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Influence of barium doping on physical properties of zinc oxide thin films synthesized by SILAR deposition technique

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Abstract: Undoped and Barium (Ba) doped ZnO thin films were deposited on glass substrates by successive ion layer adsorption and reaction (SILAR) method using zinc acetate, barium chloride and ammonium hydroxide solution. In the present work the effect of Barium doping on structural, optical and morphological properties were investigated. Structural characterization by X-ray diffraction reveals that ZnO films are polycrystalline with wurtzite structure. SEM images showed that Ba doping influenced surface morphology and grain size was found to increase with increase in doping level. Optical analysis showed that all the films had good transmittance in the visible region. The presence of defects into ZnO films was detected through photoluminescence studies.

Keywords: Zinc Oxide, Barium, SILAR Technique, Physical Properties

1. Introduction

For nearly half a century, the synthesis and characterization of ZnO thin films have been an active area of research. ZnO with wurtzite structure is an n-type semiconductor with direct band gap around 3.37eV at 300K [1], and high electronic mobility. As a wide and direct band gap semiconductor, ZnO thin films have attracted more and more attention in optoelectronic devices [2-5], photothermal conversion systems, heat mirrors, blue/UV light emitter devices, solid state sensors, transparent electrodes, heterojunction solar cells etc [6-10].

Undoped zinc oxide thin films have certain limitations in their application. In order to widen the potential areas where ZnO thin films can be applied, dopant ions have to be incorporated into them to obtain certain desired properties like lower or higher melting point, wider or narrower band gap, higher optical absorbance, etc. by applying different techniques. Different techniques have been applied to obtain ZnO nanostructured thin films such as RF magnetron sputtering [11], chemical vapor deposition [12], chemical bath deposition[13], pulse laser deposition [14], spray pyrolysis [15], sol-gel process[16], chemical co-precipitation [17], hydrothermal [18], ultrasonic irradiation assisted solution route [19], solid-state reaction[20], successive ionic layer adsorption and reaction (SILAR) [21,22] etc…Among these techniques, SILAR technique has recently attracted considerable attention because of its low cost and simplicity. Furthermore, this technique requires low temperatures and facilitates large-area deposition.

In the present work, an attempt has been made to synthesize Ba doped ZnO thin films by SILAR technique, since it involves adsorption of a layer of complex ion on the substrate followed by reaction of the adsorbed ion layer [23]. Ba doped ZnO is an important technological material used for example in varistors [24] and liquid sensors' guiding layers. Precisely, Doping ZnO with Ba procures to ZnO films a rougher surface, a stronger internal stress, and a low density crystalline structure [25]; hence the motivation to investigate the effect of Ba doping concentrations on the crystalline structure and surface morphology of ZnO thin films.

The aim of the present study was to elaborate, through a simple and accurate technique - SILAR technique-, Ba doped ZnO thin films with good structural, morphological and optical properties.

2. Experimental Details

2.1. Deposition of Films

Pure and Ba doped ZnO thin films were grown on glass substrates by the SILAR method. In the experiments, 50 ml of Zinc sulfate monohydrate ($ZnSO_4$, H_2O) with concentration of 0,1 M and concentrated ammonia (NH_4OH, 29 %) solutions were used to prepare the zinc complex $[Zn\ (NH3)_4]^{2+}$ precursor solution. NH_4OH was added slowly into beaker under stirring, until white precipitation vanished and then clear solution was obtained. For the growth of ZnO films, 50-cycles deposition was carried out. In case of Ba doped ZnO films, poundered amount of Barium chloride dihydrate ($BaCl_2$, $2H_2O$) was added to the initial solution. ZnO thin films was doped with 1 at.% and 3 at.% of Barium and designated as Ba_1ZnO and Ba_3ZnO respectively. The detailed procedures for preparing ZnO films in one cycle is described as follows: (i) the pre-cleaned glass substrates were dipped in the zinc complex solution kept at room temperature for 15 s; (ii) once $Zn(OH)_2$ precipitated on the substrates, the glass was dipped in double distilled water (DDW) for 20s; (iii) the substrates were sonicated for 30s in DDW to remove the counter ions SO_4^{2-} and loosely attached $Zn(OH)_2$ grains; (iv) the substrates were dipped in hot DDW bath maintained at 90-95°C for 20 s to generate ZnO; (v) finally, the substrates were sonicated in DDW for 30s to remove excess of the loosely attached ZnO grains, and unreacted Zn(OH) from the surface.

2.2. Films Characterization

The structure of the films was investigated by X-ray diffraction (XRD) (Rigaku Ltd., Japan, Cu Kα radiation, λ= 1.54056 Å). The surface morphologies of the samples were examined using scanning electron microscopy (SEM) (JSM-6700F). The optical properties of the ZnO thin films were characterized by an ultraviolet-visible-near-infrared (UV-VIS-NIR) spectrophotometer (JASCO, V-630) and spectrofluorometer (JASCO, FP -8200).

