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Structural and optical properties of ZnO thin film prepared by sol-gel spin coating

BALAKRISHNAN G[1,*], VIVEK SINHA[2], YOGESH PALAI PEETHALA[2], MANOJ KUMAR[2], GOLDEN RENJITH NIMAL R.J.[2], HAMEED HUSSAIN J[2], KHALID MUJASAM BATOO[3], EMAD H. RASLAN[4]

[1]Department of Nanotechnology, Bharath Institute of Science and Technology, Bharath Institute of Higher Education and Research, Chennai-600073, India

[2]Department of Mechanical Engineering, Bharath Institute of Science and Technology, Bharath Institute of Higher Education and Research, Chennai-600073, India

[3]King Abdullah institute for Nanotechnology, King Saud University, P.O. Box 2455, Riyadh-11451, Saudi Arabia

[4]Department of Physics and Astronomy, College of Science, King Saud University, P.O. Box, 2455, Riyadh 11451, Saudi Arabia

Zinc oxide (ZnO) thin films were deposited on Si (1 0 0) and glass substrates by sol-gel spin coating technique. Zinc acetate dihydrate, monoethanolamine and isopropanol were used as the sources for precursor solution and the resulting gel was used for the preparation of ZnO thin films. The films were annealed at different temperatures (100 °C to 500 °C) and the effect of annealing on the structural and optical properties was investigated. X-ray diffraction (XRD) and UV-Vis spectroscopy were used for the analysis of the films. The XRD results indicated the polycrystalline hexagonal structure of the ZnO films with (0 0 2) orientation. The optical properties of the films were studied using UV-Vis spectrophotometer in the wavelength range of 190 – 1100 nm. The optical characterization of the ZnO thin films showed the high transmittance of ∼90 % for the films annealed at 400 °C. The films showed the absorbance ∼360 – 390 nm and bandgap values of 3.40 – 3.10 eV, depending on the annealing temperature of the films.

Keywords: *ZnO thin films; sol-gel; spin coating; X-ray diffraction; optical properties*

1. Introduction

ZnO is a II-VI compound semiconductor with a wide band gap (∼3.3 eV), large excitonic binding energy, low resistivity, high chemical stability, high electrochemical coupling coefficient, high thermal and mechanical stability and high carrier mobility making it a potential candidate to use in electronics, optoelectronics and laser technology. ZnO is a multifunctional material, because of its many interesting properties such as a wide range of UV absorption, biocompatibility and biodegradability and piezo- and pyroelectricity. ZnO has a hexagonal wurtzite structure with the cell parameters of a = 3.253 Å and c = 5.215 Å. Due to its superior properties, it finds applications in the field of photo-catalysis, thin film gas sensors, varistors, light emitting diodes, spintronic devices and lasers [1–4]. The piezoelectric properties of ZnO are used in sensors, converters, energy generators and surface acoustic wave (SAW) devices. ZnO thin films are widely used in the window layers of polycrystalline solar cells and thin film silicon solar cells [5]. The wide variety of structures of ZnO are prepared in one (1D), two (2D) and three dimensional (3D) structures with many potential applications in the field of nanotechnology [6]. ZnO thin films are prepared using various techniques such as sputtering, spray pyrolysis, metal-organic chemical vapor deposition (MOCVD), pulsed laser deposition (PLD) and sol-gel process [7–10]. Among these deposition methods, sol-gel spin coating method is widely adopted for the fabrication of ZnO nanostructures due to its simplicity, low cost and lack of necessity of using vacuum. The sol-gel process also offers other advantages such as smooth surface morphology at

*E-mail: balaphysics76@gmail.com

low crystalline temperature, easy control of chemical composition and fabrication of thin films. In the present work, nanocrystalline ZnO films were prepared by sol-gel spin coating method and the effect of annealing on the structural and optical properties was investigated.

