<u>**Original Research Article**</u>

Effect of Annealing and Thickness on Some Physical Characteristics of ZnO Films

Abstract

ZnO transparent conductive films were deposited on glass substrates at 400^0 C by chemical Spray Pyrolysis Technique (CSPT). Also, the study investigated the impact of annealing of zinc oxide pieces with the rise in thickness. The structural and optical characteristics of the deposited films were studied by X-ray diffraction (XRD) and UV-VIS-NIR Spectrophotometer. The X-ray diffraction analysis detected that the polycrystalline films showed a distinctive orientation along (002) direction with a hexagonal wurtzite phase type. It is found that good crystallinity is acquired in the pieces annealed at 500^0C. All films showed an average transmittance of about 85%. The size of grain and lattice parameters of films were measured. The grain size increases as thickness increases. The values of the optical gap energy (Eg) are found to be in the range of 3.238 to 3.273 eV without annealing and in the range of 3.252 to 3.280 eV with annealing when the thickness varies from 355 to 445 nm.

Keywords: Zinc Oxide Film; Annealing; Thickness; Spray pyrolysis; Grain size; Transparent

Introduction

The II-VI compound semiconductors are of great importance due to their applications in various electro-optic devices. In materials science, ZnO is called II-VI semiconductor because zinc and oxygen belong to the 2nd and 6th groups of the periodic table, respectively [1]. ZnO is a wide band gap (3.37 eV at room temperature) semiconductor that is desirable for many applications [2] and potent exciting binding energy of 60 meV [3]. This semiconductor is of interest for UV and visible region optical devices, like laser diodes and light emitting diodes [4]. ZnO is also well-known as a piezoelectric material that has been used in acoustic wave [5] and various optoelectronic devices. ZnO thin films with high electrical conductivity and high optical transmission, nontoxicity, chemical and mechanical stability and low cost because of the high abundance [6]. Various fabrication methods have been vastly used to prepare ZnO thin films. The most intensively studied methods include, the chemical vapor deposition [7], pulsed laser deposition (PLD) [8-10], chemical bath deposition [11], sol-gel method [12-14], metal oxide chemical vapor deposition (MOCVD) [15], and spray pyrolysis technique (CPS) [16, 17]. Among these methods, chemical spray pyrolysis (CSP) is one of the most vastly applied methods because it has various merits such as, easily controlled over wide range by changing the spray parameters, cheaper and large area fabrication for applications compared with other ways which need complex equipment and accessories with very expensive parts. In present work, effect of annealing temperature at 500 °C and thickness on crystalline structure and optical Characteristics of ZnO thin film fabricated by spray method was investigated.

Experimental section

Synthesis of ZnO

ZnO thin film was prepared on glass substrate preheated at 400 ° C using the CSP. A concentration of solution of 0.1 M zinc acetate hydrate ($Zn(CH_3COO)_2$, $2H_2O$) is prepared by analyzing in mixture of distilled water. The nozzle was kept at a space of 29±1 cm from the substrate during prepared films. The solution flow rate was kept constant at 2.5 ml per minute. Air was used as the transporter gas, at the pressure of 1.56 bar. When spray aerosol droplets were near the substrates, a pyrolysis process occurs and highly adhesive ZnO samples were fabricated.

Materials Characterization

Thickness was measured using gravimetric method The transmittance of the films was measured in the range of 300-1100 nm at room temperature by using an UV/VIS/NIR analyzer (Shimadzu 1900 double beam spectrophotometer). The structural properties of the thin films were estimated by X ray diffraction system (Lab XRD-6000/Shimadzu) Cu Kα radiation (λ =1.5406 A°). In the scanning range of (2θ) was between 10° and 80°. The average crystallites were calculated by the Scherrer's formula from the expanding of the diffraction peaks.

