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The Effect of ZnO Thin Film and Its Structural and Optical Properties Prepared by Sol-Gel Spin Coating Method

Nagarani Nagayasamy, Saroja Gandhimathination, Vasu Veerasamy
School of Physics, Madurai Kamaraj University, Madurai, India
Email: nagarani1966@gmail.com

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ABSTRACT

ZnO thin films were deposited on glass substrates at different Zinc concentration and their effects on structural, morphology and optical properties were investigated. Zinc acetate dehydrate, 2 Methoxy ethanol and Monoethanolamine were used as the precursor, solvent and stabilizer respectively. The molar ratio of Monoethanolamine to Zinc acetate was maintained as 1. The crystal structure and orientation of the films were analyzed by XRD. The XRD patterns show that the ZnO films are polycrystalline with wurtzite hexagonal structure. The film with 0.5 m/l concentration has the better crystallinity. The thickness of the films was determined by thickness Profilometer. The surface morphology of the films was observed by Scanning electron microscope. The SEM images show that they are homogeneous, continuous and spindle like shape. The optical properties of the films were studied by UV-Vis-Spectrophotometer. The transmittance of the films decreases with increase of Zinc concentration. The energy band gap of the films decreases slightly, when the Zinc concentration increases from 0.25 m/l to 0.75 m/l and then increases when the concentration further increases from 0.75 m/l to 1.0 m/l.

Keywords: ZnO Thin Films; Sol-Gel; XRD; SEM; Optical Properties

1. Introduction

Zinc Oxide is an important, inexpensive, versatile n-type semiconducting material with wide direct energy band gap of 3.37 eV and large exciton binding energy of about 60meV at room temperature. ZnO has unique structural, optical and electrical properties. Due to its high transparent conducting properties, it has many potential applications like light emission display devices, piezoelectric transducers, surface acoustic devices, optoelectronic devices etc., Various deposition techniques were employed for the preparation of ZnO thin films such as magnetron sputtering [1], spray pyrolysis [2], pulsed laser deposition [3], electron beam evaporation [4] and sol-gel method [5-9]. In this work the ZnO films were prepared by an inexpensive sol-gel spin coating technique and studied the effect of concentration of the precursor on structural, morphological and optical properties.

2. Experimental Details

ZnO thin films were coated on glass substrates by sol-gel method. Zinc acetate dehydrate, 2 Methoxy ethanol and Monoethanolamine were used as the precursor, solvent and stabilizer respectively. Zinc acetate dehydrate was dissolved in a mixture of 2 Methoxy ethanol and Monoethanolamine at room temperature. The molar ratio of MEA to Zinc acetate was maintained as 1 and the concentration of Zinc acetate were 0.25 m/l, 0.5 m/l, 0.75 m/l and 1.0 m/l respectively. The solutions were stirred at 60˚C for 2 hrs to yield a clear and homogeneous solution. All of the solutions were then aged at room temperature for 1 day before spin coating.

The substrates were cleaned by soap solution, chromic acid, distilled water, acetone and finally with deionized water. Then the films were deposited on the glass substrates using spin coater. The substrates were spin at 3000 rpm for 30 sec. while the solution was dropped on to a glass substrate. In order to evaporate the solvent and remove the organic residuals the films were preheated at 300˚C for 10 minutes after each Coating. This process was repeated several times. Then the films were annealed at 500˚C for 1 hour.

The structure and orientation of the ZnO thin films

were analyzed by X-ray diffractometer with Cu-K_α radiation. The thickness of the films was determined by thickness profile meter. The surface morphology of the films was observed by Scanning electron microscope. The optical properties of the films were carried out by UV-Vis spectrophotometer.

3. Results and Discussions

3.1. Structural Properties XRD

Figure 1 shows the XRD pattern of ZnO thin films prepared at different Zinc concentrations and annealed at 500˚C for 1 hour. From the figure it may be observed that there are only three peaks with the (100) (002) (101) orientation for the sample of 0.25 m/l and 0.5 m/l concentrations. The number of orientation increases to six for the sample 0.75 m/l and seven for the sample 1.0 m/l concentration. Further it may be noted that the prepared orientation for 0.25 m/l and 0.5 m/l samples was (002) and for higher concentration (that is above 0.5 m/l) sample the preferred orientation was (101). The XRD results show that all the films were polycrystalline wurtzite hexagonal structure and have no preferred orientation. This may be due to the preferred orientation is weakened when the Zn concentration increases. The grain size of the film was calculated for different Zinc concentration by using Scherrer's formula [10]

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

where λ is the wavelength of the X-ray radiation used. β is the Full width Half Maximum and 2θ is the highest diffraction angle. The strain in the films were calculated using the formula