3. Results & Discussion

3.1. Structure Analysis

The X-ray diffraction patterns of undoped ZnO and Ba-doped ZnO films are shown in figure1. The diffractograms of the samples reveals that all the peaks are in good agreement with the JCPDS data belonging to hexagonal ZnO structure (Card No. 36-1451). Apart from ZnO characteristic peaks, no peaks corresponding to either barium or other complex oxides were detected. This observation suggests that the films do not have any phase segregation or secondary phase formation as well as Ba is incorporated into ZnO lattice. It can be seen from the XRD diffractograms that pure and Ba doped ZnO films grow preferential along (002) direction and the position of this peak shifted toward higher angle when doping. This shifting leads to the decreasing of d-spacing values as indicated in table 1. The intensity of (002) peak is found to increase when the film is doped with 1 at.% of Ba then it decreases with further doping. The decreasing of the peak intensity indicates that the crystalline quality of the films is destroyed for high doping level. This can be due to the fact that, for high doping level, Ba atoms occupy interstitial positions in the ZnO lattice. Similar results were reported by W. Water et al [26]. The grain size, D of crystallites has been calculated using the well-known Debye Scherer's formula (1):

$$D = \frac{0.9\lambda}{\beta Cos\theta} \quad (1)$$

where λ = 0.15405 nm is the x-ray wavelength, β is the peak width of half maximum and θ is the Bragg's diffraction angle. The dislocation density δ which represents the amount of defects in the film was determined using the formula (2):

$$\delta = \frac{1}{D^2} \quad (2)$$

The calculated values of particle size and dislocation density are given in Table 1. It can be seen that, the crystallite size increases when ZnO is doped with 1 at.% and decreases when the doping level reached 3 at.%. This result supportes the fact that high doping level of Ba leads to the destruction of the films' structure.

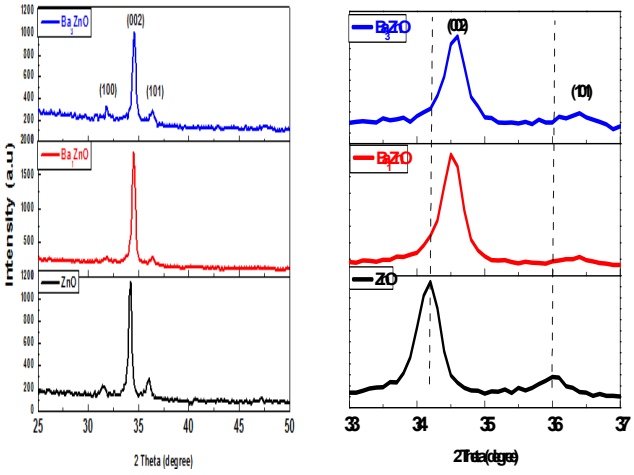

Figure 1. *The XRD pattern at (a) 2θ= 25°-50°and (b) 2θ = 33°-37° of Pure ZnO and Ba doped ZnO thin films*

The diffractograms indicated that Ba^{2+} ions of the doped ZnO samples were only incorporated in the ZnO lattice. Figure 1.(b) shows the changes in the 2θ angle values of the diffraction planes of (002) and (101) peaks at 2θ=33°-37° with increasing concentration of Ba doping. This is probably due to the difference between the ionic radius of Ba^{2+} (1.33 Å) and Zn^{2+} ion (0.74 Å).

Table 1. *Structural parameters of ZnO thin films*

Samples	2θ	hkl	d-spacing	FWHM	Crystallite size	Dislocation density
	(degree)		(Å)	(degree)	D (nm)	$\delta\times10^{14}$ (lines/m²)
ZnO	34.1400	(002)	2.62418	0.41920	19.84	25.40
Ba_1ZnO	34.4907	(002)	2.59829	0.36500	22.81	19.22
Ba_3ZnO	34.5329	(002)	2.59521	0.38250	21.77	21.10

3.2. SEM analysis

Fig 2 shows the SEM micrographs of pure and Ba doped ZnO films. It can be observed that all the films are uniform and homogenous with closely packed spherical grains. The grain size is found to increase with increase in Ba doping level. The undoped ZnO films looked porous while the doped films are compact respectively with the doping level. This can be due to the fact that the incorporation of Ba in the starting solution improves the nucleation process. Agglomeration of small grains in certain regions of the films is also evident from fig 2. Such agglomeration makes difficult to evaluate the grain size from SEM images.

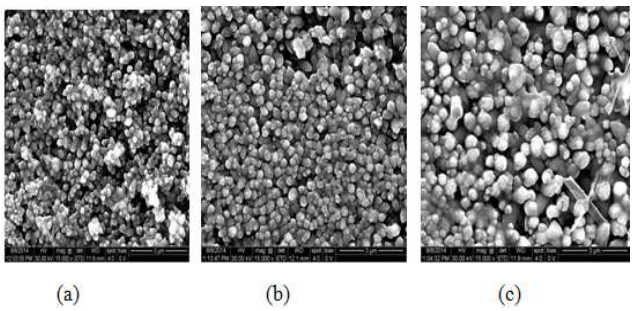

Figure 2. *SEM images of Pure ZnO and Ba doped ZnO nanoparticles. a-ZnO; b-Ba_1ZnO and c-Ba_3ZnO*

3.3. UV–Vis Absorption study

Fig 3 shows the absorption spectra of pure ZnO and Ba doped ZnO thin films recorded in the wavelength region 250–800 nm. ZnO is a non-stoichiometric oxide and is known to contain zinc-ion excess defects based on the presence of either zinc interstitial or oxygen vacancies. The spectra of Ba doped ZnO films show an absorption tail, probably related to intra-band gap transitions involving O vacancies and Zn interstitials with different charge states as reported by Balamurali et al [27]. It can be seen that the films' absorbance increases with the doping level. This can be explained by the fact that, at high doping level, films exhibit more defects leading to an increase in band gap value.