Synthesis of xerogel of the ZnO:

Zinc oxide (ZnO) sol was prepared from zinc acetate dihydrate (ZAD) precursor. Monoethanolamine (MEA) and ethanol were used as a stabilizer and solvent, respectively. Zinc acetate dihydrate (Zn $(CH_3COO)_2$ $.2H_2O$, Riedel-De-Haen, ≥99.5 %) was dissolved in ethanol (C6H6O, Sigma-Aldrich, ≥99.8 %) to prepare ZnO sol with different precursor concentration. Monoethanolamine (H2NCH_2CH_2OH, 99 %) acts simultaneously as a chemical reaction control agent and a base. Zinc oxide sol synthesis was performed in an oven dried two-necked 50 mL round bottom flask by dissolving zinc acetate dehydrate in ethanol. Monoethanolamine was then added drop-by-drop to the alcoholic solution while stirring. The mixture was continuously stirred and refluxed at 80 ^{0}C for 2 h, under N_2. The resulting solution was then cooled down to room temperature under nitrogen flow, and finally a clear and colorless sol was obtained. The prepared ZnO sols were transferred to cleaned and dried Petri dishes. The Petri dishes were semi-sealed with aluminum foil and kept for drying in an air atmosphere at room temperature for few days. The xerogel powders were obtained after gelling and drying the sol. The gel was rapidly formed at room temperature under vigorous magnetic stirring and dried at 110^{o}C for 16 h. After curing, the xerogel powders were annealed in an air atmosphere at 500 ^{o} C for 1 hour.

Results and Discussion

Structural characterization

The XRD patterns for ZnO nanoparticles are displayed in Figure. 1.The results shown broad peaks at position (31.61, 34.39, 36.11, 47.40, 56.52, 62.72, 66.29, 67.91 and 69.08 deg. as 2θ). These values are in good agreement with standard card (JCPDS 36-1451) file for ZnO and can be indexed as the hexagonal wurtzite structure. Comparable observations have been found by other investigators [18, 19]. In addition, figure. 1 shows the effect of annealing at 500 $^{\circ}$C on crystal structure, the annealed films have stronger and small width reflection peak showing an enhancement in (100); (002) and (101) peak intensity compared to without annealing. XRD results exhibit that all the samples are multiphase polycrystalline and random growth orientations, this result is due to the difference in the precursor chemistry and annealing temperatures [20]. However, there are several reported oriented along the c-axis ZnO thin films prepared on glass [21, 22]. The lattice constants shown in Table 1 are computed using the following equation [23]:

$$\frac{1}{d^2} = \frac{4(h^2+hk+k^2)}{3a^2} + \frac{l^2}{c^2} \qquad (1)$$

Where c and a are the lattice constant and d_{hkl} is the interplanar spacing.

Scanning electron microscopy is a convenient technique widely used to obtain the surface morphological information of thin film. Surface morphology of ZnO thin films was observed using Scanning electron microscopy (SEM). Figure.2 (a-b) shows the SEM micrographs obtained for the as prepared ZnO (a) as-deposited and (b) annealed at 500 ^{0} C. The morphology of the as-deposited (Fig. 2a) ZnO thin film was also observed at higher magnification is made up of very small grains and it can be seen that the grains are packed closely and well distributed on the glass substrate. Fig. 2b shows for the films annealed at 500 ^{0} C, the grains are larger in size compared to the as-deposited ZnO. The grains were uniformly stacked up, interact with each other and entirely compact are visible. It can be concluded that the annealed temperature has a great influence on the film surface.

