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EFFECT OF MULTIPLE DIPPING OF SILAR DEPOSITED ZnO THIN FILMS BY PHYSICO-CHEMICAL PROCESS

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ABSTRACT

Undoped zinc oxide (ZnO) thin films were deposited on microscopic glass substrates by a chemical technique known as 'Successive Ionic Layer Adsorption and Reaction' (SILAR). The technique involves multiple dipping of the substrates in an aqueous solution of sodium zincate kept at room temperature and deionized water kept near boiling point. The effect of multiple dipping is one of the important factors that determine the quality of film. Thin films of various thicknesses have been obtained by varying the number of dipping, while all other deposition parameters such as pH of the solution, molarity, reaction temperature, reaction time and annealing temperature were kept constant. Surface morphology and optical properties of the ZnO thin films have been studied using Scanning Electron Microscopy (SEM) with an EDAX analysis. X-Ray diffraction and Scanning Electron Microscopy studies reveal that the grain size increases with the increase in number of dipping of the glass substrate. Optial spectra were recorded using UV-Vis spectrophotometer. The optical band gap of ZnO thin film was found to increase with increase in the number of dipping.

Key words: SILAR, ZnO, Thin films, Morphology, SEM, EDAX, Optical.

INTRODUCTION

The synthesis and characterization of zinc oxide using different techniques have attracted considerable attention due to their attractive prospects in the development of material research.

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Zinc oxide is an expensive n-type semiconductor having a direct band gap of 3.3 eV and crystallizes in hexagonal Wurtzite structure (c = 5.025 nm and a = 3.249 nm)[1]. Accordingly, this binary compound has wide applications in and as chemical sensors, heterojunction solar cells, electrophotography, surface acoustic wave devices and conductive transparent conductors. However, pure ZnO thin films lack stability in terms of thermal ageing in air corrosive environments[2]. Also, zinc oxide has great potential for applications such as antistatic coatings, solid state display devices, optical coatings, heaters, etc.[3,4].

Different physical and chemical techniques have been employed for incorporating aluminium into ZnO. These include DC and RF magnetron sputtering[5,6], pulsed laser ablation[7], chemical vapor deposition[4], chemical beam deposition[8], sol-gel[9], electrolyses technique[10] and spray pyrolysis[11] among others. Even though conventional physical techniques in general produce good quality transparent films, they are very expensive and are difficult to be scaled up to industrial level. Chemical deposition techniques, on the other hand, are relatively low cost and can easily scaled up for industrial applications.

In the last two decades, chemical techniques have emerged as a good alternative for material preparation in thin film forms. Among various chemical methods employed to deposit ZnO films, spray pyrolysis is a high temperature process and the choice of suitable precursor solution is often not convenient. On the other hand, while the sol-gel process is cost effective like electroless deposition technique, they are characterized by poor coverage. One of the most effective technique is the 'Successive Ionic Layer Adsorption and Reaction' (SILAR) method. This process can be carried out on any kind of substrate and the thickness can be easily controlled enabling the preparation of both; thin and thick films.

The technique of SILAR is often termed as a modified chemical bath deposition method. In chemical bath deposition (CBD) method, deposition of thin films occurs due to the substrate being kept in contact with a diluted chemical bath. The film formation on substrate takes place when the ionic product (IP) exceeds the solubility product (SP). In SILAR technique, thin films are obtained by immersing the substrate into separately placed cationic and anionic precursors for reaction at the chosen temperatures. Between every immersion, the substrate is rinsed in distilled water or deionized water with the rinsing time being an important parameter for the formation of ionic layer. The ZnO thin film deposition process was originally reported as a multiple chemical dipping technique[12,13] and later as SILAR technique, as it involves adsorption of a layer of complex ion on the substrate followed by the reaction of the absorbed ion layer.

The advantages of this method are its simplicity in the working principle and low cost of apparatus. Since the thin film deposition is carried out in ambient atmosphere in

SILAR technique, the microstructure of the films are expected to be different from sophisticated physical techniques where the deposition is carried out in vacuum. Also they are expected to exhibit properties that are different from other techniques as well. The preparation of ZnO thin films by this technique using sodium zincate and ammonium zincate baths was reported[14,15]. The present work is thus an attempt to advance the novel interest in multiple dipping of ZnO thin films by SILAR methods.

