} + 4H_2O = Zn(OH)_2\downarrow + 4NH_4 + 2OH^- \quad (2)$$

Solid ZnO particles may be formed in aqueous solution when the temperature is over 50^oC [17]:

$$Zn(OH)_2(s) = ZnO(s) + H_2O \quad (3)$$

During the chemical reaction process in hot water, with the elapse of the time starting from the initial immersion of substrate in water, three stages will occur subsequently within the liquid film adsorbed on the substrate surface, i.e., the solution stage, the heterogeneous precipitation stage, and the homogeneous precipitation stage.

The film was heated at 100^oC for 1 hr and allowed to cool to room temperature. After 24 hrs; it was calcined at 350^oc for 3 hr in muffle furnace. The film thickness was determined by weight difference-density consideration [17] method using an electronic high-precision balance.

(c) Characterization:

The crystal structure and orientation of the ZnO films were investigated by X-ray diffraction (XRD) method employing a Philips PW 1830 x-ray diffractometer using Ni filtered *CuKα* radiation (λ=1.5418 Å). The diffractometer reflection was taken at room temperature. Scanning electron microscopy (SEM) was used to study the surface morphology and EDX measurement was done to study the composition of the film. The optical characterization was done by diffused reflectance spectroscopy.

IV. RESULTS AND DISCUSSIONS

(a) Film thickness measurement

If W_1 and W_2 are the weights of the substrate before and after film deposition in gm., A is the area of film deposition in cm^2 and ρ is the theoretical density of ZnO (5.6 gm/cm^3), then the film thickness is evaluated as:

$$t = \frac{w_2 - w_1}{A\rho} \times 10^4 \,\mu m \quad (4)$$

Film thickness was found to be 0.414 μm or 414 nm.

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(b)X-Ray Diffraction Analysis

The XRD pattern of ZnO thin film fabricated by SILAR method on glass substrates is shown in Figure 1. All the peaks of the ZnO thin films correspond to the peaks of standard ZnO (JCPDS 36-1451). For the samples, different diffraction peaks are observed in the XRD pattern, showing the growth of ZnO crystallites along different directions. Strong preferential growth is observed along (002) plane indicating that the films are oriented along c-axis [18]. The typical hexagonal wurtzite structure of thin films is inferred from the XRD pattern. The crystallites sizes (D) of the films are estimated using the Scherer formula:

$$D = \frac{K\lambda}{\beta_{2\theta} COS\,\theta} \tag{5}$$

where *k* is a constant taken to be 0.94, λ is the wavelength of X-Ray used (λ = 1.54 Å) and $\beta_{2\theta}$ is the full width at half maximum of (002) peak of XRD pattern, Bragg angle, 2θ is around 34.34°. The average value of grain size is found to be 28.92 nm. The dislocation density (δ), defined as the length of dislocation lines per unit volume, and Strain (ε) are estimated using the equation [19]

$$\delta = \frac{1}{D^2} \tag{6}$$

and

$$\varepsilon = \frac{\beta \cos\theta}{4} \tag{7}$$

The lattice constants 'a' and 'c' of the Wurtzite structure of ZnO can be calculated using the relations (8) & (9) given below

$$a = \frac{\lambda}{\sqrt{3}\sin\theta_{100}} \tag{8}$$

$$c = \frac{\lambda}{\sin\theta_{002}} \tag{9}$$

The evaluated structural parameters of thin films are presented in Table 1. The lattice parameters of ZnO thin films evaluated from XRD data are in good agreement with those reported in (JCPDS 36-1451).The calculated lattice parameters are given in Table 2.

