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Characterization of ZnO thin films grown by sol-gel spin coating technique regarding precursor solution

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ABSTRACT ZnO thin films were fabricated on glass substrates by sol-gel spin coating technique. Atomic force microscopy, X-ray diffraction and optical spectroscopy measurements were employed to analyze the effects of the precursor solution molarity. The films exhibited a hexagonal wurtzite structure with preferred c-axis orientation. The (002) peak intensity of the films decreased and full width at half maximum values reduced from 0.239° to 0.205° with increasing molarity from 0.5 M to 1.5 M. It was concluded that the molarity had affected the grain size and orientation of crystals. The grain size and the surface roughness values were 36.31 nm and 24 nm; 41.32 nm and 176 nm; 42.33 nm and 404 nm for 0.5 M, 1.0 M and 1.5 M samples respectively. The band gap values were determined as 3.28 eV, 3.23 eV and 3.16 eV, respectively for the 0.5 M, 1.0 M and 1.5 M samples.

Keywords: ZnO; Sol-gel; Thin film; Molarity effects.

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1. INTRODUCTION

Zinc Oxide (ZnO) is a wide band gap semiconductor with a direct energy gap of about 3.37 eV and a large excitation binding energy of 60 meV at room temperature [1-3]. The bandgap can be tuned by alloying with magnesium oxide or cadmium oxide. ZnO is an exceptionally important semiconductor material [4,5] for photovoltaic and optoelectronic device applications such as laser diodes or light-emitting diodes [6], display materials [7], solar cells [8], thin film or bulk acoustic resonators [9], and surface acoustic wave devices [10]. Moreover, ZnO is regarded as a promising material for these technologies owing to its non-toxicity [11], abundance on the nature [12], low cost [13] and chemical and thermal stability [14] even under hydrogen plasma [15].

ZnO thin films can be deposited by variety of deposition techniques, such as, spray pyrolysis [16], molecular beam epitaxy [17], chemical vapor deposition [18], pulse laser deposition [19], sputtering [20] and sol–gel method [21]. Among these techniques, sol–gel process has many advantages such as being simple, having low production cost, and large area coating without any need for high vacuum [22-24]. This technique is commonly used to deposit various oxide films, including ZnO thin films with higher degree of preferred c-axis orientation. Generally, organometallic or alkoxide approach is used to obtain oxide thin films. Organometallic precursors are expensive and toxic, therefore, the alkoxide approach, which uses water or alcohol solutions of metal salts such as acetates, nitrates or chlorides is preferably used in growth of ZnO films [25]. Although there are a lot of experimental works about ZnO, only a few studies on the effect of molarity on the properties of ZnO thin films exist. Babar et al. [26] and Shinde et al. [27] have used spray pyrolysis with varying the precursor solution molarity. Zaier et al. [28] have investigated the effects of solution molarity and

substrate temperature on films' properties and crystallinity and observed that the transmission increased with a decrease in the molarity and an increase in the substrate temperature. The variation of structural, morphological, optical, and electrical properties of nanocrystalline ZnO thin films with molarity of the precursor solution has been investigated in detail by Mishra et al. [29].

In this paper, ZnO films have been synthesized by using sol-gel spin coating technique. The crystalline structures, surface morphologies and absorption spectra of ZnO films prepared at various molarities of the precursor solution have been investigated.

2. EXPERIMENTAL

In this study, ZnO thin films were fabricated on glass substrates by spin coating sol-gel technique. Zinc acetate dehydrate [$Zn(CH_3COO)_2.2H_2O$] was used as a starting material. Monoethanolamine (C_2H_7NO, MEA) and 2-Methoxyethanol ($C_3H_8O_2$) were used as stabilizer and solvent, respectively. The solution was prepared as 0.5, 1.0 and 1.5 M and the molar ratios of $Zn(CH_3COO)_2.2H_2O$ to MEA were maintained at 1:1. The sol was stirred at 60 ºC for 2 h to obtain a clear and homogenous solution. The glass substrates were cleaned in acetone and methanol by using an ultrasonic cleaner. Then the substrates were rinsed with de-ionized (DI) water and dried with nitrogen. The precursor solution was dropped on glass substrate and spin-coated at a speed of 3000 rpm for 25 s. To evaporate the solvent, the as-coated film was sintered at 250 ºC for 10 minutes. This procedure was repeated for 10 times to obtain the intended thickness. The same procedure was repeated for the films prepared with different values of molarity and finally they were annealed in air ambient at 500 ºC for 30 minutes.

