Highly c-axis Oriented ZnO Thin Films by Sol-gel Method

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Abstract

This study reports the effect of annealing temperature on the structural, morphological, and optical properties of ZnO (Zinc Oxide) thin films deposited on a glass substrate by the sol-gel spin coating method. Those properties of ZnO were examined with UV-Vis, Fourier transform infrared (FTIR) and Raman spectroscopy, Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), and X-ray diffraction (XRD), before and after annealing. XRD results revealed that all the samples had a highly c-axis oriented wurtzite structure. A 1 (LO) mode in Raman spectra also confirmed the highly oriented ZnO films. Optical measurement indicated that transmittance of the films was above %85, and the optical band gap slightly decreased with the increasing annealing temperature from 350 to 550 °C. Morphological analysis displayed that increasing annealing temperature improved surface morphology and enlarged the grain size from 2-3 nm for as-deposited samples to 150 nm for annealed at 550 °C.

1. Introduction

ZnO has attracted the attention of many researchers for many years due to some of its properties such as wide band gap (3.30eV), high exciton binding energy (60MeV) at room temperature, stable hexagonal wurtzite structure with space group P63mc [1, 2]. These features have made it desirable for several applications including photocatalysis [3], surface acoustic wave devices [4], photodetectors [5], gas sensors [6], light-emitting diodes [7, 8], and solar cells [9].

ZnO films has been produced using various methods such as thermal evaporation[10], pulsed laser [11], sol-gel spin-coated [12, 13], spray pyrolysis [14], rf sputtering [15, 16], electro deposition [17], dc-rf magnetron sputtering [18, 19], metal-organic chemical vapor deposition[20], and so on. Among these coating methods, the sol-gel method is preferred by many researchers because of its advantages such as its simplicity, low cost, large area coatings, homogeneous composition, enabling film thickness control [21-27]. However, it is challenging to grow high-quality ZnO thin films using a sol-gel based technique. Therefore, it is important to put efforts in the growing of high quality ZnO films by sol-gel methods. It is well known that the annealing temperature changes the properties of the films. Therefore, it has been the subject of many studies. Chaitra et al. [28] investigated the relationship between annealing temperature and the structural, microstructural, and optical properties of the sol-gel grown ZnO thin films. They annealed the films at various temperatures and showed that with the increasing annealing temperature, the crystal quality of the films enhanced, the surface roughness increased and the band gap decreased. Meng et al. [29] reported the relationship between the annealing temperature and the structural properties of the sol-gel spin coated ZnO films. They showed that as the annealing temperature reaching 500°C, the organic compounds and water in the film completely vanished. They also demonstrated that with the increasing annealing temperature, film crystallinity improved and the average grain size increased. Daniel et al. [30] investigated that how the annealing temperature affected the structural and optical properties of the ZnO thin films grown by RF magnetron sputtering. They stated that as-deposited films were amorphous, but with annealing, their crystallinity improved and that the prominent (002) orientation was observed. They achieved better crystallinity at 400°C in accordance with their AFM results. They also

showed that the crystallite size increased with increasing annealing temperature. Additionally, they observed that the bandgap decreased as the annealing temperature reaches 400°C, but the bandgap increased with the further increase of the annealing temperature.

In this study, ZnO thin films were grown by the sol-gel spin coating technique on glass substrates. In order to improve the qualities of the films, the effect of annealing processes on the structural, morphological, and optical properties has been studied in detail. ZnO thin films with highly pronounced c-axis orientation were acquired by post-annealing.

2. Experimental Procedure

Firstly, the starting solution was consisted of zinc acetate dehydrate (ZAD, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, %98.9) dissolved in ethanol. Monoethanolamine (MEA, $\text{C}_2\text{H}_7\text{NO}$) was added into the solution dropwise as a stabilizer. The stoichiometry of starting solution (ZAD solution) to stabilizer (MEA) was kept at 1.0. The molarity of Zinc acetate was 0.5. This mixture was magnetically stirred for 2 hours at a temperature of 60°C to acquire a transparent homogeneous solution and was left to age for 24 h at room temperature. Before the coating, the glass substrates were ultrasonically cleaned in distilled water, ethanol, and acetone, respectively, and dried with high-pressure nitrogen gas. The dimension of the glass substrate was 2 cm × 2 cm. The spin coating method was used to deposit the ZnO films on glass substrates, where the rpm value was 3000 and the duration was 30 s. The films were pre-heated in the air for 10 min at 300 °C for the purpose of vaporizing the unintentional residues and solvent in the films. The coating and pre-heating procedures were performed six times to attain films of suitable thickness. Lastly, post-annealing treatments were performed at temperatures between 350, and 550 °C for 1 h in the air atmosphere.

