



# Influence of post heating temperature on structural and optical properties of spin coated Zinc Oxide thin films

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## ABSTRACT

Multi layer Zinc Oxide thin films with different post heating temperatures were prepared by sol-gel spin coating technique. Zinc acetate solution of 0.5M dissolved in isopropanol stabilized by Monoethanolamine was spin coated on glass substrates at 2000 rpm for 30s. After each deposition the films were pre-heated at 200°C for 10 minutes and post heated at 250,350 and 450°C in air atmosphere for 60 minutes. The structural properties were investigated by using X-ray diffraction technique and grain size was calculated. Elemental analysis and surface morphology were studied using EDX spectrum and SEM micrograph. Absorbance spectra were measured by using UV-Vis spectrophotometer and the optical band gap was calculated. The influence of post-heating temperatures on the structural and optical properties of zinc oxide thin films were reported.

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## Introduction

The application of ZnO have attracted much attention in recent years. With a wide band gap (3.37eV) and a larger binding energy (60meV), ZnO is potentially useful in various optoelectronics applications such as optical sensors and light emitters [1,2], etc. In additions, ZnO is also potentially useful in semiconductors [3], piezoelectric devices [4], transparent electrodes [5], solar cells [6], sensors [7], photocatalyst [8] and an antibacterial agent [9], because of its excellent electrical, optical and chemical properties. Investigations of applications of its photocatalytic activity have probably been the one area that has achieved the most interesting results [10, 11]. Photocatalytic activity occurs when the ZnO absorbs photons with an energy equal to or greater than its band gap energy and generates such reactive species as H<sub>2</sub>O<sub>2</sub>, superoxide anion radicals (•O<sub>2</sub><sup>-</sup>) and hydroxyl radicals (•OH) [12]. These photo generated reactive species are very strong oxidizing agents that can degrade organic and dye molecules.

Recently, ZnO have been prepared by sputtering [13], Chemical vapour deposition (CVD) [14], Molecular beam epitaxy (MBE) [15], spray pyrolysis [16], pulsed laser deposition [17] and the sol gel process [18,19]. Among these methods, the sol-gel process is particularly attractive because of its simplicity and acceptable cost, however the crystalline quality of the ZnO films prepared by the sol-gel process might be inferior to the other methods.

In this paper, structural and optical properties of sol gel spin coated ZnO thin films were studied and the effect of post heating temperature on structural and optical properties were reported.

## Experiment

### Preparation of precursor sol

Zinc acetate dihydrate (Zn(CH<sub>3</sub>COO)<sub>2</sub> · 2H<sub>2</sub>O), monoethanolamine (MEA, H<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH), isopropanol ((CH<sub>3</sub>)<sub>2</sub>CHOH, Merck) were used to prepare the coating solution. All chemicals were of analytical grade and were used without further purification. The molar ratio of MEA to zinc acetate dihydrate was maintained at 1.0 and the concentration of zinc acetate dihydrate was 0.5 mol/l. Zinc acetate dihydrate was

used as a starting material. Isopropanol and monoethanolamine were used as the solvent and stabilizer respectively. Zinc acetate dihydrate was first dissolved in isopropanol, then MEA was added drop by drop in the solution. The resultant solution was stirred at 50°C for 2h to yield a clear and homogeneous solution. Finally the solution was aged at room temperature for 24h. The pH value of the solution was observed as 7.5.

### Preparation of thin films

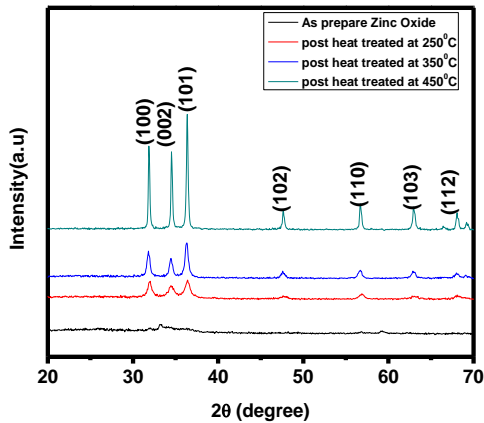
The ZnO thin films were prepared on glass substrates by repeated coating. The solution was dropped on the cleaned glass substrates and the substrates were rotated at 2000 rpm for 20s (Apex Instruments Co SCU -2008C) and the ZnO thin films were prepared by repeated coating. After each coating films were heated at 200°C for 10 min to evaporate the solvent and the organic residuals (named as pre-heat treatment). After the pre-heat treatment, the ZnO thin films were allowed to cool to room temperature to avoid cracks. The spin-coating and pre-heating process were repeated for ten times. For crystallization, the ZnO thin films were heated in a furnace in air atmosphere at 250,350 and 450°C for 60 minutes and allowed to cool to room temperature gradually. The post heat treatment is to convert the organic coating containing Zn<sup>2+</sup> into its respective oxide [20].