Quantitative information concerning the preferential crystal orientation can be obtained from the texture coefficient, *TC*, defined as [20-23]

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{(1/n)\sum_n I(hkl)/I_o(hkl)} \tag{10}$$

where *TC*(*hkl*) is the texture coefficient, *n* is the number of diffraction peaks considered, *I*(*hkl*)is the measured x-ray intensity and $I_{o(}$ *hkl)* is the corresponding recorded intensity according to JCPDS card [24] and $I_{o(}$ *hkl)* represents the x-ray intensities from standard ZnO powder with randomly oriented grains or with no preferred orientation [24]. Since three diffraction peaks were used ((100), (002), (101)), the maximum value *TC* (*hkl*) possible is 3. The texture coefficient for the (002) orientation has been found to be 2.56 in our film.

(c) SEM & EDAX Study

Surface morphology of thin films is very important tool to investigate microstructure of thin films. Figure2 shows the surface morphology of the prepared film in our report. SEM results are found to be very good with Stoichiometric formation of ZnO nanocrystals of spherical shape and obviously demonstrate aggregation of the particles. The aggregation of particles should had been originated from the large specific surface area and high surface energy of ZnO nanoparticles [25].The aggregation occurred probably during the process of drying [26,27].

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The EDAX Study of the prepared sample is shown in Figure 3. This shows that the sample contains only Zinc and Oxygen and no other impurity are present in the sample

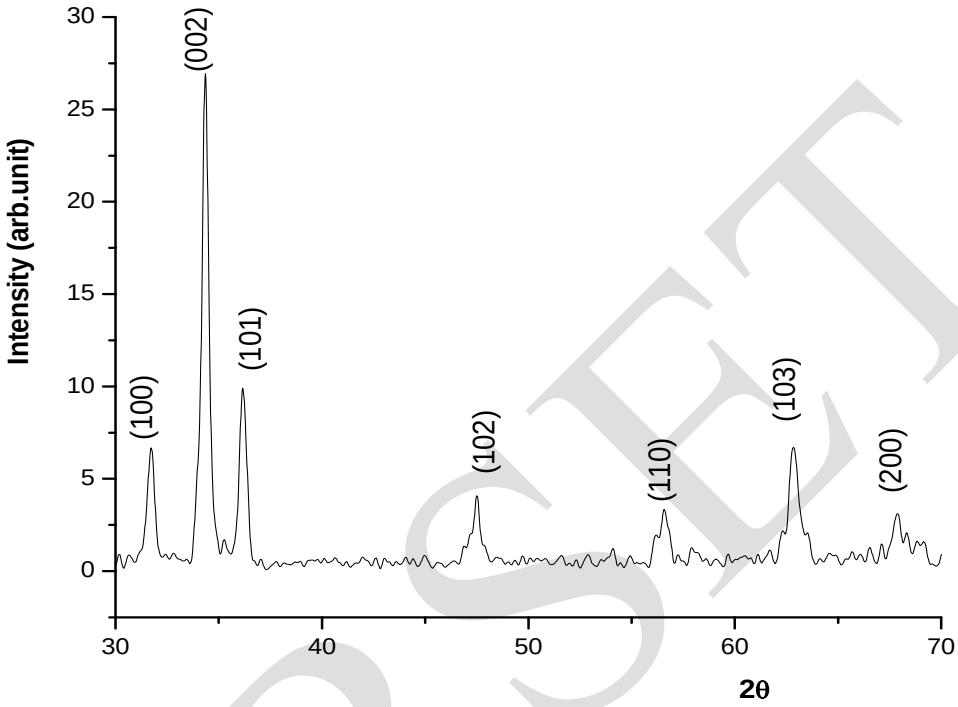

Figure 1:XRD pattern of ZnO thin film

Table1. Structural parameters of ZnO thin films.