Vibrational modes, the structural, morphological, and optical properties were characterized by various analysis methods for all the samples. The optical properties of the ZnO films were performed by a Perkin Elmer UV/Vis/NIR Lambda 2S spectrometer. The spectra were measured ranging from 190 to 1100 nm at room temperature. The structure of ZnO films was analyzed by Rigaku Miniflex X-Ray diffractometer with Cu/K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the range of 20°-70°. The surface morphology analysis was performed using Park System Atomic Force Microscopy and **FEI Quanta 650 Field Emission Model Scanning Electron Microscopy**. **The vibration mode characterizations were carried out by RENISHAW In Via Qontor Raman Spectroscopy**. **FTIR spectrometer analysis** was performed using a **JASCO FTIR -6700**.

3. Results And Discussion

3.1 XRD Analysis

Fig. 1 depicts the XRD patterns of films that were as-deposited (ASD) and annealed at 350, 400, 450, 500, and 550 °C. The results of XRD measurement indicated that the films switched to single c axis (002) orientation when annealed at temperatures of 350 °C and higher temperature [31]. In addition to this, all the films were indexed as hexagonal wurtzite ZnO structure (JCPDS 36-1451)[32]. Fig. 2 displays the

diffraction angles and the intensity of the (002) peak as a function of the post-annealing temperature of ZnO thin films. Based on the experimental finding in Fig. 2, the increment of the annealing temperature of the films up to 500 °C led to an increment of the intensity of (002) peak. It is important to point out the values and the deductions to be made from Fig. 2, with the increase of the annealing temperature, the intensity of the XRD peak increased to around 5500 counts for the sample annealed at 500 °C, which was about 300 counts for the sample that was unannealed. On the other hand, with the temperature above 500 °C, it was seen the decrement of the intensity of (002) peak, indicating that the crystallinity began to deteriorate after that temperature [33]. In addition, the position of the (002) peak shifted towards higher angles as the annealing temperature increased to 450 °C. But when the annealing temperature rose from 450 to 550 °C, it was seen that this peak shifted to lower angles. When Table 1 is scrutinized, it can be understood in more detail how the FWHM and the d_{spacing} values of the (002) peak changed with the increase of annealing temperature. As seen in Table 1, the FWHM value fell from 2.77 for as-deposited sample to 0.208 for the sample annealed at 550 °C, and also decrement in the d values were observed as the annealing temperature increased up to 450 °C.

The average crystallite size of the films was calculated by the following Scherrer formula using XRD data for (002) orientation,

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

where D is crystallite size, λ is the wavelength of the XRD and ω is FWHM. The calculation was carried out for the preferentially oriented (002) plane. Crystallite sizes are given in Table 1 as 31.14, 273, 300, 337, 395, and 417 Å for unannealed and annealed samples at 350, 400, 450, 500, and 550 °C, respectively. These calculations indicated that thermal treatment increased the grain size and improved the crystallinity. Hence, these were in consistent with SEM and AFM findings. Finally, it can be explained as follows that the crystallinity of the films first improves up to the annealing temperature of 500 °C, and then begins to deteriorate with the further increase in temperature. According to Wei et al.[34], the reason for this change after 500 °C is due to the contention between press stress and strain stress. The (002) peak position was 34.22° for as-deposited films and it shifted to higher angles up to the 34.553° for the sample annealed at 450 °C. It is important to note that the 2θ value is 34.42° for stress-free bulk ZnO [35]. The conclusion drawn from this is that as the temperature increased, tensile stress decreased and transformed into compressive stress with further increasing annealing temperature[36]. Considering all the XRD results, the most optimal annealing temperature was 500 °C from the structural perspective.[37].

3.2 SEM Analysis

SEM images taken at 100000x illustrated in Fig. 3 were used for depicting surface morphology of the thin films annealed at 350, 400, 450, 500, 550 °C, and unannealed. At first glance, it is seen there were no cracks at the grain boundary and unannealed samples had a particle size of several nm which means grain formation is almost absent or it is very hard to determine the grains boundary. On the other hand, grain structure and grain boundaries in annealed samples are frankly seen [38]. SEM images show the

particle sizes were approximately 20, 20, 50-70, 70-100, and 100-150 nm, which corresponds to 350, 400, 450, 500, and 550 °C post-annealing temperature treatment, respectively. It is important to notice that the SEM images were examined in detail that it is clearly seen that small grains integrated into large grains at samples annealed 450, 500, 550 °C. In the event that the situation in which small grains merged and formed the greater grains, the average grain size was roughly 20-30 nm and grain size became greater with increasing temperature. Crystallite and grain size calculated from XRD and SEM respectively were consistent with each other [39], and with the increment of the annealing temperature, both crystallite and grain size became larger.