### Characterization of thin films

The crystallinity of each ZnO film was determined by X-ray diffraction using an (XPRT-PRO) X-ray diffractometer with CuK<sub>α</sub> radiation source in the range of 20-70° with 0.05° step size. Elemental compositions and surface morphological analysis of the prepared samples have been studied using scanning electron microscope (Hitachi VP-SEM S-3400N). The optical properties were studied by using a UV-Visible spectrophotometer (JASCO Corp., V-570).

### Results and discussion

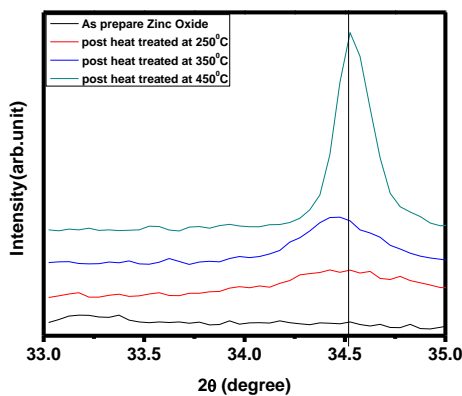
Fig. 1 shows the X-ray diffraction patterns of ZnO thin films post heated at various temperatures of 250,350 and 450°C for 60 minutes. It shows that as prepared films exhibit non crystalline nature and other post heat treated films are polycrystalline.



**Fig.1. X-ray diffraction patterns of ZnO thin films post heated at different temperatures**

The very strong (100), (002) and (101) peaks corresponding to the  $2\theta$  values of  $31.80^\circ$ ,  $34.442^\circ$  and  $36.278^\circ$  and the very weak (102), (110), (103), and (112) peaks corresponding to the  $2\theta$  values of  $47.62^\circ$ ,  $56.7^\circ$ ,  $62.94^\circ$ , and  $68.0^\circ$  are in good agreement with the standard JCPDS card (36-1451) for hexagonal wurtzite ZnO [20]. The relative intensity of the (100), (002), (101) peaks tends to increase with an increase in the post heating temperature. The increase in peak intensities indicates an improvement in the crystallinity of the films because it is generally noted that the crystallinity can be enhanced while increasing the post heating temperature [21].

The fig. 2 shows (002) diffraction peaks in  $2\theta$  region from  $33^\circ$  to  $35^\circ$ . These main peaks of ZnO films shift to higher diffraction angle ( $34.442^\circ$  to  $34.532^\circ$ ) with an increase in the post heating temperature. The increase of  $2\theta$  of the (002) peak may be related to a decrease of the lattice parameters which comes from the oxygen deficiency and strain caused by crystallization during the post heating process [22, 23].



**Fig.2. X-Ray diffraction peaks in  $2\theta$  region from  $33.0^\circ$  to  $35.0^\circ$ .**

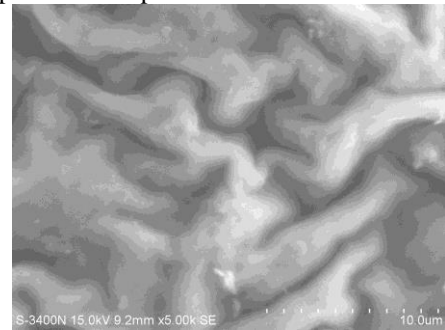
The grain size of the ZnO thin films has been estimated from FWHM of (002) diffraction peak using the Scherrer formula [24]