X-ray diffraction (XRD) patterns were taken using a Rigaku D/Max-IIIC diffractometer. The diffractometer reflections were investigated at room temperature and the values of 2θ were altered between 20º and 80º. The incident wavelength was 1.5406 Å. Morphological properties of the films were determined with dynamic mode atomic force microscopy (D-AFM), (Produced by Nanomagnetics-Inst). Atomic force microscopy images were obtained at 5 μm x5 μm planar in tapping mode, in 512x512 resolution and with speed of 3 μm/s. The optical absorbance of the thin films was recorded in spectral region of 360-460 nm at 300 K using a Perkin Elmer UV/VIS Lambda 2S Spectrometer which works in the range of 190-1100 nm and has a wavelength accuracy of better than ±0.3 nm. The average film thickness was obtained from SEM image and determined with Nova Nanosem 430.

3. RESULTS

The crystal structures of the ZnO thin films prepared using 0.5 M, 1.0 M and 1.5 M solutions, samples S1, S2 and S3, respectively, were analyzed by XRD method. Fig. 1 shows the XRD spectra, where all the peaks of are indexed to ZnO with the hexagonal wurtzite structure [22]. It is comprehensible that all the films exhibit the growth of ZnO with higher degree of preference along the *c*-axis perpendicular to the substrate surface, except S3 sample. The dominant peak was observed as the (002) reflection for all samples.

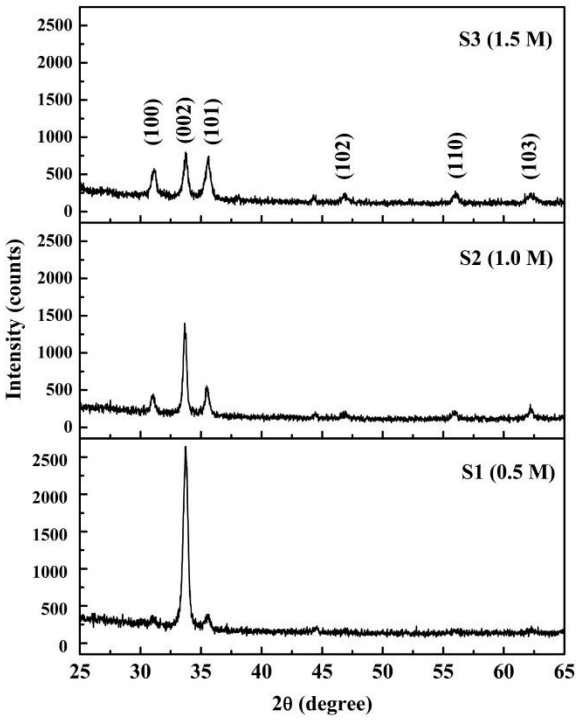

Figure 1. *XRD spectra of ZnO films prepared at various molarities of the precursor solution.*