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

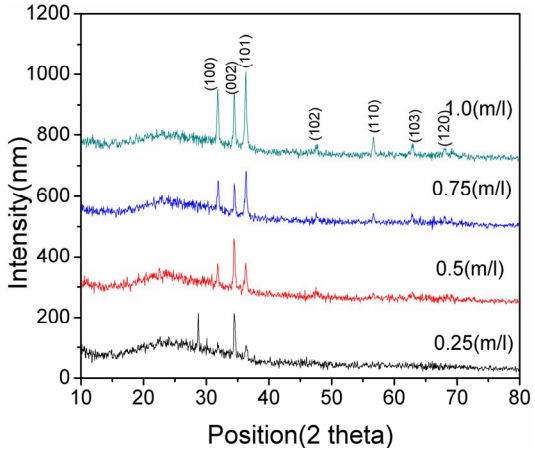


Figure 1. XRD spectra of ZnO thin films at different Zinc concentration (a) 0.25 m/l; (b) 0.5 m/l; (c) 0.75 m/l (d) 1.0 m/l.

The value of particle size, strain and FWHM values are tabulated in **Table 1**. From the table it may be observed that the strain value of the film decreases with increase in particle size. For the concentration of 0.5 m/l, FWHM value is very small indicating larger particle size compared to other concentrations.

Figures 2 (a) and **(b)** show the relation between strain and particle size of the films as a function of Zinc acetate concentration. The thickness of the film was tabulated in **Table 1**. It may be observed that the thickness of the film increases with increase of Zinc Concentration. This is because of the increased fluid Viscosity.

3.2. Surface Morphology

Figures 3 (a)-(d) show the SEM images of ZnO thin films for different concentration of ZnO 0.25 m/l, 0.5 m/l, 0.75 m/l and 1.0 m/l deposited on glass substrates. The films deposited at different concentration have smooth and spindle like structure and uniformly covering the overall surfaces with good adherence. The SEM images show the grains of spindle like shape without any cracks and pores.

3.3. Optical Properties

Figure 4 shows the optical transmittance spectra of ZnO

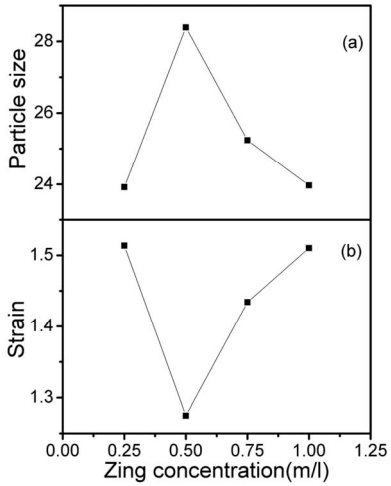
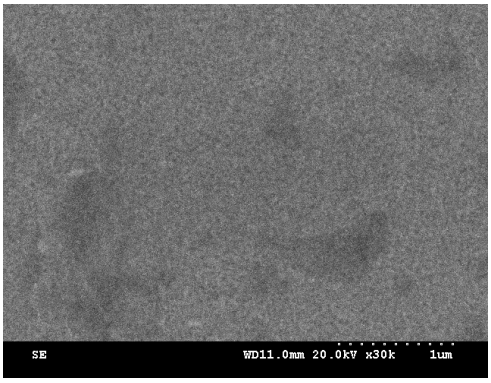


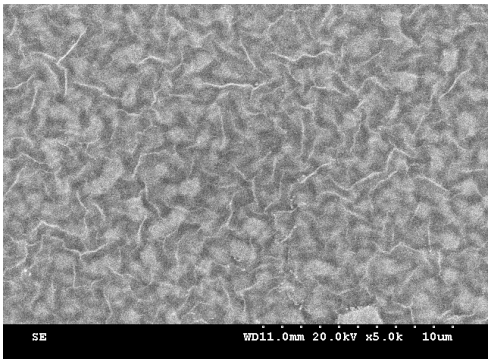
Figure 2. (a), (b) the relation between strains, particle size with respect to Zinc concentration.

Table 1. The structural parameters of the ZnO thin films.

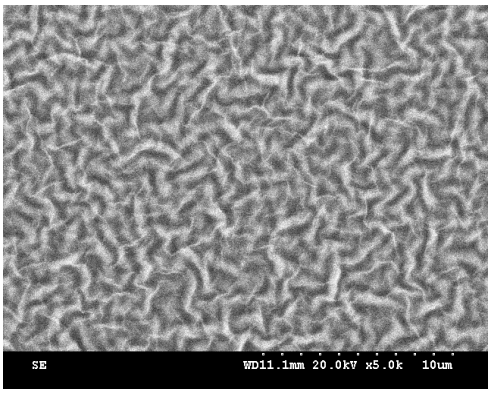
Zinc concentration	Position (2θ)	(hkl)	FWHM	Strain ($\beta\cos\theta/4$)	Particle size (nm)	Thickness (μm)
0.25 m/l	34.4672	(002)	0.3634	1.5137	23.92	0.26
0.50 m/l	34.4367	(002)	0.3061	1.2751	28.39	0.40
0.75 m/l	36.3110	(101)	0.3461	1.4342	25.24	0.44
1.00 m/l	36.2727	(101)	0.3644	1.5102	23.97	0.49