$$d = k\lambda / \beta \cos \theta$$

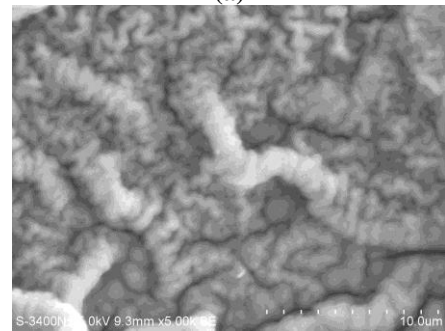
where  $\lambda$  is the X-ray wavelength of  $1.54\text{\AA}$ ,  $\theta$  is the Bragg diffraction angle in degrees,  $k$  is a fixed number of 0.9 and  $\beta$  is the FWHM of (002) plane. By increasing the post heating temperature the grain size of the ZnO thin films gets increased and good grain size was obtained at  $450^\circ\text{C}$ .

As the micro structure of the ZnO thin films has an influence on the optical and structural properties, it is very

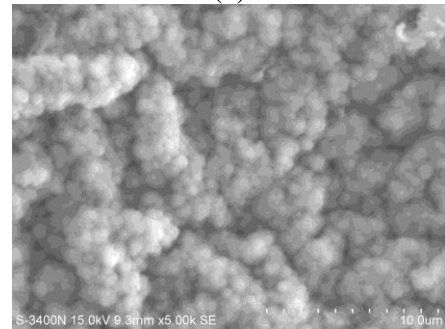
important to investigate the surface morphology of the ZnO thin films. Fig. 3(a-d) shows the SEM images of as prepared film and films post heated at  $250^\circ\text{C}$ ,  $350^\circ\text{C}$ , and  $450^\circ\text{C}$ . By increasing the post heating temperature, the grains become denser and larger which can be considered as a coalescence process induced by the thermal treatment. For ZnO nanoparticles, there are many Frenkel defect, such as Zn interstitials and oxygen vacancies at grain boundaries [21,25]. As a result, these defects are favorable to coalescence process to make larger grains with an increase in the post heating temperature [21]. These results are in agreement with the XRD analysis. The crystalline size increases with increasing post heat temperature from  $250$  to  $450^\circ\text{C}$ .



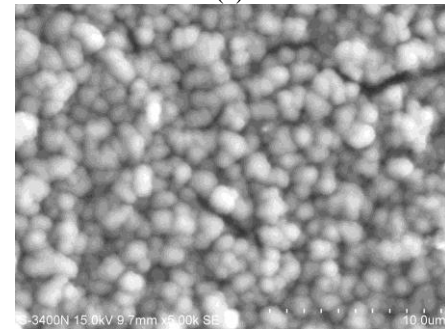
(a)



(b)

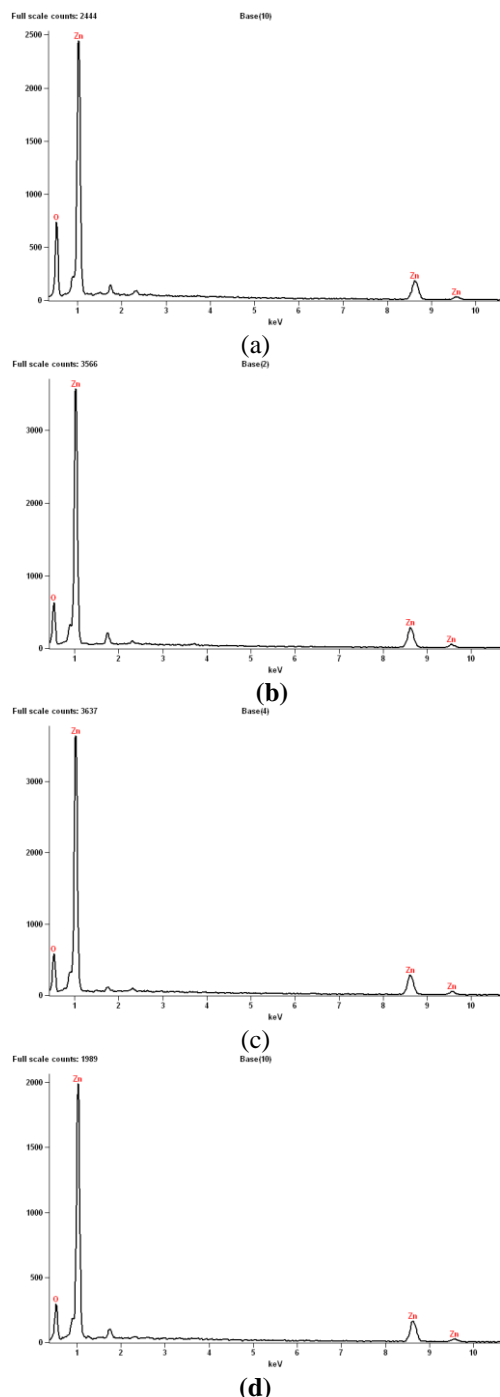


(c)



