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Impact of different post-annealing temperatures on photoluminescent and structural properties of ZnO films prepared by sol-gel technique

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Abstract

In this work, the effects of different post-annealing temperatures on the prepared ZnO glass films were studied. The deposited ZnO films were prepared by a sol–gel spin coating technique. The influence of the annealing temperature on the photoluminescent, elemental, optical, structural, crystallite size properties were investigated. The PL spectra show a blue shift in DLE and the intensities of the DLE emission decreased due to the annealing temperature increasing. EDS peaks confirm the successful synthesis of ZnO film. The optical transparency of ZnO films was measured at different annealing temperatures and showed a visible transmittance of 94%. The optical band gap of ZnO film was increased as the annealing temperature increased. The XRD results show the deposited ZnO film has a hexagonal wurtzite structure. Diffraction intensity and crystal size increase with the increase in annealing temperature, while full width at half maxima decreases.

Keywords post annealing, photoluminescent, wurtzite structure

1. Introduction

Zinc oxide thin films have received a lot of attention due to their high potential for a variety of applications such as light-emitting diodes, solar cells, UV photo detectors, gas sensors, photocatalytic agents, transparent electrodes, and so on. They have unique physical and chemical properties, like high chemical stability, high photo-stability, a wide range of absorption light. It has an n-type semiconductor oxide material with a large band gap energy of 3.37 eV, a high exciton binding energy of 60 meV, a wide resistivity range, and high transparency at room temperature [1-3]. In the literature, several factors have been reported that influence ZnO thin films: shape, size, and optical properties, both individually and collectively. Precursors, concentrations, temperature, stirring time, duration, surfactant concentrations, dopant concentrations, and annealing temperature are all factors to consider during synthesis [4-5]. Spray pyrolysis, Pulsed laser deposition, chemical bath deposition , chemical vapour deposition and sol-gel are some of the methods now used to make ZnO thin films [6-9]. Among these methods, sol-gel is one of the best due to its simplicity and the low cost of the required equipment. In this work, the annealing effects of ZnO sol–gel deposited using the spin coating method onto glass samples were investigated. The primary goal of this work is to optimise ZnO thin film crystallinity using an annealing treatment. This post-annealing treatment was performed in an open air furnace to compare the effects on the crystalline orientation of ZnO thin films. Photoluminescence (PL), UV-Vis and X-ray diffraction (XRD) analysis were used to investigate the Photoluminescence and structural properties.

2. Procedure

For the deposition of the sol–gel ZnO thin films, the precursor zinc acetate dehydrates [($C_4H_6O_4Zn.2H_2O$)] was used, with 2-Methoxyethanol [($C_3H_8O_2$)] and ethanolamine [($H_2NCH_2CH_2OH$)] serving as the solvent and stabilizer, respectively. The molar ratio of the zinc acetate dihydrate mixed with ethanolamine was maintained at 1.0, and the zinc acetate concentration was fixed at 0.5 M. The solution was stirred on a hot plate at 75°C for 1 hour in order to get a well-mixed precursor solution. After that, the solution was allowed to age for 24 hours. Before deposition, the glass substrate samples were cleaned with distilled water, chromic acid, acetone, and de-ionized water. Spin coater was used for the deposition of ZnO thin films onto glass substrate samples at 2000 rpm for 30 seconds. After each coating, the as-deposited films were dried at 200°C in the air for 10 min to evaporate the organics. The procedures from deposition coating to drying were repeated fifteen times to increase the thickness. Finally, all the films were post-annealed in an open-air furnace at 250, 275, 300, 325, and 350^0C for 1 hour. The samples were characterized by XRD, model Rigaku Miniflex 600. Optical characteristics were studied using the Shimadzu UV-2600. Photoluminescence spectra were measured using a spectrofluorometer, HORIBA Fluoromax-4.

3. Results

3.1 Photoluminescence

Fig. 1 depicts the room-temperature photoluminescence (PL) emission spectra of ZnO films annealed at various temperatures and excited at 320 nm. In these films, there was one emission peak that could be seen, which was located in the visible region. The films PL spectra showed a wide range of emission peaks in the visible range, from 430 nm to 600 nm. All five annealed ZnO thin films absorbed the emission peaks at Deep Level Emission (DLE). The emission band for a 250°C annealed sample has a high intensity emission at DLE. When the annealing temperature was increased from 250°C to 350°C, the emissions shifted slightly blue. The intensity of the DLE emission decreased due to oxygen ion vacancy. This means that when the annealing temperature is increased, there are fewer zinc ions in the material and more oxygen vacancies, which makes the intensity of DLE lower [10-11].