2. Materials and methods

The preparation procedure of ZnO thin films by sol-gel technique consisted of three major steps: (i) preparation of the solution, (ii) film deposition and (iii) heat treatment. The solution was prepared by dissolving zinc acetate dihydrate [$Zn(CH_3CO_2)_2 \cdot 2H_2O$] (Merck, 99.98 %) in dehydrated isopropyl alcohol (Merck, >99.9 %). The solution was stirred thoroughly with a magnetic stirrer for 30 min and a milky solution was obtained. Then, monoethanolamine (MEA) [$NH_2C_2H_4OH$] (Merck, +99 %) was added dropwise to the solution as stabilizer until it became transparent. Zinc acetate dihydrate, isopropyl alcohol and monoethanolamine were used as starting material, solvent and stabilizer, respectively. The solution was mixed using a magnetic stirrer at 70 °C for about 2 h. To yield a stable, clear and homogeneous gel, it was kept at room temperature for about 24 h. Finally, the gel was deposited using spin coating technique. The silicon and glass substrates were ultrasonically cleaned with tap water and detergent solution. Then, they were cleaned with deionized water. The substrates were once again ultrasonically cleaned using acetone. The cleaned substrate was placed at the centre of a spin holder and one drop of the gel was poured on the substrate, which was rotated at a certain rpm and the gel was spread across the substrate due to the centrifugal force. The deposition was carried out in three steps at different spinning speeds such as 1000 rpm for 30 s, 2000 rpm for 30 s, and 3000 rpm for 60 s.

Silicon and glass slides were used as substrates and 5 samples were prepared and annealed at temperatures of 100 °C, 200 °C, 300 °C, 400 °C, and 500 °C and then each sample was kept for 30 min in a furnace and cooled down to room temperature. The crystal structure of ZnO films on Si (1 0 0) was analyzed using X-ray diffraction (XRD-Rigaku Dmax 2200) with Cukα radiation. Grazing measurement program operated at 40 kV and 30 mA in an angular range of $20° \leqslant 2\theta \leqslant 80°$. The optical studies were carried out on ZnO thin films deposited on glass substrates using UV-Vis-NIR spectrophotometer (Model UV-1800, Shimadzu) in the wavelength range of 190 – 1100 nm.

3. Results and discussion

3.1. Structural studies - X-ray diffraction (XRD)

Crystallinity of the ZnO thin films was investigated by X-ray diffraction (XRD) technique. The intensity versus 2θ values was obtained from the computer aided data acquisition system. Fig. 1 shows the XRD patterns of the ZnO thin films annealed at different temperatures. The XRD patterns of annealed films show the peaks at the angles of 33.3°, 34.7°, 47.8°, 56.5° and 61.8° corresponding to (0 0 2), (1 0 1), (1 0 2), (1 1 0) and (1 0 3) reflections indicating the hexagonal wurzite structure of ZnO films [3, 7, 8]. The intensity of (0 0 2) peak increased with the increase of annealing temperature up to 300 °C and thereafter the intensity decreased. At higher annealing temperatures, re-evaporation of the materials took place and hence, the intensity decreased at higher temperatures. Therefore, the optimum annealing temperature is 300 °C at which the high peak intensity and small FWHM is observed. The Scherrer formula was used to calculate the crystallite size in the ZnO films from the full width at half maximum (FWHM) of (0 0 2) reflection:

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad (1)$$

where β is the full width at half maximum (FWHM) of the XRD peaks, K is a constant (∼0.9), θ is the diffraction angle and λ is the X-ray wavelength corresponding to CuKα radiation (λ = 1.5418Å). The contribution of the instrumental broadening was calculated as $\beta = \sqrt{(B^2 - b^2)}$, where B is the FWHM of the film and *b* is the instrumental broadening of the bulk specimen. The (0 0 2) peak was used to calculate the crystallite size, which was found in the range