The optical transmittance spectra of ZnO and Ba doped ZnO thin films are shown in Fig 4. All the films exhibit good transmittance in the visible region. However, high transmittance (about 95%) is obtained for ZnO films doped with 1 at.%. Beyond this doping level the transmittance is found to decrease. This can be due to the fact that at higher doping level, more Ba atoms occupy interstitial position in the ZnO lattice which causes light scattering.

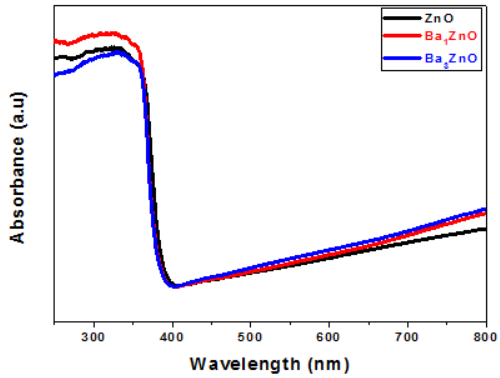

Figure 3. *Absorption spectra of pure ZnO and Ba doped ZnO thin films*

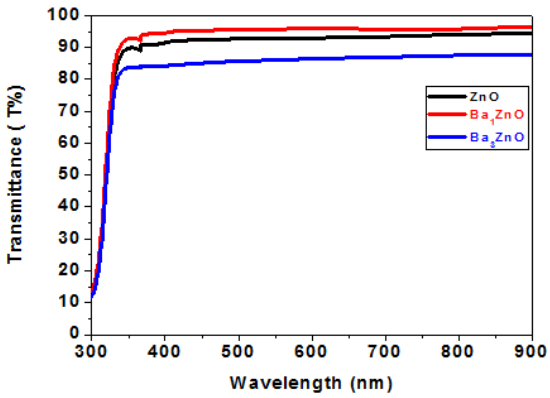

Figure 4. *Transmittance spectra of pure ZnO and Ba-doped ZnO thin films*

3.4. Photoluminescence Study

Fig. 5 shows the photoluminescence spectra at room temperature of pure ZnO and Ba doped ZnO films under the excitation of 325 nm. It is found that strongest ultraviolet (UV) emission peak centered at 392 nm corresponds to near band emission (NBE). The two peaks observed at 420 nm and 469 nm are attributed to intrinsic defects such as zinc interstitials and single ionized oxygen, respectively. We remarked that the intensity of the NBE peak is high for sample obtained with 1 at.% of Ba doping. This can be explained by the fact that these samples had less defects as they exhibit uniform and homogenous surface along with good crystalline structure. The decrease of the NBE peak observed for the undoped and 3 at.% Ba doped ZnO films indicated the presence of a large number of defects. It is well known that pure ZnO films have native defects such as zinc interstitials, zinc vacancies, oxygen interstitials and oxygen vacancies. In the case of 3 at.% Ba doped films, the increase in the number of defects may be due to the interstitial incorporation of Ba in the ZnO lattice.

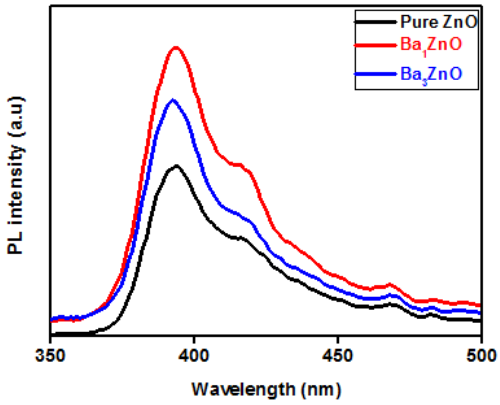

Figure 5. *Photoluminescence spectra of Ba-doped ZnO and pure ZnO thin films.*

4. Conclusion

Undoped and Ba doped ZnO thin films with different percentage (1 at.% and 3 at.%) of Ba content have been successfully synthesized by SILAR technique on glass substrates. The XRD studies confirmed the growth of ZnO thin films with hexagonal wurtzite structure. The SEM images indicated that the grain size, thus the roughness, increased with increase in Ba doping level. Optical analysis showed that all the films had good transmittance in the visible. However, the highest transmittance is obtained for 1 at. % Ba doped ZnO thin films. Such Ba doped ZnO films, with possible further improvements, can be used in varistors, liquid sensors' guiding layers or organic solar cells.

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