Effect of annealing on structural and optical properties of ZnO thin films prepared by Sol-Gel technique

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Abstract: Zinc oxide thin films were prepared by sol gel method and spin coating technique, using zinc acetate as precursor solution on glass substrate. The prepared films were annealed at three different temperatures to study the effect of annealing on the structural and optical properties of ZnO thin films. The deposited and annealed films were characterized by X-ray diffraction (XRD), UV-Vis-NIR spectroscopy and scanning electron microscopy (SEM) coupled with microanalysis (EDX). The XRD pattern shows that ZnO films are polycrystalline in nature and crystallite size increases with the increase in annealing temperature. Optical transmittance measurements were taken using UV-Vis-NIR spectrophotometer and the calculated values of the direct band gap energy, Eg was between 3, 28 and 3, 42 eV.

Keywords: ZnO thin films, Sol-Gel, Annealing, XRD, Transmittance.

1. Introduction

Recently, wide band gap semiconductors have actively been studied for their application in optoelectronic devices. GaN and ZnO are examples of wide band gap semiconductors which have been used for light emitting diodes and laser diodes. ZnO is mostly chosen for its better excitonic properties compared to GaN, with an excitonic binding energy of 60 meV at room temperature [1]. Besides that, because of its high transparency in the visible region and its high conductive properties, ZnO is widely used as a transparent conducting oxide (TCO), in photovoltaic devices, and sensors. ZnO is naturally n-type due to defects such as oxygen deficiency and zinc excess [2]. It is chemically and mechanically stable, non-toxic, and high abundant. Various deposition methods have been applied to grow high quality ZnO thin films such as molecular beam epitaxy (MBE) [3], thermal chemical vapor deposition (CVD) [4], metal-organic cvd (MOCVD) [5], r.f. sputtering [6], and sol-gel methods [7]. Among the methods, sol-gel spin coating is favorable because of its simple, non-expensive preparation of homogeneous thin film, along with excellent compositional control, lower crystallization temperature and uniform film thickness [8].

In this work we have studied the effect of post-deposition annealing on structural and optical properties of ZnO films.

2. Experimental procedure

ZnO thin films have been deposited by sol–gel associated with spin coating method onto glass substrates. Zinc acetate dihydrate, 2-methoxyethanol and (MEA) Mono-ethanolamine were used as starting precursor, solvent, and sol stabilizer, respectively. The molar ratio of MEA to zinc acetate dihydrate was maintained at 1.0 and the concentration of zinc acetate was 0.75M solutions were stirred at 60°C for 2 h to yield a clear and homogeneous solution, which served as the coating solution after cooling to room temperature. The coating solution was dropped into a glass substrate, which was rotated at 3000 rpm for 30s. After depositing by spin coating, the film was dried at 200°C for 10 min in a furnace to evaporate the solvent and remove organic residuals. The procedures from coating to drying were repeated 5 times. The films were then inserted into a tube furnace and annealed in air at (450,500 and 550°C) for 2 h.

3. Results and discussion

3.1. XRD studies

X-ray diffraction (XRD) studies have been performed to measure the crystallite sizes, texture coefficients and the lattice constants ‘a’ and ‘c’.