Therefore, the crystalline quality of ZnO films can be evaluated by the intensity and the full-width at half-maximum (FWHM) of the (002) peak [30]. The other peaks of low intensities correspond to (100) and (101) planes. The relative intensities of the (002) diffraction peaks are much stronger than those of the (100) and (101) peaks. We have also observed an increase in the intensities of the peaks (100) and (101) and a decrease in the intensity of peak (002) with increase in molarity. These results implied that the orientation of the substrate had some impact on the orientation of the deposited ZnO [31]. In addition to the reduction in XRD peak intensities, it is clear in Fig. 1 that crystal structures of the films changed from single to poly crystalline nature with molarity increasing from 0.5 M to 1.5 M. It may be concluded that molarity could affect the grain size and the orientation of crystals. Fig. 2 shows the relationship between XRD (002) peak intensity and molarity. Fig. 2 also shows the relationship between roughness and molarity (002) peak intensity of the films gradually decreased from 0.5 M to 1.5 M with increasing of precursor solution molarity. The lowest (002) peak intensity has been obtained for the 1.5 M ZnO film. This may be due to high molarity meaning the excessive density could increase defects in the ZnO films and deteriorate the structural quality. At higher temperatures, similar behavior has been observed by Zaier et al. [28].

Table 1. *The molarity, FWHM, grain size and surface roughness values for the S1, S2, and S3 samples.*

Sample	Molarity (M)	FWHM (°)	Grain size (nm)	Roughness (nm)
S1	0.5	0.239	36.31	24
S2	1.0	0.210	41.32	176
S3	1.5	0.205	42.33	404

The average size of the crystalline grains in the films is estimated from the full-width at half-maximum (FWHM) of (002) diffraction peak by using the following Debye–Scherrer equation [32] by assuming a homogeneous strain across the films.

$$D = \frac{k\lambda}{B\cos(\theta)} \quad (1)$$

Where k is the shape factor (0.9), λ is wavelength of the X-ray, θ is the diffraction angle and B is the full width at half maximum (FWHM) of the (002) diffraction peak. When the molarity increased from 0.5 M to 1.5 M, the

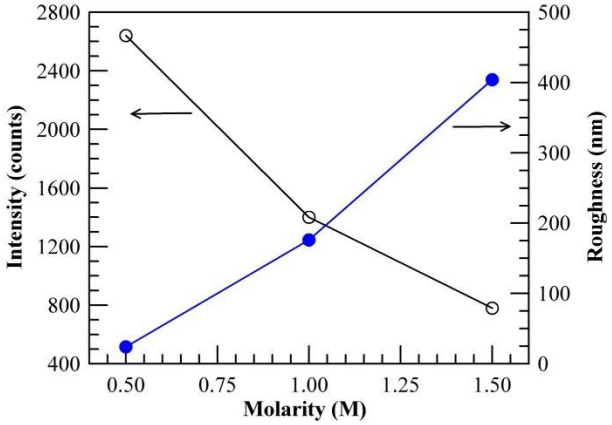

Figure 2. *Intensity of (002) XRD peak and the corresponding calculated surface roughness versus molarity.*

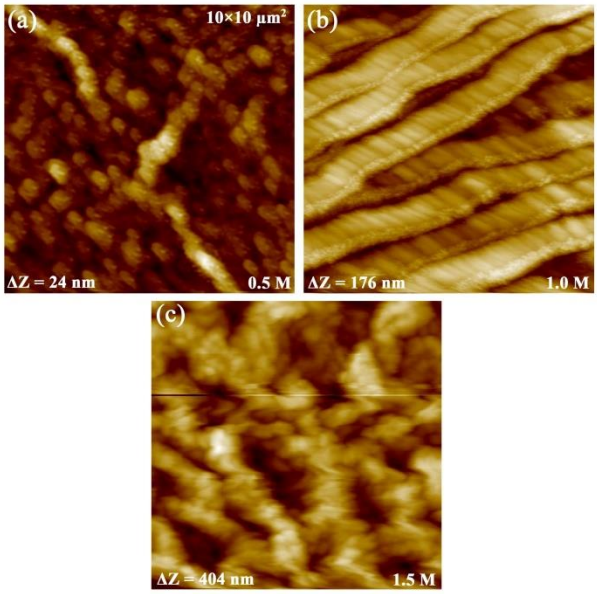

Figure 3. *AFM images of the films grown using precursor solution of molarity* ***(a)*** *0.5 M;* ***(b)*** *1.0 M;* ***(c)*** *1.5 M.*

value of the FWHM decreased from 0.239° to 0.205°. The calculated values of grain size and FWHM values are given in Table 1. Grain size increases gradually from 36.31 to 42.33 nm with increasing molarity. This behavior is consistent with the results obtained by Korotcenkov et al. [33], Mishra et al. [29] and Shinde et al. [27]. It was also pointed out in each of the aforementioned studies that the grain size of ZnO films increases with an increase in precursor solution molarity. Moreover, Fang et al. [30] has found it that the grain size of ZnO thin films increases gradually with increasing annealing temperature.