Planes	Interplaner spacing (Å)	FWHM β (10^{-3}radian)	Grain size D (nm)	δ (10^{14})(lines/m^2)	ε (10^{-3})
(100)	2.818	6.87	20.97	22.74	1.603
(002)	2.608	4.81	30.16	10.99	1.149
(101)	2.480	6.87	21.22	22.21	1.633

Table2. Lattice parameters of the ZnO thin film.

a (Å)		c (Å)	
Calculated 3.257	Standard 3.253	Calculated 5.215	Standard 5.215

V. OPTICAL CHARACTERIZATION

In the Figure 4 the absorption spectrum of ZnO thin film are shown. The exciton absorption at 360 nm is observed in the absorption spectrum. When photons of higher energy are larger than band gap of the semiconductor, an electron is transferred from the valence band to the conduction band where there occurs an abrupt increase in the absorbency of the material to the wavelength corresponding to the band gap energy. The optical band gap E_g of the thin film was calculated from Tauc plot as shown in Figure 5. The presence of a single slope in the plot suggests that the films have

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direct and allowed transition. For such transition we have $(\alpha h\nu)^2 = A(h\nu - E_g)^n$ where α is absorption coefficient, hν is photon energy, E_g is optical band gap, n is 1 for direct transition & A is a constant. The band gap energy is obtained by extrapolating the straight line portion of the plot to zero absorption coefficient. The band gap value of ZnO thin film is found to be 3.24 eV. These values are in good agreement with the values reported by others [**28**]. This red shift of the band gap energy is due to agglomeration of the nanocrystallites into larger crystallites as reported by various authors in different literatures.