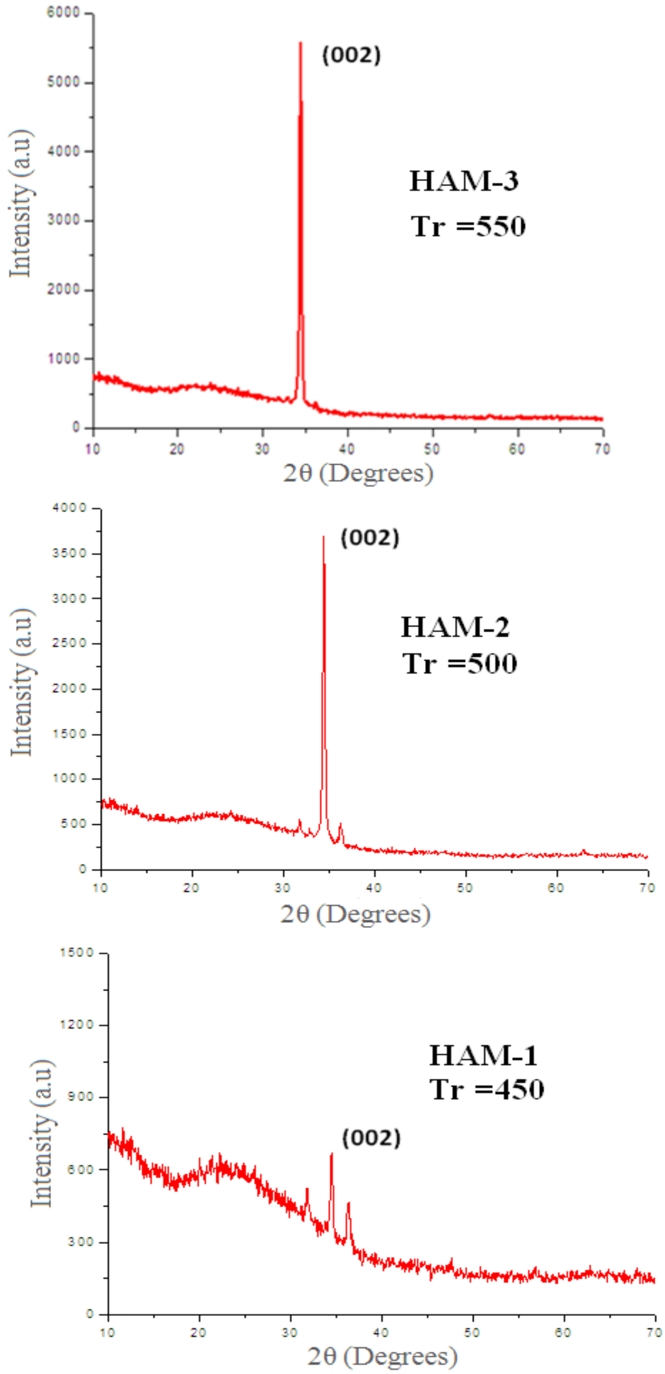

Fig 1: X-ray diffraction pattern of the ZnO thin film

The XRD pattern of the film is shown in Fig 1. Shows that all of the films have the same crystal structure but the intensities (002) changed with different annealing temperature [9] .The XRD result suggest that the ZnO thin film has the polycrystalline structure. The film was crystallized with the hexagonal wurtzite structure (JCPDS 36-1451) and a strong preferred orientation along the direction (002) which is located at 2 θ = 34.44 along the c axis with lattice parameters a = 0.3258 nm and c = 0.5225 nm, very close to the theoretical values a = 0.3256 nm and c = 0.5237 nm [10]. The lattice constants 'a' and 'c' of the Wurtzite structure of ZnO can be calculated using the relations (1) and (2).

$$c = \frac{\lambda}{\sin\theta} \quad (1) \qquad a = \sqrt{\frac{1}{3}}\,\frac{\lambda}{\sin\theta} \quad (2)$$

The crystallite size of the ZnO films annealed at different temperatures was calculated by using Scherrer's formula [11].

$$D_{hkl} = 0.94\,\frac{\lambda_{hkl}}{\beta_{hkl}\cos(\theta_{hkl})}$$

$\mathbf{D_{hkl}}$ is the crystallite diameter, $\boldsymbol{\lambda}$ is the wavelength of the incident radiation (λ = 0,152 nm) $\boldsymbol{\beta_{hkl}}$ the width at half height of the diffraction peak, $\boldsymbol{\theta_{hkl}}$ the half-angle Bragg diffraction expressed in radians. The results are reported in Table1. These results indicate that the grain size changes with temperature annealed [9].

Table 1: Crystallite size along prominent diffraction planes for ZnO films annealed at 450 °C, 500 °C and 550 °C.

