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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

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## 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 ( $ZnSO_4 \cdot H_2O$ ) with concentration of 0,1 M and concentrated ammonia ( $NH_4OH$ , 29 %) solutions were used to prepare the zinc complex  $[Zn(NH_3)_4]^{2+}$  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, powdered amount of Barium chloride dihydrate ( $BaCl_2 \cdot 2H_2O$ ) 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  $K\alpha$  radiation,  $\lambda=1.54056 \text{ \AA}$ ). 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 figure 1. 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):

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where  $\lambda = 0.15405 \text{ nm}$  is the x-ray wavelength,  $\beta$  is the peak width of half maximum and  $\theta$  is the Bragg’s diffraction angle. The dislocation density  $\delta$  which represents the amount of defects in the film was determined using the formula (2):

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

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 supports the fact that high doping level of Ba leads to the destruction of the films’ structure.

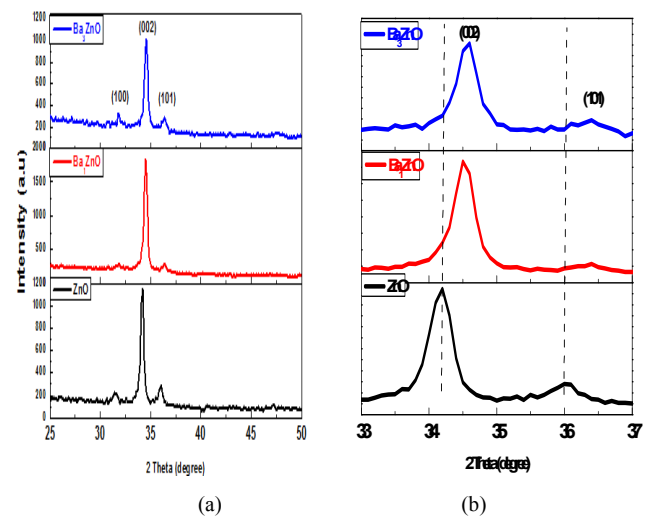


Figure 1. The XRD pattern at (a)  $2\theta = 25^\circ-50^\circ$  and (b)  $2\theta = 33^\circ-37^\circ$  of Pure ZnO and Ba doped ZnO thin films

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  $2\theta$  angle values of the diffraction planes of (002) and (101) peaks at  $2\theta=33^\circ-37^\circ$  with increasing concentration of Ba doping. This is probably due to the difference between the ionic radius of  $Ba^{2+}$  ( $1.33 \text{ \AA}$ ) and  $Zn^{2+}$  ion ( $0.74 \text{ \AA}$ ).

Table 1. Structural parameters of ZnO thin films

Samples	2 $\theta$ (degree)	hkl	d-spacing (Å)	FWHM (degree)	Crystallite size D (nm)	Dislocation density $\delta \times 10^{14}$ (lines/m <sup>2</sup> )
ZnO	34.1400	(002)	2.62418	0.41920	19.84	25.40
Ba <sub>1</sub> ZnO	34.4907	(002)	2.59829	0.36500	22.81	19.22
Ba <sub>3</sub> ZnO	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.

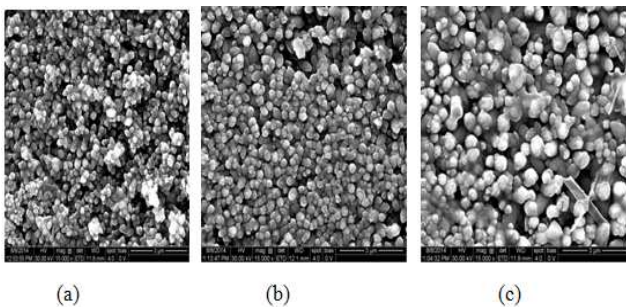


Figure 2. SEM images of Pure ZnO and Ba doped ZnO nanoparticles. a-ZnO; b-Ba<sub>1</sub>ZnO and c-Ba<sub>3</sub>ZnO