EXPERIMENTAL

Deposition of ZnO films was carried out from 0.125 M sodium zincate (Na_2ZnO_2) solution and hot water bath. Sodium zincate bath was prepared by the addition of sodium hydroxide (NaOH) in zinc sulphate ($ZnSO_4.7H_2O$) solution. The pH of the zincate solution was maintained at a value of 9.0 ± 0.2. Film deposition was carried out by alternatively dipping a pre-cleaned microscopic glass substrate in zincate bath kept at room temperature and hot water bath maintained between 96-98°C[16-22]. ZnO thin films were then prepared from solution in aqueous media with 50, 75, 100, 125 and 150 dipping. The prepared ZnO films were found to adhere strongly to the glass substrate. They appeared white in colour and were very stable under typical environmental conditions. The deposited films were subsequently annealed in air at 200°C for 30 minutes. The effects of number of dipping of substrate were studied using various characterization techniques and the optimized deposition parameters were arrived for ZnO thin films.

The measurement of film thickness was carried out using gravimetry technique[23]. The method involves measuring the weight change of the ZnO film formed on the substrate due to film deposition to the theoretical density of ZnO. The crystalline structure was determined by X-ray diffraction using X'pert PRO (PANalytical) diffractometer with *CuKα* radiation ($\lambda = 1.5405$ Å) and employing a scanning rate of 5^{o} min^{-1}. The particle size and morphology were examined using Scanning Electron Microscope (SEM) Hitachi S-3000H model. For SEM studies, the samples were sputter coated with '*Au*' using Fine Cote ion sputter JFC-1100 model instrument. Optical transmittance was measured by Perkin-Elmer Lambda 35 UV- Vis spectrometer. All the analytical characterizations were performed at room temperature.

RESULTS AND DISCUSSION

Film thickness

The thickness of the ZnO thin films deposited by SILAR method was found using gravimetry technique with the film thickness being determined by the weight gain method using the formula –

$$t = \frac{m}{A\rho} \qquad \ldots(1)$$

Where '*t*' is the thickness of the film, '*m*' is the weight gain, 'A' is the area of the coated film and '*ρ*' is the density of ZnO (5.6 gcm^{-3}). Table 1 gives the thickness values for the film deposited with different number of dipping.

Table 1: Effect of the number of dipping on the thickness of ZnO thin films

Number of dipping	Thickness of the film (μm)
50	0.47
75	0.83
100	1.39
125	1.54
150	1.89

Thus, the result clearly indicates that the thickness values increase with increasing number of dipping.

XRD Results

Fig. 1 shows the X-Ray diffractometer (XRD) pattern of the ZnO films with different number of dipping deposited from sodium zincate bath. The material was scanned in the range of 30º-70º (*2θ*). The peaks in the XRD spectrum correspond to those of the ZnO patterns form the JCPDS data[24] which has a hexagonal Wurtzite structure with a *c*-axis value of (002). In addition to the (002) peak, other peaks such as (100), (101), (102), (110), (103) and (112) were also observed for samples with higher thickness corresponding to the hexagonal ZnO phase.

The intensity of (002) plane was found to increase as the number of dipping of the substrate is increased. Polycrystalline nature of the film is clear from Fig. 1. However, the peak position of the principal (002) orientation matches closely with the JCPDS data for the films grown from 50 dipping (Fig. 2). The lattice constants '*a*' and '*c*' of the Wurtzite structure of ZnO are also calculated. The crystalline size of the ZnO films prepared by different number of dipping of substrate was calculated using Scherrer's formula[25]. The enlarged region of the (002) plane in Fig. 2 indicates the shift in XRD peaks, which is due to the number of dipping.

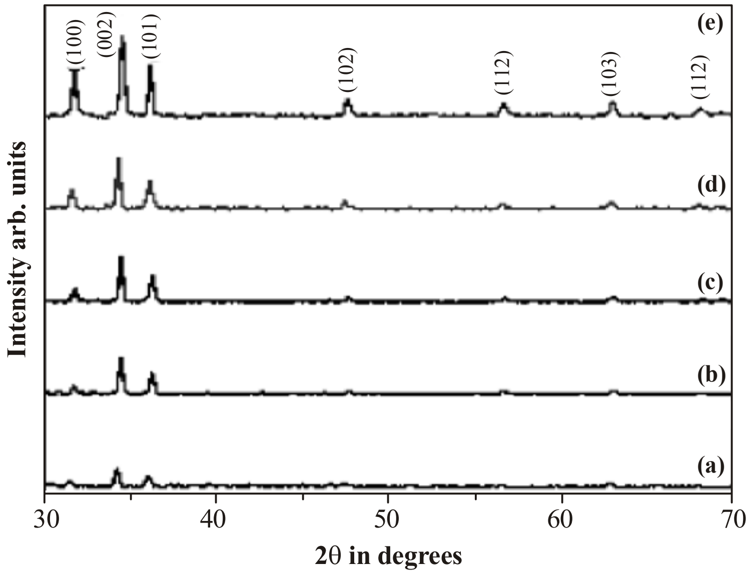

Fig. 1: The effect of number of dipping on the XRD patterns of ZnO thin films (a) 50 (b) 75 (c) 100 (d) 125 and (e) 150