The strain ε values in samples were evaluated using the relation [24];

$$\varepsilon = \frac{C-C_0}{C_0} \times 100\% \qquad (2)$$

where $\mathcal{E}$ is the main strain in ZnO thin film (table1), C is the lattice parameter of ZnO films and C_0 the lattice parameter of bulk (standard C_0 = 0.5206 nm). In thin films, strains are

produced fundamentally due to mismatch between the film and the substrate and difference in coefficients of thermal expansion of the film and the substrate. The crystallite size (D) can be presented by the following equation [25];

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (3)$$

Where k is about 0.9 and β is the Full Width at Half Maximum (FWHM). Table 1 gives the lattice parameter, particle size and strain (ε) % of the as-deposited and annealed at 500^0C ZnO thin films. The resulted c and a are in agreement with the standard values according to the ICDD card no. 75-0576. The average uniform strain ε, along the c-axis in the film, increases as the thickness increases. The crystalline quality of the film gets better as the film grows thicker. Figure. 3 shows the change of strain at different thicknesses for as prepared and annealed films. In larger thickness the crystallinity becomes better. Figure. 4 shows the increasing the thickness and the heat treatment decrease the FWHM value, showing a better crystallinity of the films. The particle size increases with heat treatment, but decreases with lower thickness, like previous work [26].

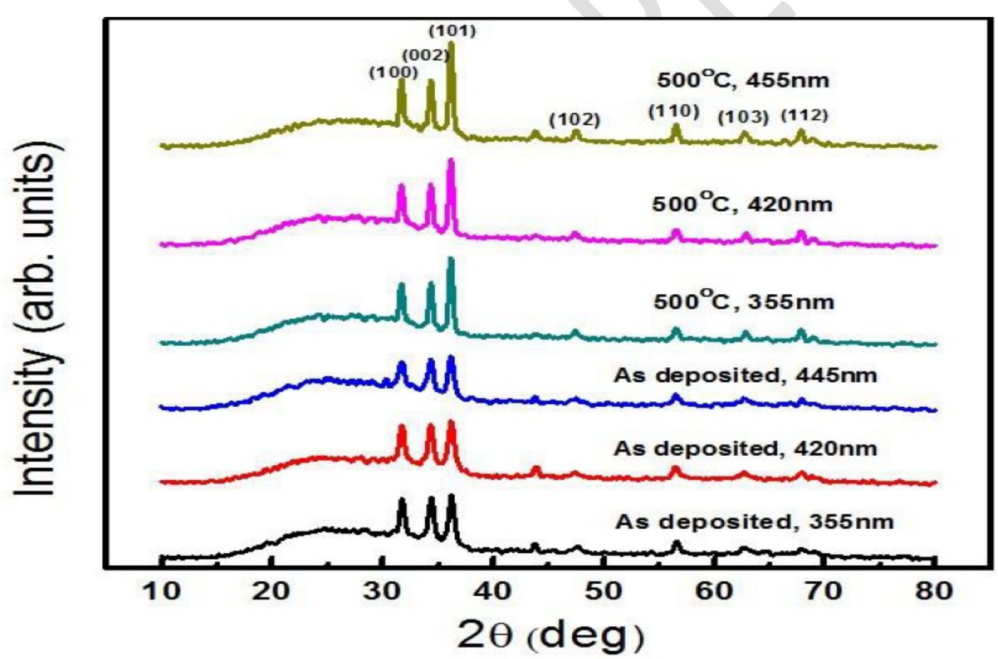

Fig. 1 X-ray diffraction patterns of as-deposited and annealed ZnO thin films with different thicknesses