### 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.

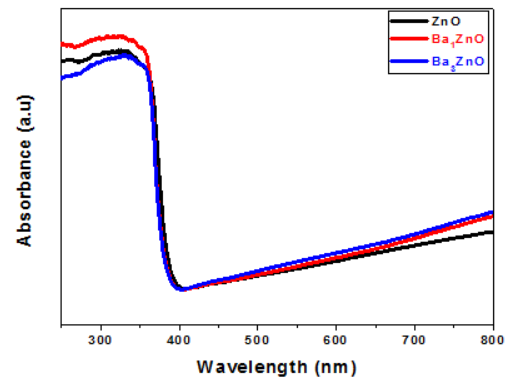


Figure 3. Absorption spectra of pure ZnO and Ba doped ZnO thin films

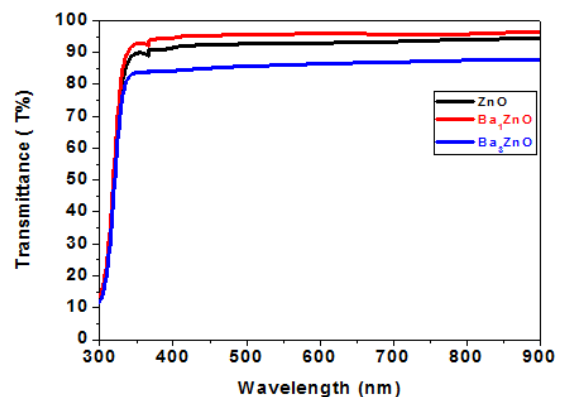


Figure 4. Transmittance spectra of pure ZnO and Ba-doped ZnO thin films

### 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.

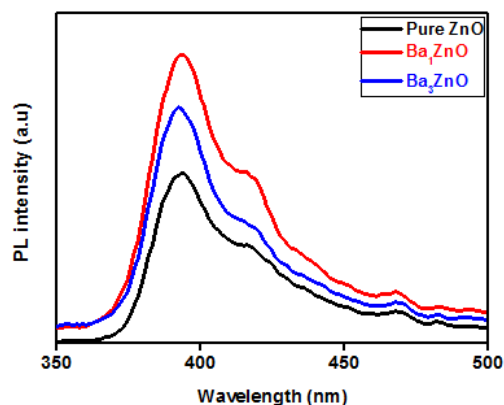


Figure 5. Photoluminescence spectra of Ba-doped ZnO and pure ZnO thin films.

## 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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## References

- [1] M Nirmala and A Anukaliani "Structural and optical properties of an undoped and Mn doped ZnO nanocrystalline thin film" *Photonics Lett. Pol.* Vol 2, No 4, pp.189-194 (2010).
- [2] G. Xiangdong, L. Xiaomin, and Y. Weidong, "Preparation and characterization of highly oriented ZnO film by ultrasonic assisted SILAR method," *J. Wuhan Univ. Technol.-Mat. Sci. Edit.*, vol.20, No.3, pp. 23-25, 2005.
- [3] T. Yen, D. Strome, S. J. Kim, A. N. Cartwright, and W. A. A derson, "Annealing studies on zinc oxide thin films deposited by magnetron sputtering," *J.of Electronic Materials*, vol. 37, no. 5, pp. 764-769, 2008.
- [4] V. Shelke, B. K. Sonawane, M. P. Bhole, and D. S. Patil, "Electrical and optical properties of transparent conducting tin doped ZnO thin films," *J. of Materials Science: Materials in Electronics*, vol. 23, no. 2, pp. 451-456, 2012.
- [5] B. Zhou, A. V. Rogachev, Z. Liu, D. G. Piliptsov, H. Ji, and X. Jiang, "Effects of oxygen/argon ratio and annealing on structural and optical properties of ZnO thin films," *Applied Surface Science*, vol. 258, no. 15, pp. 5759-5764, 2012.
- [6] T. Negami, Y. Hashimoto, S. Nishiwaki, "Cu(In,Ga)Se2 thin-film solar cells with an efficiency of 18% ", *Sol. Energy Mater. Sol.Cells* 67, 331, 2001.
- [7] Y.Natsume and H.Sakata "Zinc Oxide Films Prepared by Sol-Gel Spin-Coating", *Thin Solid Films*, 372, pp. 30-36, 2000.
- [8] X Wang, W P Careg and S Yee "Monolithic thin film metal oxide gas sensor arrays with application to monitoring of organic vapors" *Sens. Actuators B28* vol. 28, 1995, pp 63-70, 1995.
- [9] S.Roy, M.Boro, D.Mohanta, A.Choudhury and G.A.Ahmed, "Size quantification of sub-micron ZnSe semiconductor particles by laboratory scattering methods", *Indian J. Phys.* 84 705, pp 705-709, 2010.
- [10] D P Gogoi, G A Ahmed, D Mohanta, A Choudhury and G A Stanciu "Structural and optical properties of Mn doped ZnS semiconductor nanostructures", *Indian J.Phys.* 84 (10), pp.1361-1367, 2010.
- [11] V. Ghafouri, M. Shariati, A. Ebrahimzad "Photoluminescence investigation of crystalline undoped ZnO nanostructures constructed by RF sputtering" *Sci. Iran. Trans. F*, 19 (3) (2012), pp. 934-942, 2012.
- [12] Dong-Suk Kang, Seok Kyu Han, Sang Mo Yang, Jae Goo Kim, Wook Jung Hwang, Soon-Ku Hong, Jae Wook Lee, Jeong Yong Lee, Jung-Hoon Song and Takafumi Yao "Growth and Characterization of Zinc Oxide Nanostructures on (111) Silicon Substrates with Aluminum Compound Layer" *J. Korean Phys Soc.* Vol 53, No1, pp.292-298, 2008.
- [13] Patwari G, Bodo B.J., Singha R and Kalita P.K. "Photoluminescence Studies of H<sub>2</sub>O<sub>2</sub> Treated Chemically Synthesized ZnO Nanostructures", *Res. J. Chem. Sci.*, Vol.3 (9), pp.45-50, 2013.
- [14] Kentaro Sakai, Kohei Noguchi, Atsuhiko Fukuyama, Tetsuo Ikari and Tatsuo Okada, "Low-Temperature Photoluminescence of Nanostructured ZnO Crystal Synthesized by Pulsed-Laser Ablation" *Jpn. J. Appl. Phys* Vol. 48, 085001, 2009.
- [15] Yaxin Cai, Xiaowei Li, Yang Liu, Sisi Du, Pengfei Cheng, Fengmin Liu, Kengo Shimanoe, Noboru Yamazoe and Geyu Lu, "Hollow cylinder ZnO/SnO<sub>2</sub> nanostructures synthesized by ultrasonic spray pyrolysis and their gas-sensing performance", *CrystEngComm*, 16, 6135, 2014.
- [16] Mohammed Hadi Shinen, "Preparation of Nano-thin films of ZnO by Sol - Gel method and applications of solar cells Heterojunction", *J.Nat.Sci. Res.*, Vol.4, No.1, pp. 98-106, 2014.
- [17] Samira Bagheri, Chandrappa K. G and Sharifah Bee Abd. Hamid, "Facile synthesis of nano-sized ZnO by direct precipitation method", *Der Pharma Chemica*, Vol.5 (3), pp.265-270, 2013.
- [18] S. Thakur, J. Kumar, J. Sharma, N. Sharma, P. Kumar, "Structural and optical study of nickel doped ZnO nanoparticles and thin films for dye sensitized solar cell applications", *J.Opt. Adv. Mat.*, Vol. 15, No. 7- 8, pp. 989 - 994, 2013.
- [19] X. D. Gao, X. M. Li, and W. D. Yu, "Structural and morphological evolution of ZnO cluster film prepared by the ultrasonic irradiation assisted solution route," *Thin Solid Films*, vol. 484, no. 1-2, pp. 160-164, 2005.