24 – 46 nm. The increased crystallites growth was found with the increase of temperature up to 300 °C. This can be explained by considering the annealing, induced coalescence of small crystallites through grain boundary diffusion, resulting in enhanced crystallites growth. The XRD results are in agreement with the other researchers [11–14]. Harish Bahadur et al. [11] prepared ZnO thin films by sol-gel spin method and characterized their crystallinity. The films consisted of nanostructures in the form of nanocrystals in the range of 15 – 60 nm. Transparent Al-doped ZnO thin films were prepared on silicon substrates by spray pyrolysis and air annealed at 450 °C. XRD patterns showed that annealing process improved the crystallinity of the films [12]. The XRD pattern showed the preferred orientation along the c-axis and the grain size of ∼16 nm. Only (0 0 2) peak at $2\theta = 34.34°$ appeared. The as-deposited films revealed a transparency > 80 % in the 400 – 800 nm wave range. The optical band gap energy was 3.296 eV [13]. ZnO thin films were deposited by sol-gel using dip coating and spin coating techniques. The films were deposited on glass substrates at room temperature and preheated at 225 °C for 15 min. The structure of ZnO films prepared by dip coating, investigated using X-ray diffraction (XRD) revealed that the film was polycrystalline and highly oriented along (0 0 2) plane. The structure of thin films, prepared by spin coating technique was amorphous which was confirmed by the low intensity and wide peaks [14].

3.2. Optical properties - UV-Vis spectroscopy

UV-Vis spectroscopy technique was used to analyze the optical properties of the ZnO films. The transmittance and absorbance spectra were recorded for each sample. Fig. 2 shows the absorbance spectra of ZnO thin films annealed at different temperatures. The absorption observed at ∼380 nm, confirms the transition from valence band to conduction band and gives the band gap of the films. The frequency dependent absorption coefficient α (λ) can be calculated from the equation:

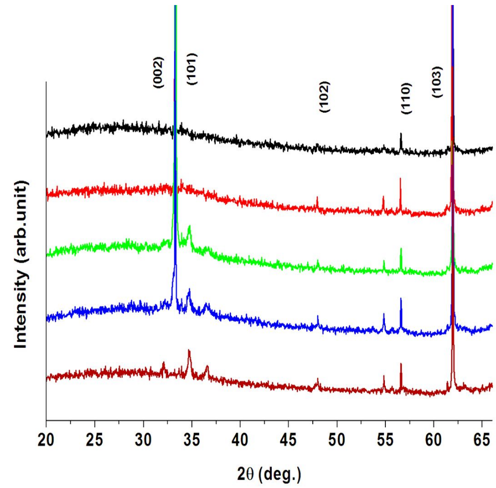

Fig. 1. XRD patterns of the ZnO thin films deposited on Si (1 0 0) substrates and annealed in the temperature range of 100 °C – 500 °C.

$$\alpha(\lambda) = 2.303\frac{A}{t} \tag{2}$$

where t is the thickness of the film and A is the optical absorbance of the film [15].

The optical band gap of the ZnO thin films was estimated by extrapolation of the linear portion of $(\alpha h\nu)^2$ versus hν plots using the relation

$$\alpha h\nu = A(h\nu - E_{opt})^n \tag{3}$$

where A is a constant which depends on the properties of the material, hν is the photon energy of incident radiation, the exponent n can have values of 1/2, 3/2, 1, 2 and 3, depending on the nature of electronic transition and E_{opt} is the optical band gap. Among different n values, a good linearity was observed for n = 1/2 (direct allowed transition), which was found to give the best fit for these films [8, 11]. It is noticed that the plots of $(\alpha h\nu)^2$ versus hν are linear over a wide range of photon energies indicating the direct type of transitions. The intercepts (extrapolations) of these plots (straight lines) on the energy axis give the energy band gaps. The band gap, Eg = 3.10 eV was obtained from the intercept with energy axis for the films annealed at 500 °C as shown in the Fig. 3.

Fig. 4 shows the transmittance of the ZnO thin films whose value is ∼70 – 90 % in the visible

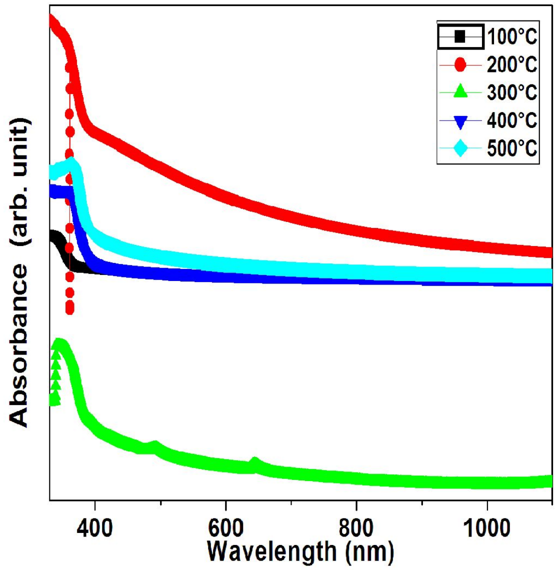

Fig. 2. Absorption spectra of the ZnO films annealed at different temperatures.