(d)

**Fig.3. SEM Micrographs of ZnO Thin films (a) as prepared (b) post heated at  $250^\circ\text{C}$ , (c)  $350^\circ\text{C}$ , (d)  $450^\circ\text{C}$**

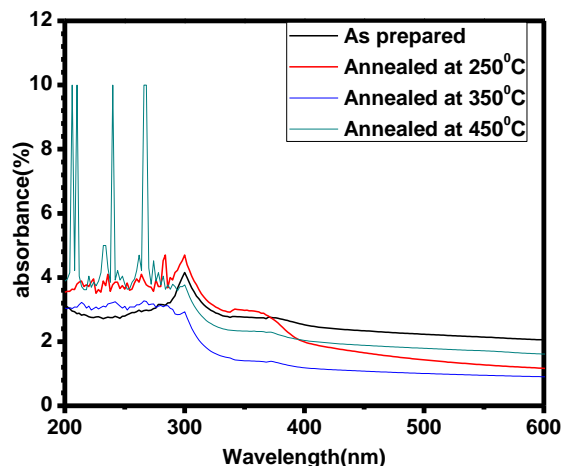


**Fig. 4. EDX spectrum of ZnO thin films (a) as prepared (b) post heated at 250°C, (c) 350°C, (d) 450°C**

The crystalline greatly grows at 450°C and the pores of the surface are partly formed by the coalescence of microvoids. It indicates that the pores in the surface are related with the decomposition reaction of the precursor and the evaporation of residual organics in gel films [26].

Energy dispersive X-ray (EDX) analysis reveals that the ZnO thin films were mainly compounds of Zn and oxygen. Fig. 4(a-d) shows the EDX spectrum of the thin films as prepared and post heat treatment at 250, 350, and 450°C. It can be seen that the net count of the oxygen atoms get decreased when the post heating temperature of the ZnO thin film is increased. If oxygen atoms get decreased it leads to increasing in oxygen vacancies and oxygen defect.

Fig .5 shows the optical absorption spectra of ZnO thin films post heat treated at 250, 350, and 450°C.



**Fig .5. UV-Vis absorption spectra of the ZnO thin films post heated at different temperatures**

It can be seen that the intensity of the UV peaks increases with increase in the post heating temperatures and sharp peaks with maximum intensity in UV-C region are observed for the film post heat treated at 450°C.

**Table 1. Influence of post heating temperature on grain size and optical band gap**

Post Heating Temperature (°C)	Grain Size (nm)	Band Gap(eV)
As prepared	--	3.68
250	14.62	3.28
350	22.535	3.24
450	32.743	3.22

It is well known that the optical absorbance determines the optical band gap and ZnO thin films have a direct band gap. The optical band gap of as prepared ZnO thin films and films post heated at 250, 350, and 450°C was found to decrease from 3.68eV, 3.28eV , 3.24eV to 3.22eV respectively. It is observed that as the post heat temperature increases the grain size increases while the band gap decreases as shown in table.1.

### Conclusion

ZnO thin films were prepared by the sol gel spin coating method and post heat treated at different temperatures and their structural, morphological and optical parameters were investigated. From the results of XRD and SEM , it was clearly observed that the thin films are found to be polycrystalline in nature and good quality of ZnO thin films can be fabricated at the post heating temperature of 450°C. From the investigations, it was observed that, as the post heating temperature increases the grain size and absorption intensity increase and the band gap decreases. The film post heated at 450°C shows maximum UV absorption intensity. Thus the post heating temperature influences the structural and optical properties of spin coated ZnO thin films. From the results it is clear that one can apply these high quality ZnO thin films as photocatalyst in photocatalytic decolorization of organic contaminants.

### Acknowledgement

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