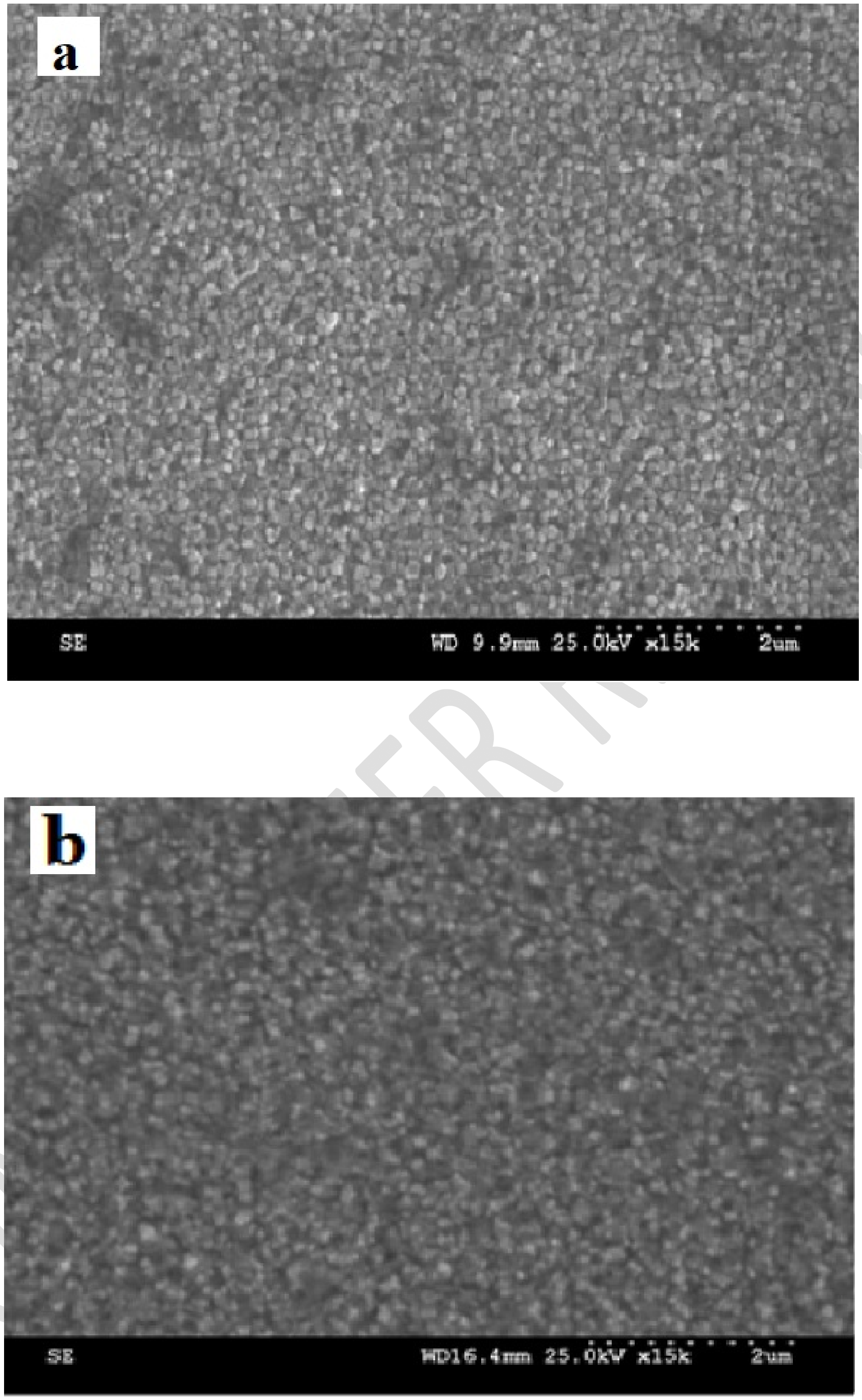

Fig. 2 SEM images of ZnO films (a) as-deposited; (b) annealed at 500℃

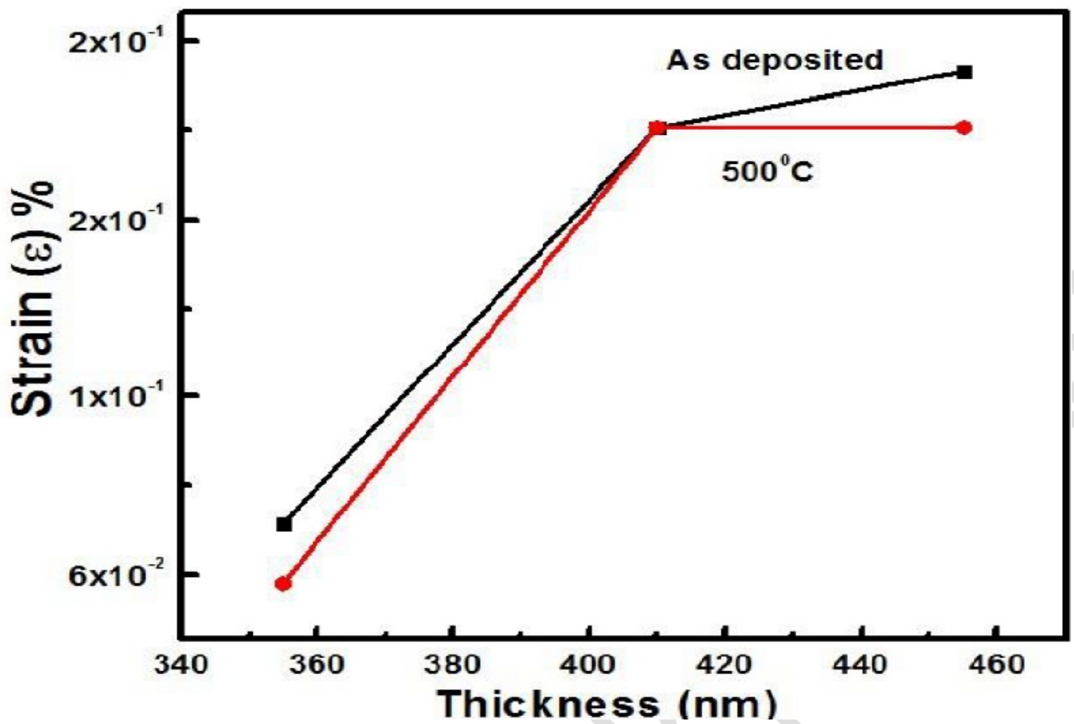

Fig. 3 The variation of strain at different thicknesses for as deposited and annealed films.

Table 1 Lattice parameters, crystallite size and strain (ε) % of ZnO thin films before and after

Thickness (nm)	**FWHM (deg.)**	**c (nm)**	**a (nm)**	**c/a**	**Strain (ε) %**	**Grain size (nm)**
355(As-deposited)	0.5200	0.5210	0.3252	1.6020	0.077	15.99
410 (As-deposited)	0.5183	0.5217	0.3254	1.6032	0.211	16.05
455 (As-deposited)	0.4800	0.5218	0.3255	1.6030	0.23	17.32
355 (500 o C)	0.2804	0.5209	0.3251	1.6022	0.057	29.66
410 (500 o C)	0.3213	0.5217	0.3256	1.6022	0.25	25.88
455 (500 o C)	0.3213	0.5217	0.3250	1.6052	0.198	25.88