Samples	Temperatures (°C)	Crystallite size (nm)
HAM-1	450	45,27
HAM-2	500	60,44
HAM-3	550	78,94

The texture coefficient (TC) represents the texture of particular plane, deviation of which from unity implies the preferred growth. Quantitative information concerning the preferential crystallite orientation was obtained from the different texture coefficient TC (hkl) defined as [12].

$$TC(hkl) = \frac{\frac{I_r(hkl)}{I_0(hkl)}}{\frac{1}{n}\sum\frac{I_r(hkl)}{I_0(hkl)}}$$

Where I_r (hkl) is the measured relative intensity of a plane (hkl), I_o (hkl) is the standard intensity of the plane (hkl) taken from the JCPDS data. n is the number of diffraction peaks. A sample with randomly oriented crystallite presents TC(hkl) = 1 while the larger value, the larger abundance of crystallites oriented at the (hkl) direction. The texture coefficient was calculated

for the highly oriented peak of (002) and is given in Table 2.

Table.2: texture coefficients value for the ZnO thin film.

Samples	(hkl)	Intensity	2θ	TC(hkl)
HAM-1	002	3750	34.44	1,49
HAM-2	002	1789	34.44	8,35
HAM-3	002	5574	34.44	15,09

3.2. Surface morphology of ZnO thin films

The microstructure and chemical of the films was observed by a field emission Scanning electron microscopy (SEM) coupled with Energy-Dispersive X-ray analysis. The SEM image in Fig.2 shows the surface morphology of ZnO thin film deposited under optimal conditions. This photo shows crystallites of hexagonal shape. This agrees well with results obtained by analyzes of diffraction X-ray.

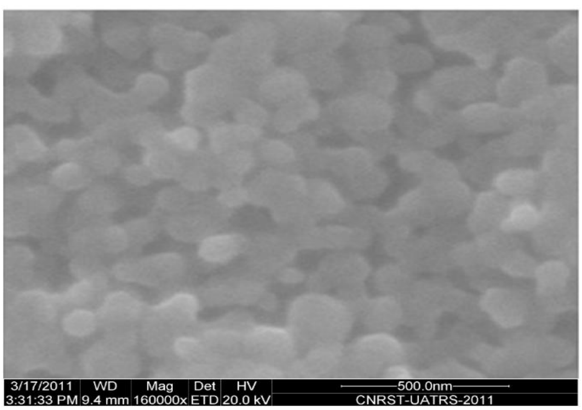

Fig 2: Surface morphology of a ZnO layer deposited under the optimum conditions.

The composition analysis by X-ray spectroscopy revealed the presence of all the expected elements with some contamination at low levels.

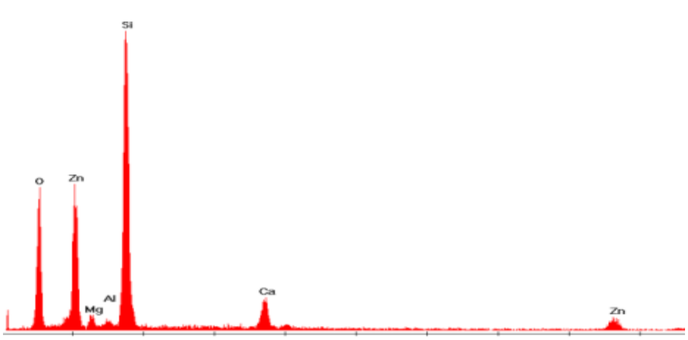

Fig 3: EDX analysis corresponding to the ZnO thin film.

The peaks associated with Zn and O elements are present parallel peaks of Mg, Al, Si and Ca are also observed, but from the substrate on which the sample was deposited. The elements are zinc and oxygen in the respective proportions of 53.63% and 46.37%. From these data the stoichiometry of the layer is estimated to be Zn / O = 0.90%.

3.4. Optical properties of the ZnO thin films

Transmittance and reflectance spectra were measured in the range of 300-1000 nm using a Perkin Elmer Lambda 900. We have studied transmittance and the band gap values, Eg, of ZnO thin films as a function of annealing temperature. As can be seen from Fig.4, all ZnO thin films annealed at different annealing temperatures were highly transparent in the visible with a transmittance of more than 85%.