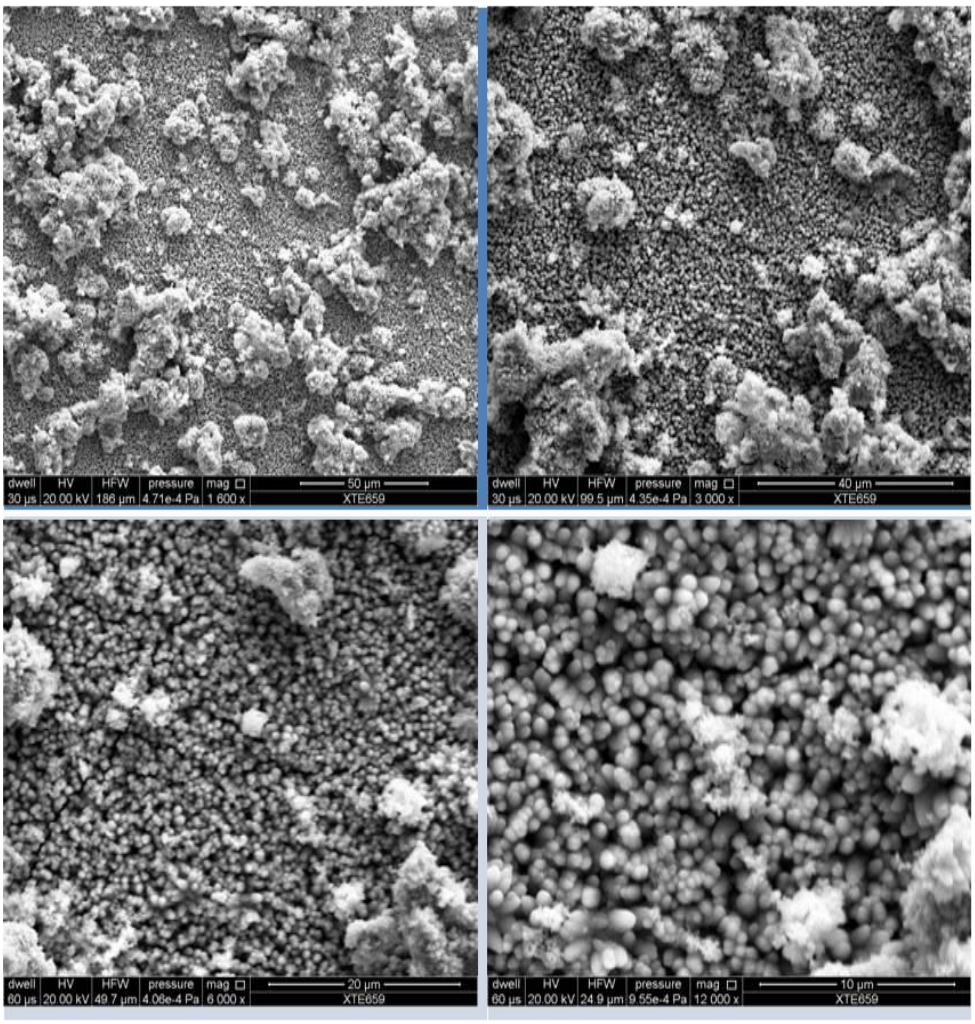

Figure 2: SEM image of prepared ZnO thin film

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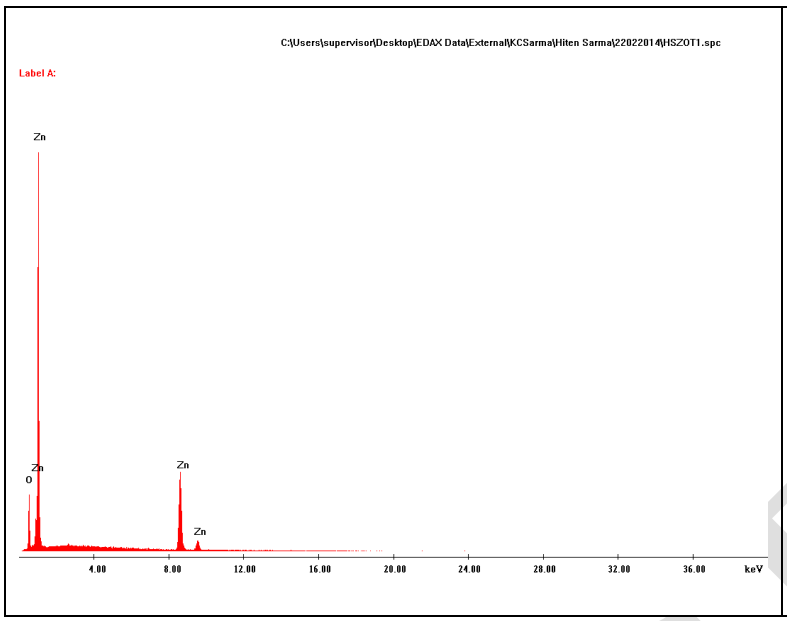