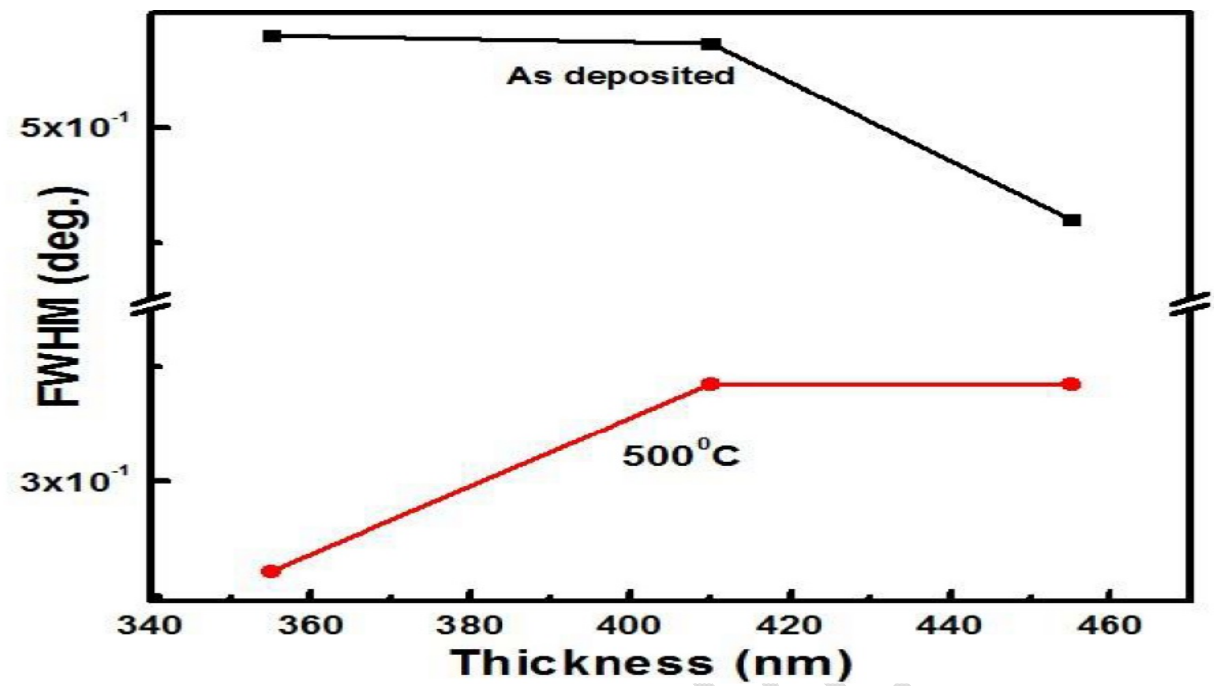

Fig. 4 FWHM at different thicknesses for as deposited and annealed samples.

Optical properties

In order to determine the influence of thickness and annealing on the optical band gap of ZnO, the optical transmission spectra of all films were recorded and shown in figures. 5(a) and 5 (b). It is clearly seen that all the films exhibit a high transmittance, around 85%, in the visible. The transmittance decreases sharply near the UV range due to the band gap absorption. When the thickness increases, the transparency decreases. This outcome was expected; since when the thickness is increased a larger number of photons are adsorbed in a film. In addition, a shift of the absorption edge proportional to the thickness values, towards larger energies is apparent from the spectra. The optical absorption at the absorption edge is in agreement with the transition from valence band to the conduction band (λ<390nm). The optical gap energy of ZnO (direct interband transition) is given by the following formula [27]:

$$\alpha h v = B \sqrt{h v - E_g} \quad (4)$$

Where ***B*** is a constant and α is the absorption coefficient. The optical gap energy ***Eg*** can be obtained from the intercept of $(\alpha h\nu)^2$ versus ***hv***. Figures. 6 (a) and 6 (b) show the curves of $(\alpha h\nu)^2$ versus ***hv*** for all samples.