AFM images of the film surfaces deposited using different precursor solution molarities are shown in Fig. 3. The surface roughness values for S1, S2 and S3 samples were 24, 176, and 404 nm, respectively, which increases with the molarity. A considerable increase in the surface roughness was observed in the 1.5 M ZnO films. The grain sizes obtained from XRD measurements were also increasing with increasing molarity. However, the increase in the roughness values of ZnO films obtained from AFM is much larger than the increase in the grain size values obtained from XRD [26]. The calculated roughness values are given in Table 1. The values of grain size and roughness were found to increase with increasing in molarity of the precursor solution. As the concentration of the precursor solution increased, grain size and roughness seem to increase; i.e, small crystallites coalesce together to make larger crystallites. This process was termed as coalescence by Fang et al. [30]. The coalescence causes larger grain size and surface roughness in crystal structure.

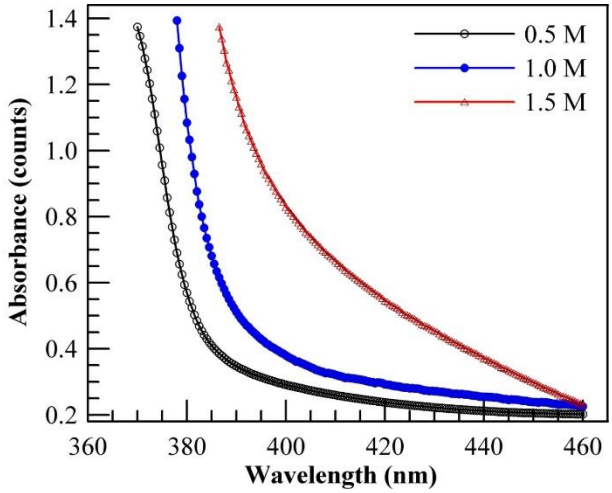

Figure 4. *The optical absorption spectra for the S1, S2 and S3 samples.*

Optical absorption spectra of S1, S2 and S3 samples within the wavelength range of 250-460 nm are shown in Fig. 4. The band edge absorption shows that ZnO films exhibit high quality. This is inconsistent with XRD results. Optical absorbance increased as the molar concentration of solution was increased from 0.5 M to 1.5 M. Similar behavior has also been reported by Shinde et al. [35]. There are several factors influencing the absorption, such as films thickness, surface scattering and grain-boundary scattering [36]. The absorption edge of ZnO film shifts slightly to longer wavelengths (red shift) from 381 to 399 nm with molarity variation from 0.5 M to 1.5 M, respectively. This shift can be attributed to the increase in grain size with molar concentration [35].

Fig. 5 shows the plots of $(\alpha h\upsilon)^2$ versus photon energy for all three films. Absorption coefficient (α) was computed from the measured absorption spectra using the following equation:

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)} = \exp(-A) \qquad (2)$$

where R is the reflectance, T is the transmittance, A is the absorbance and t is the film thickness.