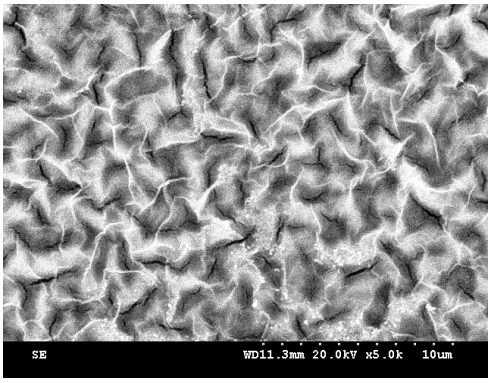
(a)



(b)



(c)



(d)

Figures 3. (a)-(c) show the surface morphology of the films at different Zinc concentration.

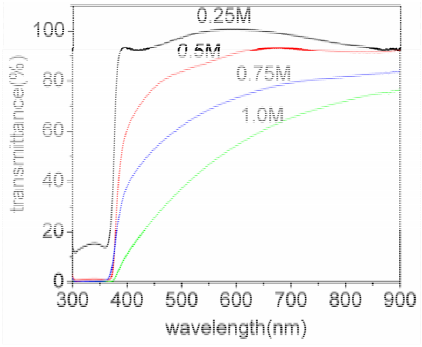


Figure 4. Transmittance spectra of ZnO films with different Zn concentration.

films with different Zinc concentration. The transmittance decreases with increase of Zinc concentration. All the samples present a sharp absorption edge in the UV region nearly 370 nm due to the onset fundamental absorption. The decrease in transmittance may be due to increase of the optical scattering caused by the grain boundaries and the increase in film thickness. The grain boundary density increases with increasing Zinc concentration. This may reduce the optical transmittance. The absorption co-efficient (α) was determined from the transmittance measurements using the relation

$$\alpha = \frac{\ln\left(1/T\right)}{t}$$

where T is the transmittance and t is the thickness of the film. The calculated absorption co-efficient values are used to determine the optical energy gap of the films. **Figure 5** shows the plot of $(\alpha h\gamma)^2$ versus $h\gamma$.

Assuming a direct transition between valance and conduction bands, the energy band gap was determined by the expression [11]

$$\alpha h\gamma = k\left(h\gamma - E_g\right)^{1/2}$$

where k is the constant. E_g is determined by extra ploting the straight line portion of the curve to $(\alpha h\gamma)^2 = 0$ and the values for different Zinc concentration are tabulated in **Table 2**. It may be observed that the energy band gap decreases slightly, when the concentration Increases from 0.25 m/l to 0.75 m/l and further increases when concentration Increases from 0.75 m/l to 1.0 m/l.

4. Conclusion

ZnO thin films were prepared with different Zinc concentration and their effects on structural, morphology and optical properties were studied. The XRD results show that the films are polycrystalline wurtzite hexagonal structure and have no preferred orientation. The film with 0.5 m/l concentration has minimum value of strain and has larger particle size compared to other concentrations.

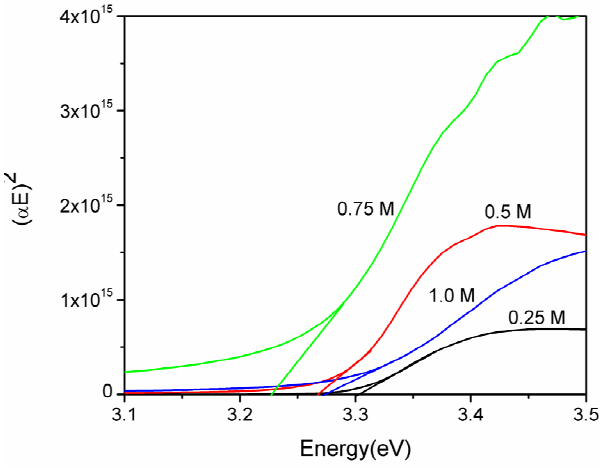


Figure 5. Band gap plot of $(\alpha h\gamma)^2$ versus $h\gamma$.

Table 2. Energy bandgap of ZnO films with different Zn concentration.

Zinc concentration (m/l)	Energy bandgap (eV)
0.25	3.3054
0.50	3.2695
0.75	3.2295
1.00	3.2757

The thickness of the films increases with increase of Zinc concentration. SEM images show that they are homogeneous, continuous and spindle like shape. The transmittance decreases with increase of Zinc concentration. This may be due to increase of optical scattering caused by the grain boundary. The energy band gap of the films decreases slightly, when the Zinc concentration increases from 0.25 m/l to 0.75 m/l and then increases when the concentration further increases from 0.75 m/l to 1.0 m/l.

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