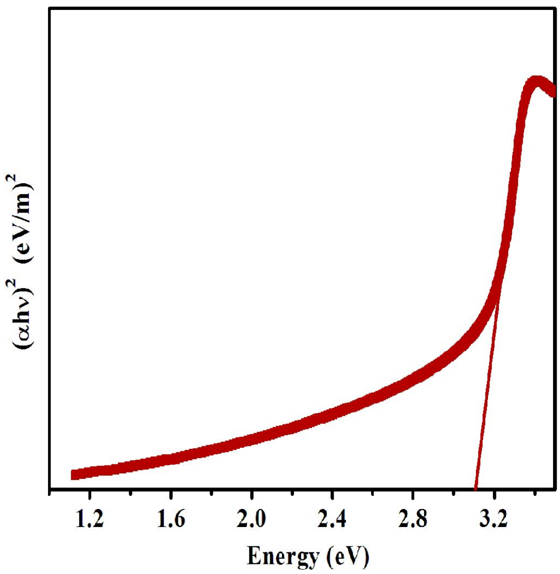

Fig. 3. Typical $(\alpha h\nu)^2$ versus $h\nu$ plot of the ZnO film annealed at 500 °C.

region of electromagnetic spectrum. The film deposited at 400 °C shows the highest transmittance. Table 1 shows the values of crystallite size and bandgap of the films with respect to the annealing temperature. Agrawal et al. [7] deposited ZnO thin film on glass substrates by reactive DC magnetron sputtering in oxygen atmosphere at different oxygen flow rates and annealed the films at 300 °C for 2 hours in vacuum environment. The band gap of the film was found to be 3.2 eV and it showed 80 % transparency at 600 nm wavelength. The XRD pattern of a ZnO thin film deposited on glass substrate by spray pyrolysis showed crystalline nature of the film and wurtzite phase with preferential orientation along the c-axis. The energy band gap of the film was evaluated as 3.28 eV [8]. ZnO thin films were deposited on glass substrates by pulsed laser deposition (PLD) in an oxygen-reactive atmosphere [9]. High quality polycrystalline ZnO films with hexagonal wurtzite structure were obtained at substrate temperatures of 100 °C and 300 °C. The films exhibited high transmittance of 90 % and energy band gap in the range of 3.26 – 3.30 eV. ZnO thin films were deposited on the glass substrates by the sol-gel spin coating method at different RPM [10]. Zinc acetate dihydrate, 2-methoxethanol and monoethanolamine (MEA) were used as a starting material, solvent and stabilizer, respectively. The grain size of the films was calculated using the Scherrer formula. The optical absorption studies revealed a direct band gap.

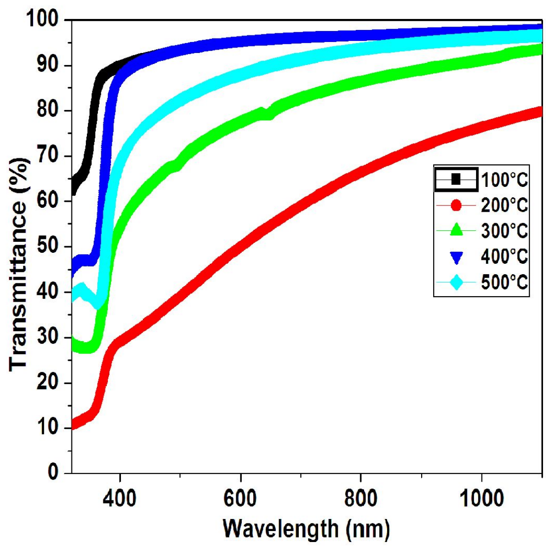

Fig. 4. Transmission spectra of the ZnO thin films annealed at different temperatures.