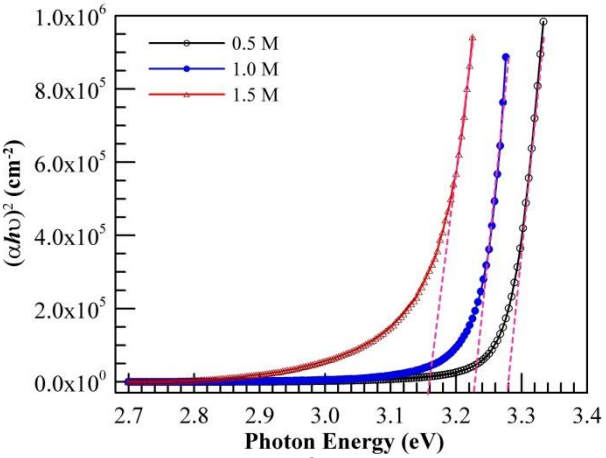

Figure 5. *The plots of $(\alpha h\upsilon)^2$ versus photon energy for the S1, S2 and S3 samples.*

The optical band gap (E_g) values of the films were determined from the intercept of $(\alpha h\upsilon)^2$ versus photon energy curve. E_g values for samples S1, S2 and S3 are 3.28 eV, 3.23 eV and 3.16 eV, respectively, at 300 K. It has been observed that bandgap changes can be as large as 120 meV with increase in molarity from 0.5 M to 1.5 M. The decrease in the optical band gap of the films with increase in the molarity of precursor solution have been attributed to the grain size enhancement by Sakthivelu et al. [37].

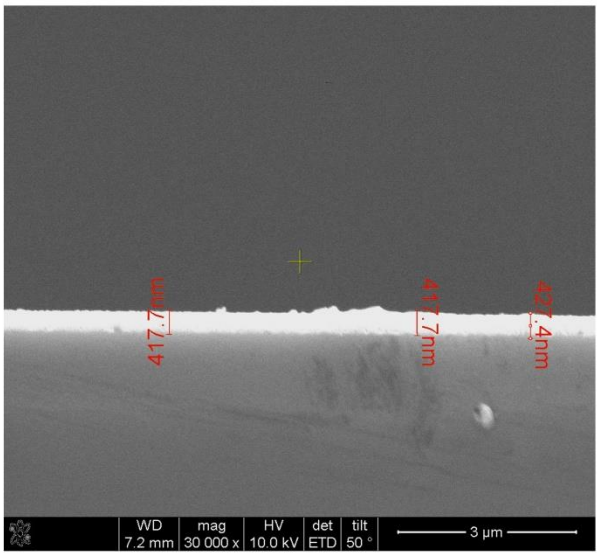

Figure 6. *The film thickness of ZnO thin film for 0.5 M sample.*

Kuo et al. [38] also reported that the band gap energy could be modulated by changing the particle or grain size in the films. The decrease in band gap with increase in particle size observed in 0.5 M, 1.0 M and 1.5 M ZnO films is in accord with the quantum confinement theory.

In addition, the average film thickness of Sol-gel growth ZnO film was obtained 417.6 nm for 0.5 M from SEM image and shown in Fig. 6. The thickness of the prepared film has a significant effect on the surface roughness and optical properties [34].

4. CONCLUSION

The influence of the molar concentration of zinc acetate precursor solution on the optical and structural characteristics of ZnO films prepared by sol-gel spin coating method was studied. The grown ZnO films exhibit a higher degree of preference along the *c*-axis perpendicular to the substrate surface, except S3 sample, as determined from XRD measurements. The (002) peak intensity of the films gradually decreased, the crystal structures of the films changed from single to poly crystalline and the value of the FWHM decreased from 0.239° to 0.205° with increasing molarity from 0.5 M to 1.5 M. It may be concluded that molarity could affect the grain size and the orientation of crystals. The calculated values of grain size and roughness were 36.31 nm, 24 nm; 41.32 nm, 176 nm; and 42.33 nm, 404 nm for samples S1, S2 and S3, respectively. The optical band gap values of the films were determined as 3.28 eV, 3.23 eV and 3.16 eV, respectively for S1, S2 and S3 samples at 300 K. In conclusion, the molarity can influence the structural and optical properties of ZnO films and appropriate molarity (0.5 M) can improve ZnO crystallinity, such as high c-axis orientation, and regular and smooth surface.

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