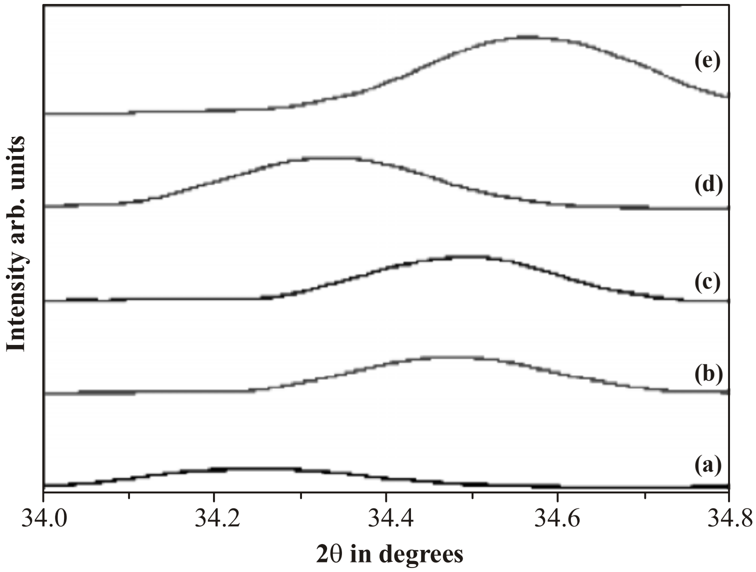

Fig. 2: Enlarged region of the (002) plane indicating the shift in XRD peaks due to the effect of number of dipping (a) 50, (b) 75, (c) 100, (d) 125 and (e) 150

Table 2 gives the lattice constants and crystalline size along prominent diffraction planes for films prepared under different dipping. It is clear from the results that the RMS strain, dislocation density and stacking fault probability decreases as Zn^{++} concentration increases. Also, it is found that the degree of preferred orientation $I_{(002)}/I_{(101)}$ for the ZnO film prepared by 100 times dipping is much higher than those of others. Hence, this concentration is chosen for the subsequent depositions.

Table 2: Effect of dipping on the microstructural parameters of zinc oxide thin films

Number of dipping	Parameters					Lattice constants		$\frac{I_{(002)}}{I_{(101)}}$
	t (μm)	D (nm)	$(e^2)^{1/2}$ (10^{-4})	α (10^{-4})	P (10^{14})	a (nm)	c (nm)	
50	0.47	73	33.214	30.477	26.384	3.286	5.242	1.73
75	0.83	89	32.289	24.314	22.418	3.247	5.204	1.68
100	1.39	121	19.472	17.618	10.762	3.245	5.202	1.77
125	1.54	132	15.224	14.435	9.616	3.259	5.216	1.71
150	1.89	139	11.318	10.318	4.762	3.237	5.194	1.55

Microscopic analysis

Scanning Electron Microscopy is a convenient method for studying the microstructure of thin films. The microstructure of ZnO films on glass substrate is shown in Fig. 3 (a-e). The micrograph clearly illustrates the uniform distribution of hexagonal shaped grains for 50 dipping (Fig. 3a). The films prepared at 75 and 100 times dipping (Fig. 3b & 3c) shows hexagonal shaped nano rods. The well aligned and uniformly shaped ZnO nano rods are observed for films that were prepared by 125 dipping (Fig. 3d). Flower like structures were observed for the films dipped at 150 times (Fig. 3e). Fig. 3 (*f*) shows the EDAX elemental mapping of a 125 times dipped sample, wherein the uniform distribution of *Zn* and *O* elements, indicate the formation of ZnO films.

Optical studies

Fig. 4. shows the optical transmittance spectra of ZnO films with different number of dipping using UV-Vis Spectrophotometer. These spectra reveal that films grown under the same parametric conditions have low absorbance in the region from 350 nm to 850 nm. Fig. 4 also shows that the absorption increases with the increase in the thickness of the film.