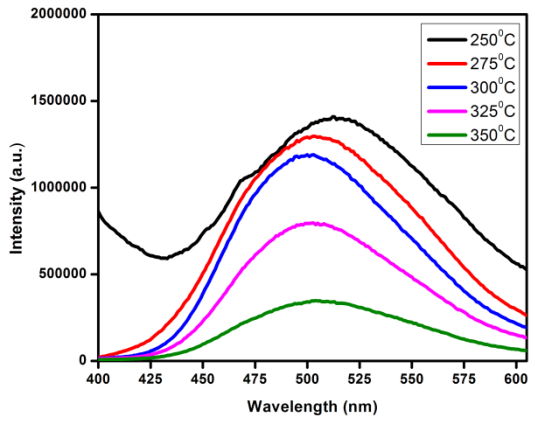

Fig. 1 shows PL spectra of ZnO films at 250, 275,300, 325 and 350°C annealing temperatures

3.2 Energy-Dispersive X-Ray Spectroscopy

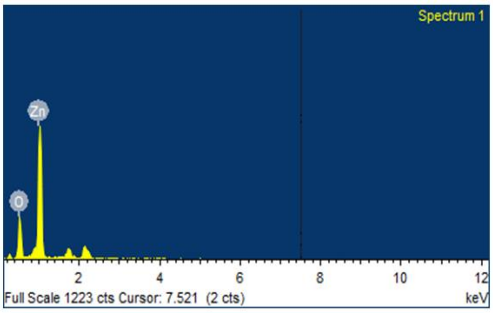

Fig. 2 shows EDS spectra of ZnO films at 350°C annealing temperatures

Energy-Dispersive X-Ray Spectroscopy (EDS) Fig. 2 shows the sharp peaks for O and Zn were found in annealed 350^0C ZnO thin films, confirming the formation of ZnO. The other spectrum appears as a result of the glass substrate.

3.3 Optical Properties

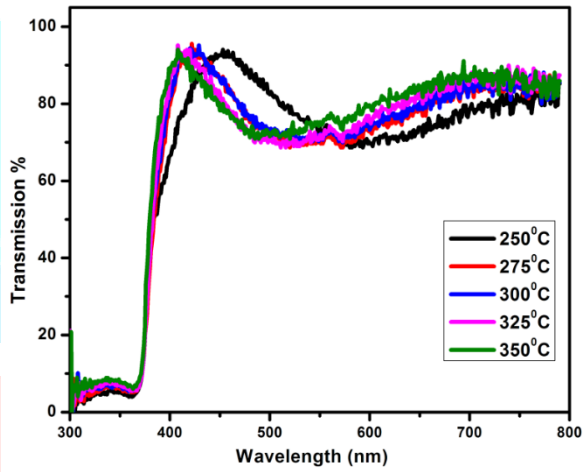

Fig. 3 shows transmission spectra of ZnO films at 250, 275,300, 325 and 350°C annealing temperatures

Fig. 3 depicts the optical transmittance spectra of ZnO films at various annealing temperatures. Although the transmission in the visible wavelength range of 300–800 nm is temperature dependent, it appears that the film annealed at 250 to 350^0C has transmission edges shifted to lower wavelengths, indicating that the crystallisation quality effects on optical properties [12]. In this visible region, the average transmittance of all films was determined to be 94%. This demonstrates that the films are highly transparent in the visible wavelength range. For the various annealed ZnO sol–gel films, we used Tauc's equation for direct band gap semiconductors and the absorption edge to figure out the optical band gap (E_g) [13]:

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

Where α stands for the absorption coefficient, hv for the energy of the photons, and Eg for the optical band gap and A stands for a constant. The optical band gap values were calculated by plotting $(\alpha h\nu)^2$ against the photon energy hv. As shown in Fig. 4, the optical band gap of the ZnO sol–gel thin films were determined to be 3.2416, 3.2721, 3.2733, 3.2736, and 3.2763 eV. As the annealing temperature increases, the optical band gap values also increase. For the post-annealing effect, the band gap energies shift from 3.2416 to 3.2733 eV.

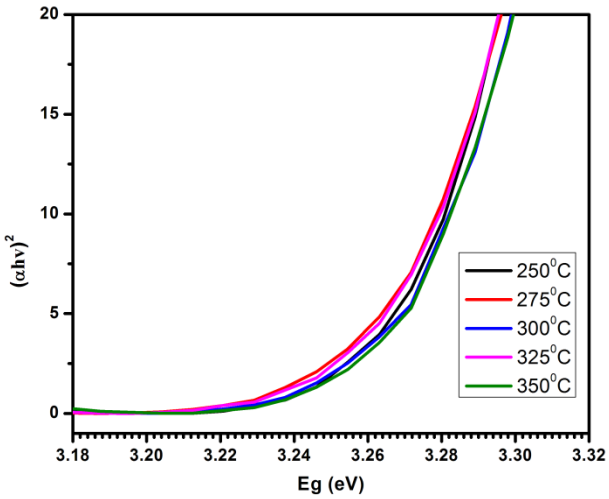

Fig. 4 The optical band gap spectra of ZnO films values by plotting $(\alpha hv)^2$ vs photon energy Eg