Fig. 4 illustrates the cross-section image taken from SEM at 20000x magnification to determine the film thickness. According to the cross-sectional image, the average thicknesses of the samples were about 450 nm.

3.3 AFM Analysis

To obtain more detailed information about the surface morphology of the thin films, AFM image was employed. Fig. 5 presents images for the surface morphology of the as-deposited and annealed ZnO thin films. The microstructures of thin films were composed of homogeneous. The RMS (Root Mean Square) values along the red and green lines of the ZnO thin films shown in Fig. 5 were presented in Table 1. As-deposited films had RMS values of 2.93 nm for the Red line in Fig. 5 and corresponding RMS values increased to 30.25 nm for the sample annealed at 550 °C. This proves that an increment in the annealing temperature increased the surface roughness of the thin films. In addition, it is also reported in AFM images clearly show that grain formation began and the size increased with increasing temperature[40, 41]. The grain size increased to 150 nm for the sample annealed at 550 °C. This result state that with increasing annealing temperature, there was a noticeable improvement in structural order by reduction of nonbridging oxygen type of defect which caused the formation of hexagonal structure. Here, ZnO nanoparticles cohered with each other to constitute larger grains during the post-annealing process with the help of more energy in the thermal procedure[42].

These deductions were in agreement with XRD and SEM results which indicated crystalline quality and grain sizes were in direct proportion to annealing temperature.

3.4 Raman Analysis

Fig. 6 depicts the room temperature Raman spectra of as-deposited film and the ZnO thin films annealed at temperatures between 350 and 550 °C. Two broad bands at about 565 cm^{-1} and 1100 cm^{-1} were observed in the Raman spectra. These bands represented the $A_1(\text{LO})$ and $2A_1(\text{LO})$ modes of wurtzite ZnO, respectively [43-48]. In A_1 mode dominated by oxygen, the atoms move parallel to the c-axis. In this phonon mode, the neighboring ions move in the same direction, therefore, the displacements of atoms cause net polarization. Consequently, a long-range electrostatic field formed by the polarization of A_1 in a unit cell splits the polar mode into transverse optical (TO) and longitudinal optical (LO) components. [43,

49]. $A_1(\text{LO})$ modes can be observed for highly oriented ZnO films [43, 46, 50]. Thus, these results are consistent with XRD results [43, 46, 50].

3.5 FTIR Analysis

Fourier Transform Infrared (FTIR) spectra measurement was performed to identify the molecular structures of the ZnO films. Fig. 7 shows the FTIR spectra of the glass substrate, as-deposited film, and the ZnO thin films annealed at temperatures between 350 and 550 °C. The peak at about 560 cm^{-1} was related to the vibration of the ZnO bond in the ZnO lattice [51-54]. The peak at 3380 cm^{-1} was related to O-H stretching vibrations of water or OH [55-58]. This peak disappeared after annealing treatment. Two peaks observed around 2850 and 2920 cm^{-1} had been attributed to C-H stretching vibrations of alkane groups. Meanwhile, these peaks were strongly consistent with frequencies of the C-H_2 symmetric stretch and C-H_2 asymmetric stretch respectively. [55, 59]. The peaks around 1590 and 1400 cm^{-1} were related to asymmetric and symmetric stretch vibrations of COO^- bonds which were from organic residues [58, 60, 61]. Organic residues were disappeared with increasing temperature.

3.6 UV/Vis/NIR Spectrometer Analysis

The optical transmittance (%T) spectra of ZnO thin films in the wavelength range of 300 to 1100 nm (UV-VIS-NIR spectrum region) are depicted in Fig 8. The optical transmittance of all the ZnO thin films was over 85% in the visible region. As seen in Fig. 8, there was a slight decrease in the transmittance of the ZnO thin films by increasing the temperature from 350 °C to 500 °C and an eminent decrease at 550°C. AFM images indicated that the surface roughness increased with the increasing temperature, thus the decrement of the optical transmission could be ascribed to the increment of optical scattering in consequence of the increase in the roughness of the surface [62]. Moreover, the optical spectra of ZnO thin films showed a sharp and rapid decrease at about 380 nm, indicating the high quality and purity of the samples [63]. Additionally, the interference fringes seen in Fig. 8 indicated that the films had a good crystalline structure with constant interplanar spacing and a uniform atomic density, but the interference fringes disappeared at 550 °C, indicating that the crystallinity of the films deteriorated at this temperature as highlighted in XRD analysis [64].