Nagarani et al. [16] studied the effect of annealing temperature on structural and optical properties of ZnO thin films. The ZnO thin films were prepared on glass substrates by spin coating method. The prepared films were annealed at different temperatures from 350 °C to 550 °C. The XRD studies indicated the wurtzite structure with (1 0 0) (0 0 2) and (1 0 1) reflections in all the ZnO thin films. The intensity of (1 0 1) reflection increased with annealing temperature, indicating the preferential orientation. The crystal structure and orientation of the films were investigated using X-ray diffraction (XRD) and the optical energy band gap was evaluated in the range of 3.27 eV – 3.31 eV [16]. Nanda Shakti et al. [17] studied the structural and optical properties of ZnO thin films prepared by sol-gel spin coating process. The ZnO thin films were prepared on quartz substrates and annealed at 400 °C, 500 °C and 600 °C. XRD patterns of the films showed the polycrystalline nature. The photoluminescence studies revealed UV emission ∼380 nm [17]. Anil Kumar et al. [18] deposited ZnO thin films on quartz substrates using RF magnetron sputtering and the films were annealed in air at RT, 200, 400, 600 and 800 °C for 2 h. The XRD patterns showed the (0 0 2) diffraction peak in all the films indicating the preferred orientation along the c-axis. The intensity of this orientation increased with annealing temperature. All the films showed a high transmittance of ∼90 % in the visible range with a sharp absorption edge of ∼380 nm. Jamilah Husna et al. [19] deposited ZnO thin films using RF magnetron sputtering on ITO coated soda-lime glass substrates and the films were annealed in the temperature range of 250 – 450 °C. XRD analysis indicated the hexagonal wurtzite structure and polycrystalline nature of the annealed ZnO films with (0 0 2), (1 0 1) and (0 0 1) orientations. The as-deposited ZnO films showed the (1 0 1), (1 0 2) and (0 0 2) peaks and the films treated at annealing temperature above 400 °C showed the dominant (0 0 2) peak. The band gap of the films annealed at a temperature of 400 °C ranged between 3.1 eV and 3.23 eV [19]. Zaier et al. [20] produced ZnO thin films on glass substrates by thermal evaporation technique at room temperature and the films were annealed at different temperatures from 200 °C to 500 °C for 2 h in air. XRD studies indicated the hexagonal wurtzite structure with the strong (0 0 2) preferential orientation of the ZnO thin films. The optical studies showed the transmittance > 90 % in the visible region and the band gap values were found between 3.13 and 3.25 eV. It has been suggested that due to annealing, the surface energy is minimum along (0 0 2) orientation and the grain growth is maximum [21]. The (0 0 2) texture of the ZnO thin films is in an effective equilibrium state, where an adequate surface mobility is revealed by the atoms deposited/annealed at certain conditions [22]. The structural and optical properties of all the studied ZnO thin films showed that the annealing conditions, rotational speed, concentration of reactants (precursor and solvent) strongly affect the orientation and the properties of the films.

Table 1. Crystallite size and bandgap of the films with annealed temperature

S. No.	Annealing temperature [°C]	Crystallite size [nm]	Optical bandgap [eV]
1	100	24	3.40
2	200	27	3.25
3	300	32	3.25
4	400	38	3.10
5	500	46	3.10

4. Conclusions

Nanocrystalline ZnO thin films were deposited on glass and silicon (1 0 0) substrates by sol-gel spin coating technique. The ZnO films prepared by spin coating method have shown homogeneous and dense surface. The XRD patterns indicated the hexagonal structure of the ZnO thin films with (0 0 2) orientation. The optical transmittance of the films was ∼90 % for the films annealed at 400 °C. The absorption edge was found at ∼380 nm and the energy band gap values were in the range of 3.40 – 3.10 eV. From the XRD and UV-Vis studies, it was confirmed that the good quality ZnO thin films were obtained and the films can be used for the industrial applications in electronics, optoelectronic devices and solar cells.

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