- [20] Yantao Shi , \* Kai Wang , Yi Du , Hong Zhang , Junfu Gu , Chao Zhu ,Lin Wang , Wei Guo , Anders Hagfeldt , Ning Wang and Tingli Ma “Solid-state synthesis of ZnO nanostructures for quasi-solid dye-sensitized solar cells with high efficiencies up to 6.46%”.*Adv.Mater.* 25(32), pp.4413-4419, 2013.
- [21] Lee, Pay-YuChang,Sheng-PoChang,Jui-FuHsu, En-Hao Chang, Shouu-Jinn “Highly Transparent Nanostructured Zinc Oxide Photodetector Prepared by Successive Ionic Layer Adsorption and Reaction”, *Int. J. Electrochem. Sci.*, 8, pp.6425-6432, 2013.
- [22] P. Suresh Kumar, J. Sundaramurthy, D. Mangalaraj, D. Nat raj, D. Rajarathnam, M.P. Srinivasan, “Enhanced super-hydrophobic and switching behavior of ZnO nanostructured surfaces prepared by simple solution–Immersion successive ionic layer adsorption and reaction process”,*J. Colloid Interface Sci.*, 363, pp. 51-58,2011.
- [23] A U Ubale and A N Bargal “Characterization of nanostructured photosensitive cadmium sulphide thin films grown by SILAR deposition technique”, *Indian J. Phys.* 84 (11), pp.1497-1507, 2010.
- [24] J. Fan, R. Freer, “Varistor properties and microstructure of ZnO-BaO ceramics” *J. Mater. Sci.* 32 (1997) 415.
- [25] E. Ando, M. Miyazaki, *Thin Solid Films* 516 (2008) 4574.
- [26] Walter Water, Te-Hua Fang, Liang-Wen Ji, Teen-Hang Meen and Yin-Shiang Yan “Surface Morphology and Liquid Sensor Sensitivity of Barium-Doped ZnO Thin Film”,*J. Sci. Innov.*, Vol. 1, No. 1, pp.25-32,2011.
- [27] S. Balamurali, R. Chandramohan, N. Suriyamurthy, P. Parameswaran, M. Karunakaran, V. Dhanasekaran, T. Mahalingam “Optical and magnetic properties of Mn doped ZnO thin films grown by SILAR method”, *J Mater Sci: Mater Electron* 24, pp.1782–1787, 2013.