3.4 XRD

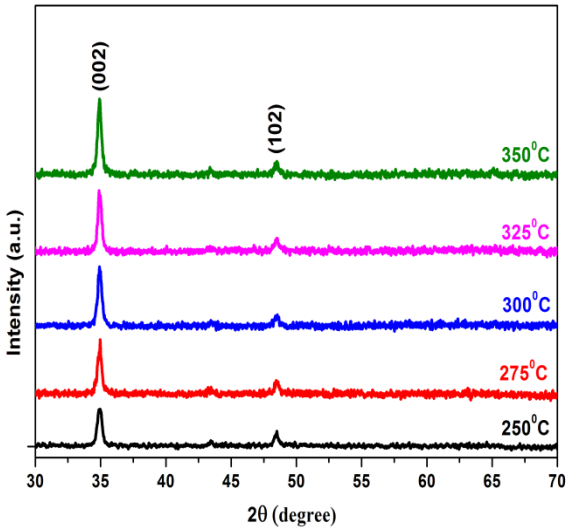

Fig. 5 XRD patterns of ZnO films at 250, 275,300, 325 and 350°C annealing temperatures.

Fig. 5 shows the XRD patterns for the ZnO sol-gel thin films on glass samples with different annealing at 250, 275, 300, 325, and 350^0C. The peaks are associated with (002) and (102) and match the hexagonal wurtzite structure of ZnO. No diffraction peaks of other phases were detected. However, the annealed temperature leads to a change in the XRD intensity. The intensity peak (002) was found to be increased with increasing annealing temperature and it was greater for the 350°C ZnO sample. The saturation of newer nucleating centres may affect the subsequent increase in (002) peak intensity for higher annealed temperatures. ZnO crystallizes in the wurtzite structure, which is a hexagonal network composed of two interpenetrating sub-networks of Zn^{2+} and O^{2-}ions, with each Zn ion surrounded by a tetrahedron of oxygen ions and vice versa. This configuration produces polar symmetry along the hexagonal longitudinal axis (c axis). The Debye–Scherrer formula was used to calculate the mean crystallite size (D) based on the broadening of the highest intensity peak corresponding to the (002) diffraction plane [14].

$$D = \frac{k\lambda}{\beta(\cos\Theta)}$$

Where k is a constant set to be 0.94, λ is the wavelength of the X-rays(λ=1.54059), β is the full width at half maximum (FWHM) of the XRD pattern's (002) peak, and Θ is the angle of the diffraction peak. As observed in Table 1, we obtained smaller FWHM values and larger crystal sizes (ranging from 23.26 nm to 26.12 nm) for ZnO sol–gel thin-films as the annealing temperature increased in the open-air furnace. These results indicate the better crystallization of the ZnO sol–gel thin-films annealed in the furnace.

The strain (ε) and density of dislocations (δ) in ZnO thin films are calculated using the equations shown below [15].

$$\varepsilon = \frac{(\cos \Theta)\,\beta}{4}$$

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

A lattice strain range from 0.000944 to 0.000787 was observed. As we increased the annealing temperature, the lattice strain became weaker. Also, the dislocation density ranged from 0.009841 to 0.003695. The dislocation densities in the ZnO thin films studied decreased as the annealing temperature increased, as shown in Table 1.

Table 1 shows information about 2Θ (°) values, FWHM, grain size, lattice strain and dislocation density for corresponding samples for different post-annealing temperature.

Annealing Temp. (^{0}C)	**2 Θ (^{0})**	**FWHM (^{0})**	**Crystal size D (nm)**	**Lattice strain (ε)**	**Dislocation density (δ) (nm)$^{-2}$**
250	34.92	0.374	23.26	0.000944018	0.009841551
275	34.88	0.350	24.85	0.000883309	0.00161952
300	34.92	0.363	23.96	0.000916253	0.004627701
325	34.92	0.312	27.88	0.000787523	0.003911137
350	34.91	0.333	26.12	0.000840499	0.003695492

Conclusions

The sol–gel spin coating method was used to deposit ZnO films on glass substrates. The temperature of the post-annealing process has been studied to see how it affects photoluminescence, EDS, optical, and structural properties. Peaks in visible regions were observed in the PL emission spectra of deposited ZnO films. The PL emission peaks of deposited ZnO films were temperature independent after annealing. The intensity of PL emission decreased as the annealing temperature increased. Optical transparency with a visible transmittance of approximately 94% The band gap of the ZnO film grows from 3.2416 to 3.2733 eV as the annealing temperature rises. The hexagonal wurtzite structure of ZnO films was confirmed by XRD. The crystallinity of the synthesised films has improved as the FWHM decreases with increasing temperature. The crystalline size was found to be between 23.26 nm and 26.12 nm. This fact, combined with the ease with which the films can be prepared, makes them appealing for potential applications in optoelectronic devices.

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