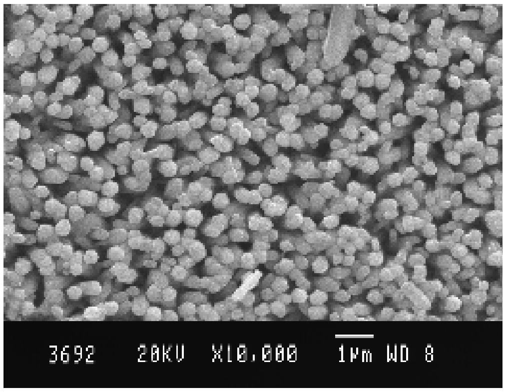

Fig. 3(a): ZnO film with 50 dipping

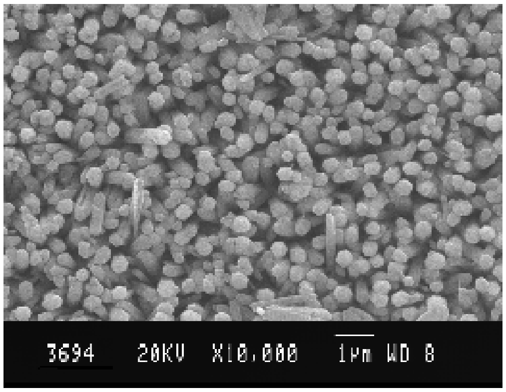

Fig. 3(b): ZnO film with 75 dipping

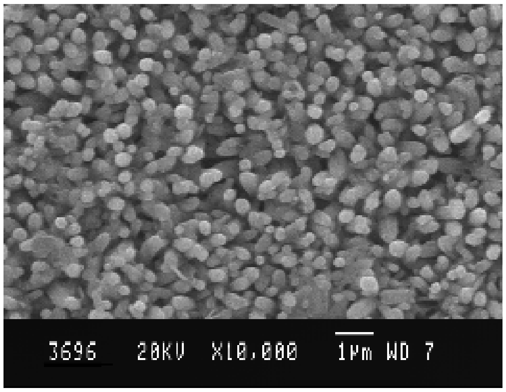

Fig. 3(c): ZnO film with 100 dipping

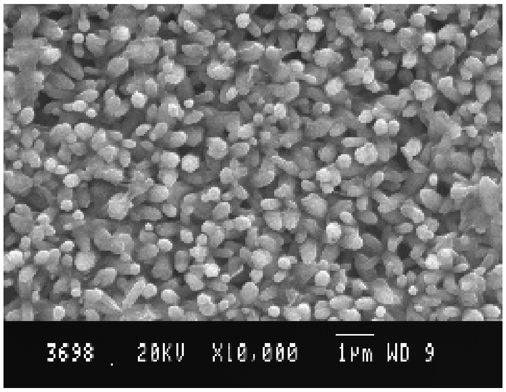

Fig. 3(d): ZnO film with 125 dipping

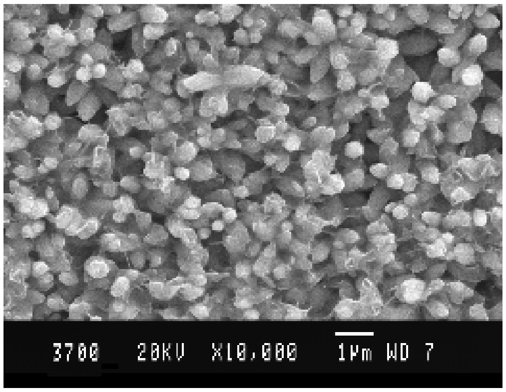

Fig. 3(e): ZnO film with 150 dipping

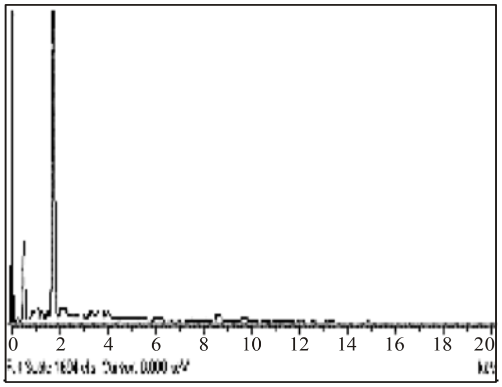

Fig. 3(f): EDAX spectrum of a ZnO film grown at 125 dipping

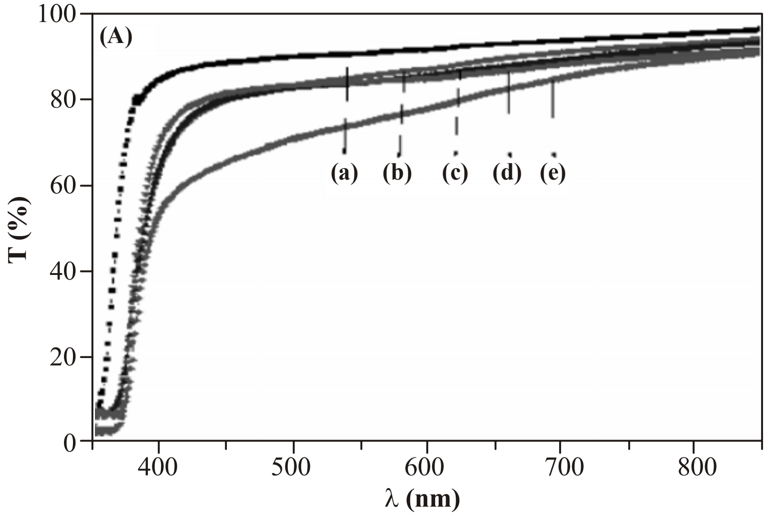

Fig. 4: Optical transmittance spectra of ZnO thin films prepared from different dipping (a) 50, (b) 75, (c) 100, (d) 125 and (e) 150

From the optical energy gap E_g and absorption coefficient α of the ZnO films prepared at different dipping rates, the variations of $(h\nu)$ *vs* $(h\nu\alpha)^2$ are obtained and shown in Fig. 5. Direct band gap values could be observed from the linear extrapolation of these curves towards the intersection with X-axis. These values were found to decrease from 3.37 to 3.22 eV with the increase in number of dipping of the substrate from 50 to 150. The values are found to vary marginally compared to those reported in literature[26]. Table 3 gives the values of E_g of the ZnO films deposited at different dipping. The band gap energy, a constant value of the materials for bulk samples is known to vary in thin films due to particle size effects. It has been reported that the band gap energy can be modulated by changing the particle or grain size in the films[27]. The decrease in the optical band gap of the films with increase in the number of dipping of substrate could be attributed to the grain size enhancement.