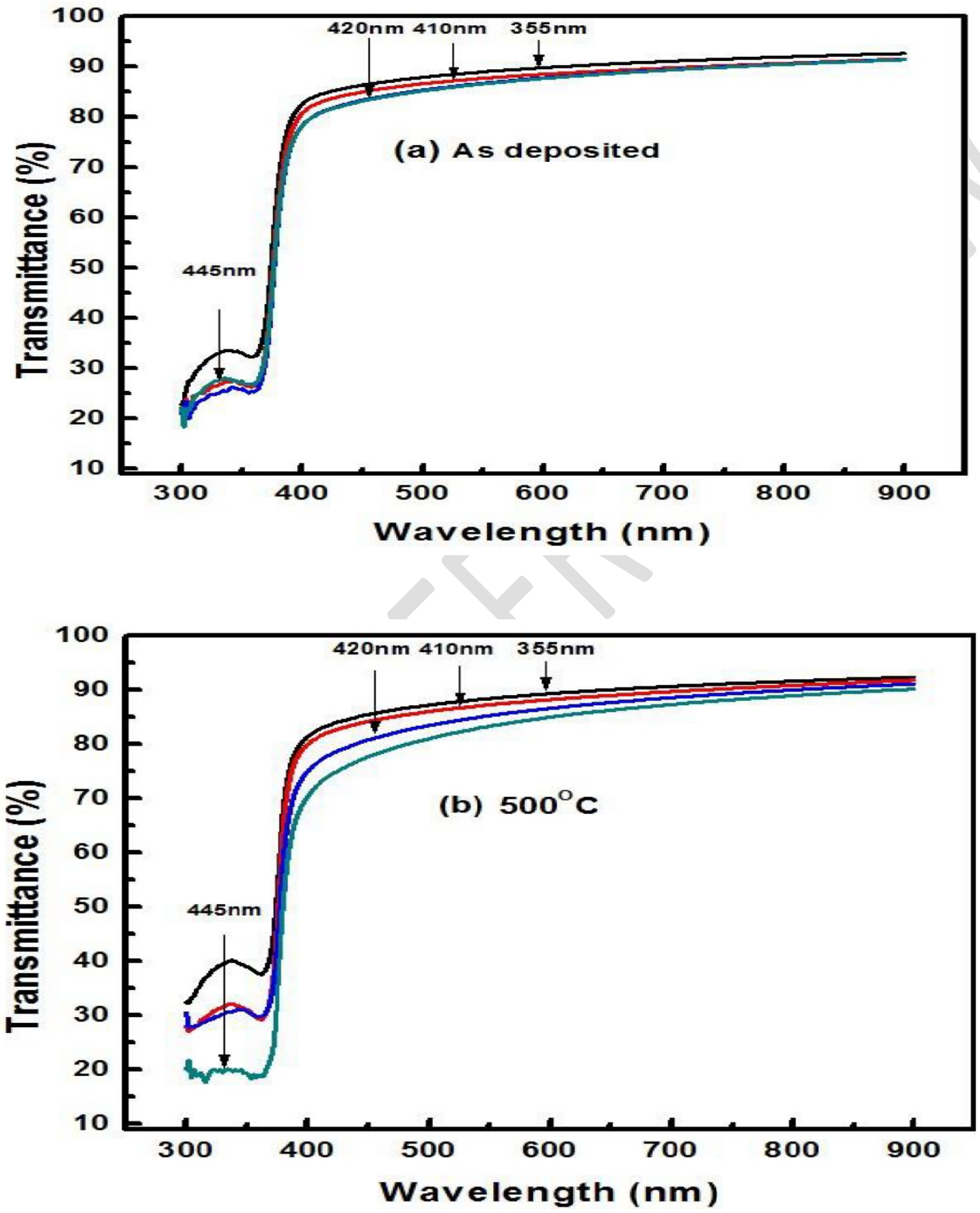

Fig. 5 The UV-visible transmission spectra of ZnO films, (a) without and (b) with annealing for different thicknesses.

The values of the optical band gap are found to be between 3.238 to 3.273 eV without annealing and from 3.252 to 3.280 eV with annealing when the thickness changes from 355 to 445 nm. We can explain the rise in optical gap energy by the oxygen diffusion with heat treatment [28]. The increase in optical band gap with the thickness increase is also proportionate with increasing trend in the strain. Previous research reported that strain variation of the interatomic distance in semiconductors influences the energy gap [28].