Element	Atomic %	Weight %
O K	50.29	19.84
Zn K	49.71	80.16
TOTAL	100	100

Figure 3: EDX of prepared ZnO thin film

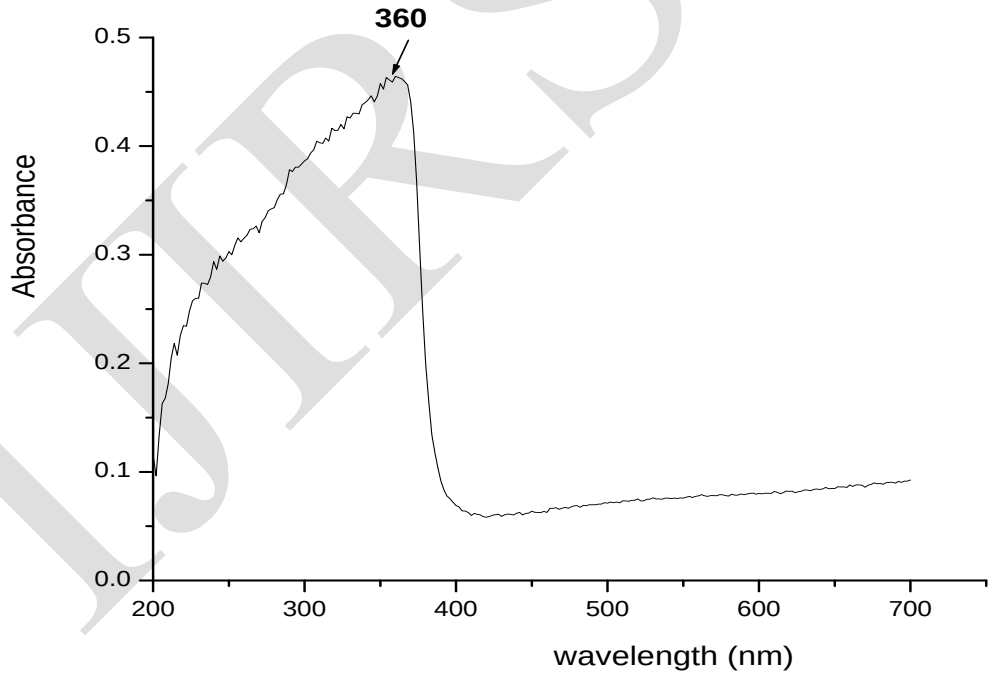

Figure 4:Absorption spectra of ZnO thin film

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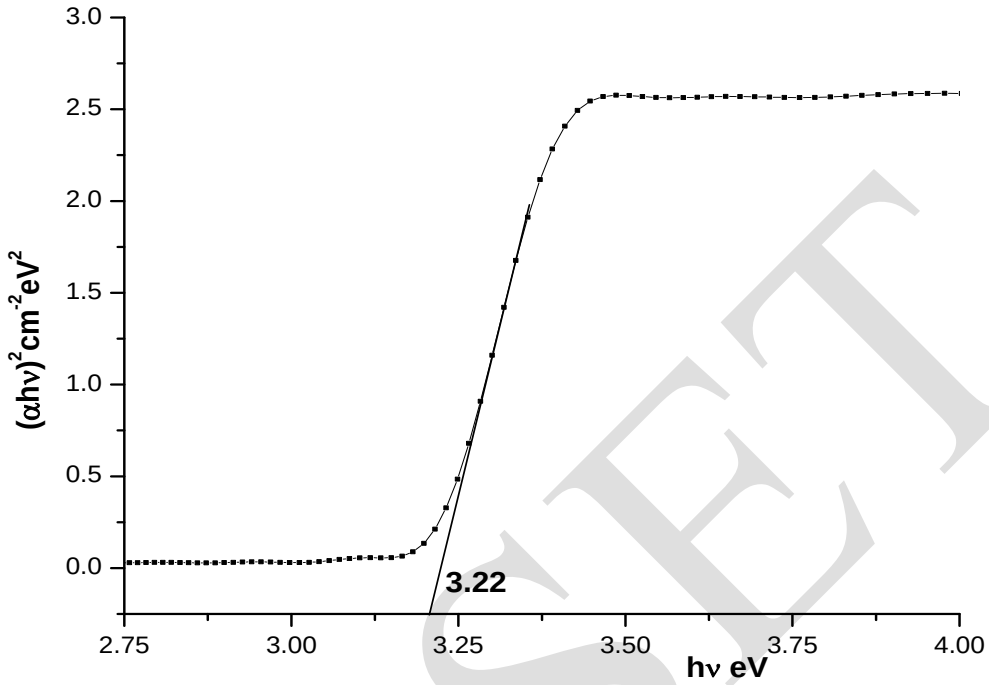

Figure5:Tauc plot for band gap determination

VI. CONCLUSION

The ZnO nanoparticles with hexagonal structure have been synthesized by simple cost competitive precipitation method after annealing the precursor at 350°c. The prepared ZnO particles were characterized by XRD, SEM, EDAX and diffused reflectance study. XRD and SEM studies confirmed the nanostructures for the prepared ZnO nanoparticle. SEM micrographs illustrates that the particle size increases at high annealing temperature. The ZnO nanoparticles can be used in different industrial applications, namely, luminescent material for fluorescent tubes, active medium for lasers, sensors, and so forth

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