Table 3: Optical parameters of zinc oxide thin films on the effect of number of dipping

Preparation condition	Parameters	Thickness (µm)	Transmittance (%)	Band gap (eV)
Number of dipping	50	0.47	92	3.37
	75	0.83	88	3.28
	100	1.39	86	3.27
	125	1.54	85	3.26

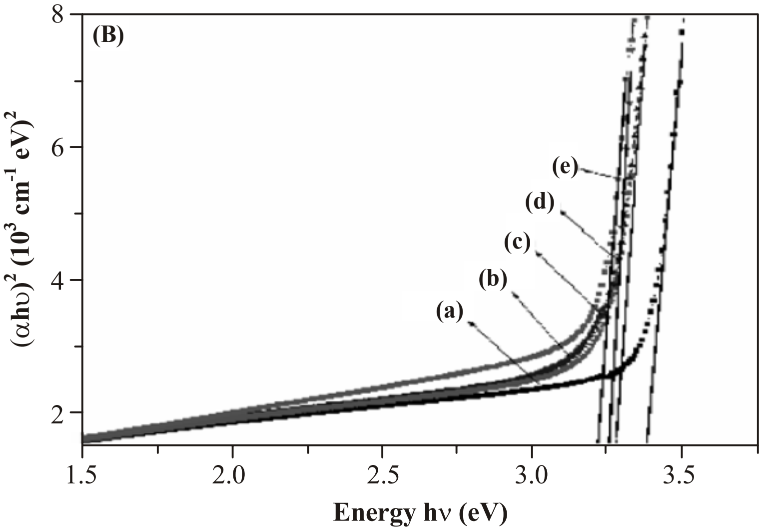

Fig. 5: Plot of (hν) vs $(h\nu\alpha)^2$ of ZnO thin films prepared from different number of dipping (a) 50, (b) 75, (c) 100, (d) 125 and (e) 150

CONCLUSION

Zinc oxide thin films were prepared on glass substrates by SILAR process with different number of dipping (50, 75, 100, 125 and 150 times). The thickness of the films was measured using gravimetry method. The structural characteristics of the films were done by X-ray diffraction (XRD) method. From the XRD spectrum, the characteristic reflection planes of ZnO was verified. The calculated lattice constants agreed with the values for that of the bulk ZnO. Crystallite sizes of the films were found to be less than 100 nm. The variations in optical constants with number of dipping were found to be dependent on the thickness of the film. The surface morphology of the films reveals that grain size depends on the number of dipping of the substrate.

The transmission spectra of the films were recorded by UV-Vis Spectrophotometer showing a high transparency (> 75%) in the visible region. With the increase in the number of dipping, the transmittance of the film was found to decrease. The band gap energy of the films was found to decrease from 3.37 to 3.22 eV with increasing number of dipping. The dipping range will be increased in our future work for more genetic applications.

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