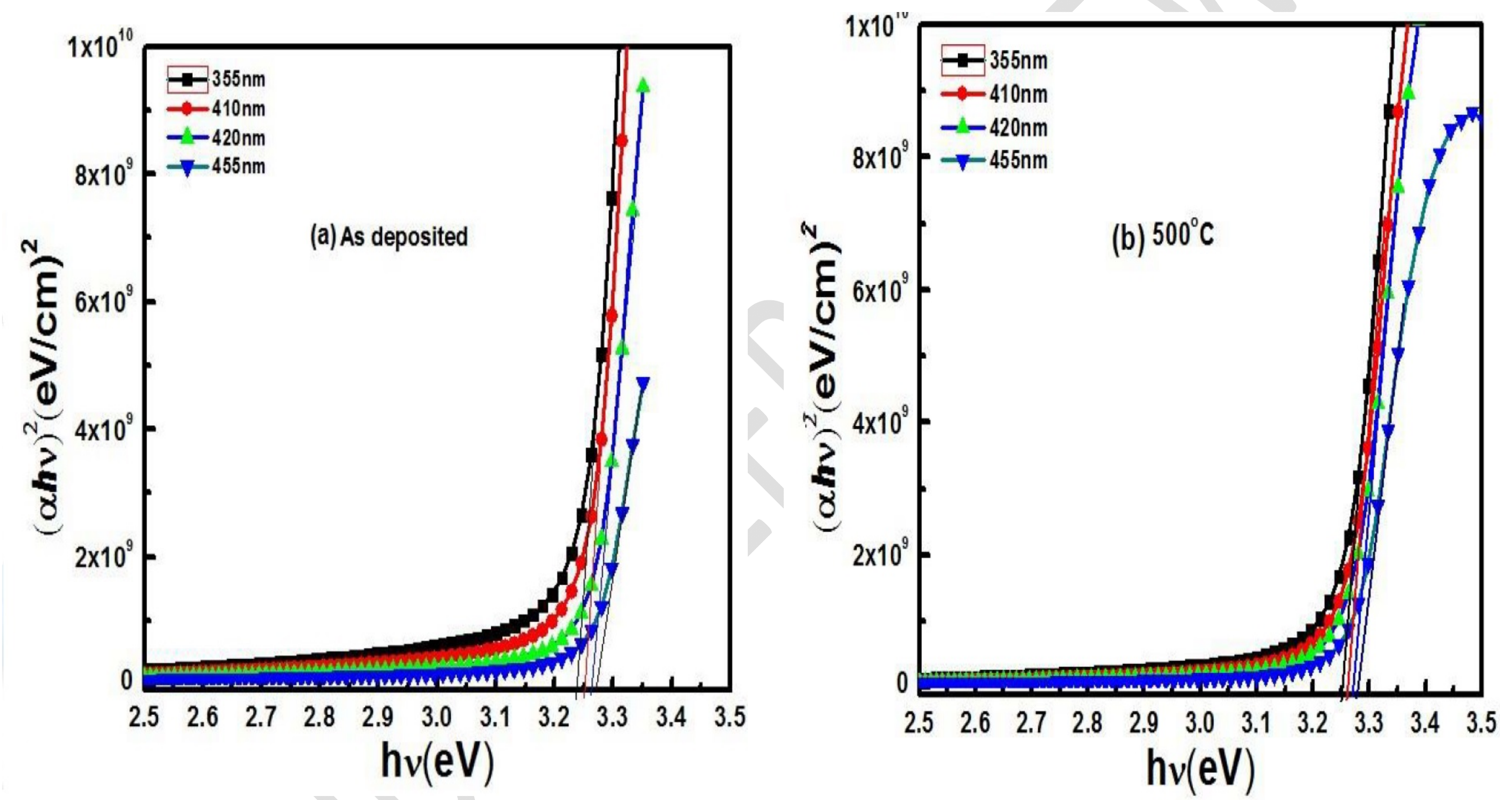

Fig. 6 The typical variation of $(\alpha h\nu)^2$ versus photon energy of ZnO thin films, (a) without and (b) with annealing.

Conclusions

A thin film of ZnO prepared by CSP technique on TCO glass substrate showed good adherence to the substrate. The structural, optical and electrical properties of the ZnO thin films have been found to be influenced by the thickness of the film. The crystalline quality of the films gets better and the strain increases as the thickness increases. The values of the optical gap energy (Eg) are found to be in the range of 3.238 to 3.273 eV without annealing and in the range of 3.252 to 3.280 eV with annealing when the thickness varies from 355 to 445 nm.

COMPETING INTERESTS

Author have declared that no competing interests exist.

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