The optical band gap was estimated by using the Tauc relation [65] for direct band gap thin films given by the following Equation (2).

$$\alpha h\nu = A(h\nu - E_g)^2 \quad (2)$$

where A is constant, $h\nu$ is the photon energy, E_g is the optical band gap, h is the Planck constant, and α is the absorption coefficient. E_g was estimated by extrapolation of the graph to x-axis (Energy/ $h\nu$) as seen in Fig. 9. From this graph, the optical band gaps for films as-deposited, annealed at 350, 400, 450, 500, and 550°C were estimated as 3.26, 3.29, 3.29, 3.28, 3.28, and 3.27 eV respectively. The optical band gap values were close to the 3.30 eV

and in good agreement with the results reported in the literature [37, 66]. As the annealing temperature increased from 350 to 550°C, a decrease was observed in the optical bandgap. The results of XRD, SEM, and AFM analysis showed that grain size increased as the annealing temperature increased. Thus, the decrease of the band gap with increasing annealing temperature from 350 to 550°C was probably due to the increase of the grain size with increasing annealing temperature [28].

4. Conclusion

The sol-gel spin coating method has been used to deposit ZnO thin films on the glass substrate. The films as-deposited and annealed at the temperatures of 350, 400, 450, 500, and 550 °C were thoroughly characterized. The XRD analysis presents that all the films were highly c-axis preferred (002) oriented. These results were also confirmed by Raman spectroscopy. AFM and SEM images have also displayed that high annealing temperature increased the grain size of the samples. In addition, the optical band gap slightly decreased by annealing temperature. ZnO thin films with 500 °C annealing temperature had the highest diffraction peak intensity and the most homogeneous surface morphology compared to other films, indicating that 500°C was the optimum annealing temperature for this study. Determining the optimum annealing temperature has crucial importance in extending this study for doping mechanism investigations. Finally, it should be mentioned that the sample produced with such high intensity (002) orientation by wet chemical methods is very rare in the sol-gel literature, generally, studies with low-intensity peaks are encountered.

Declarations

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Table

Table 1. Represent the calculation of peak position (2θ), lattice spacing (d), FWHM and crystallite size (D) of as-deposited and annealed ZnO thin films at temperatures between 350 and 550 °C for (002) peak obtained from XRD results and RMS values of the films calculated from AFM measurements.

Annealing Temp. (°C)	002 peak position, 2θ (deg)	d (Å)	FWHM (deg)	D (Å)	RMS(nm) along RED/ GREEN line
As-deposited	34.22	2.618	2.77	31.14	2.93/2.68
350	34.414	2.6038	0.318	273	2.94/2.65
400	34.545	2.5942	0.289	300	3.93/4.80
450	34.553	2.5937	0.258	337	7.56/8.80
500	34.533	2.5952	0.22	395	14.13/15.47
550	34.446	2.6015	0.208	417	30.25/36.75

Figures

Figure 1

X-ray diffraction pattern of as deposited film and the ZnO thin films annealed at temperatures between 350 and 550 °C (colored)

Figure 2

002 peak diffraction angle and intensity of as-deposited and annealed thin films (▲ shows diffraction angle and ■ shows intensity) (colored)

Figure 3

SEM image taken 100000x of as deposited ZnO film and the ZnO thin films annealed at a) 350 °C b) 400 °C, c) 450 °C d) 500 °C, and e) 550 °C (colored)

Figure 4

Cross-sectional SEM image of ZnO thin film annealed at 500 °C (colored)

Figure 5

AFM images of as deposited ZnO film and the ZnO thin films annealed at a) 350 °C b) 400 °C, c) 450 °C d) 500 °C, and e) 550 °C (colored)

Figure 6

Raman spectra of as deposited film and the ZnO thin films annealed at temperatures between 350 and 550 °C (colored)

Figure 7

The FTIR spectra of glass substrate, as deposited film and the ZnO thin films annealed at temperatures between 350 and 550 °C (colored)

Figure 8

Optical transmittance spectra of as deposited film and the ZnO thin films annealed at temperatures between 350 and 550 °C (colored)

Figure 9

Plot of $(\alpha h\nu)^2$ vs. photon energy of as deposited film and the ZnO thin films annealed at temperatures between 350 and 550 °C (colored)