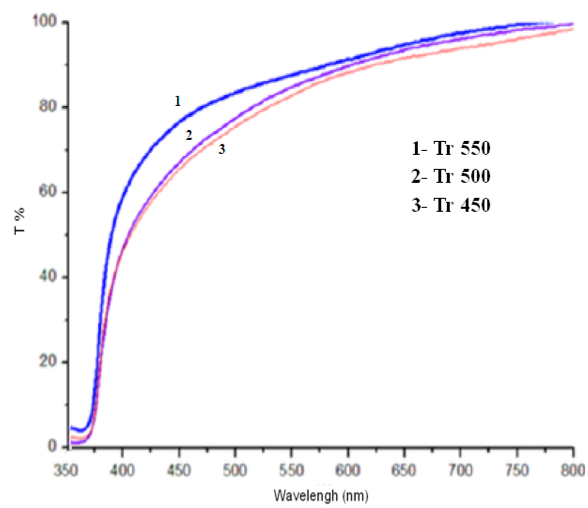

Fig 4: Transmission of ZnO thin films under different annealing temperatures.

From the transmission curve, we can calculate the direct band gap by the following equation, which represents the variation of $(\alpha.h\upsilon)^2$ with $(h\upsilon)$ [13].

$$(\alpha.h\upsilon)^2 = B\,(h\upsilon - E_g) = f\,(h\upsilon)$$

Where $h\upsilon$ is the energy of incident photons, Eg the optical gap and B is a constant.

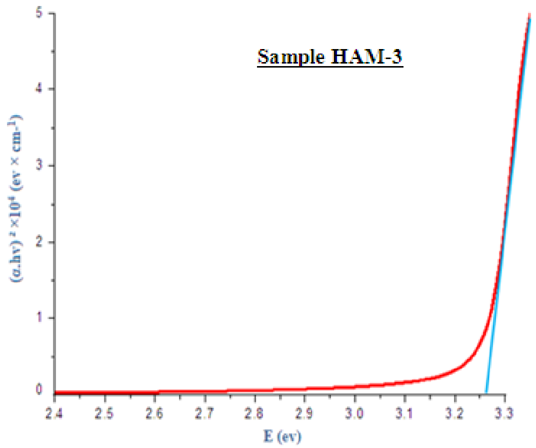

Fig 5: Determination of the energy gap by extrapolation method from the variation of (α.hυ) ² according to (hυ) for a thin layer of ZnO.

The values of energy gap Eg of the samples showed good transmission curve by the method of extrapolation from the change $(\alpha.h\nu)^2$ according to hv a thin layer of ZnO. The table 3 below summarizes the values of the energy gap for the samples deposited at different recruit.

Table 3: Values of the energy gap.

Samples	Temperatures (°C)	Energy gap (eV)
HAM-1	450	3,42
HAM-2	500	3,37
HAM-3	550	3.28

The optical band gap (Eg) of the ZnO thin films annealed at 450 °C, 500 °C, and 550°C obtained from Tab. 3 by the naked eye is 3.42 eV, 3.37 eV and 3.28 eV, respectively. The shifts of the optical band gap edge may be attributed to the increasing grain size and the texture coefficient TC (hkl).

4. Conclusion

ZnO thin films prepared on glass substrate by sol-gel spin coating process with post annealing temperatures at 450ºC, 500ºC and 550ºC. The structural characterization of the film was done by X-Ray Diffraction (XRD). From XRD spectrum of the film the characteristic reflection planes of ZnO was verified. The lattice constants were calculated, which agreed with that of bulk ZnO. Crystallite size of the films was found to be less than 80 nm. The transmission spectrums of the films were recorded by UV-VIS Spectrophotometer. The films showed high transparency (>85%) in the visible region. The band gap energies determined from the transmission spectra for thin films deposited on glass are 3.28 to 3.42 eV.

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