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Review

Influence of annealing temperature on the structural, morphological and optical properties of Cu doped ZnO thin films deposited by the sol–gel method

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ABSTRACT

In this work, the characteristics of 5 wt% Cu doped ZnO thin films deposited by sol gel on glass substrates were studied. The objective of the present work is to study the influence of different annealing temperatures on the structural, morphological and optical properties of 5 wt% Cu doped ZnO thin films. For this purpose we have used XRD, AFM and UV–visible spectroscopy for films characterization. Structural analysis showed that all films are polycrystalline with hexagonal wurtzite structure and preferred orientation (002) which gradually improves with increasing the annealing temperature. The grain size is calculated by the Scherrer method ranges from 21.65 nm to 36.47 nm. The AFM study showed an increase in surface roughness with increasing annealing temperature. Optical characterization in the visible range from 300 to 1100 nm showed that the deposited layers have a high transmission factor (>78%). The calculated gaps vary between 3.28 and 3.36 eV in the whole investigated annealing temperature range.

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Contents

1. Introduction

In recent years, Zinc oxide (ZnO) thin films have been widely investigated and considered as the most ideal semiconductor materials for many potential applications. ZnO is a binary material, semiconductor wide direct band gap (3.37 eV), a large excitonic binding energy of 60 meV [1], strong emission, large saturation velocity (3.2×10^7 cm s^{-1}) and a high breakdown voltage [2]. Because of their physical, optical and electrical properties, high chemical and thermal stability, non-toxicity and its abundance in nature, ZnO is well suited for various applications such as photodetectors [3], acoustic devices [4], thin film transistors [5], gas sensors [6], solar cells [7], ceramics [8], lasers [9], and light emitting diode [10].

Several methods of ZnO thin films preparing have been developed such as chemical vapor deposition (CVD) [11], RF magnetron sputtering [12], molecular beam epitaxy (MBE) [13], pulsed laser deposition [14], spray-pyrolysis [15], filtered cathodic vacuum arc method [16] and sol–gel method [17]. Among these techniques, sol–gel method has several advantages such as simplicity, precise composition control, low cost, excellent uniformity, easy control of the thickness and low crystallization temperature [18,19].

Experimental and theoretical results already on Cu doped ZnO have been reported [20–23]. Most research is based on the study of the influence of different concentrations of Cu on the structural properties, morphological and optical ZnO thin films. However, the influence of the annealing temperature on the structural and optical properties of Cu doped ZnO thin film has not reported. The present work deals with the investigation of the effect of annealing temperature on the structural, morphological and optical properties of Cu-doped ZnO thin films. We study the behavior of structural, morphological and optical properties of 5 wt% Cu doped ZnO thin films for different annealing temperatures (400–550 °C).

2. Experimental procedure

5 wt% Cu doped ZnO thin films were prepared by dip-coating technique. Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), copper acetate ($Cu(CH_3COO)_2$), was dissolved in a mixture of 2-methoxy ethanol($C_3H_8O_2$) and monoethanolamine ($HOCH_2C_2NH_2$). The molar ratio of zinc acetate to MEA was 1:0 and the concentration of zinc acetate was maintained at 0.5 mol. The resulting mixture solution was stirred by a magnetic stirrer at 333 K for 2 h to yield homogeneous solution. Afterwards the solution was kept in a covered for 24 h at room temperature. The glass substrates were ultrasonically cleaned in acetone for 20 min, methanol for 20 min, rinsed in deionized water. The films were prepared by dip coating technique with withdrawal speeds of 100 mm/min at room temperature. After dip coating process, the films were dried at 150 °C for 10 min. This coating procedure was repeated 20 times. Finally, the films were annealed at 400, 450, 500, and 550 °C for 2 h.

To study films properties, various characterization techniques were used. The X-ray diffraction (XRD, Bruker AXS-8D) with Cu Kα radiation (Cu Kα = 0.1541 nm) to study the structural properties, films morphology was also characterized by atomic force microscopy (A 100-AFM) and UV–Visible spectrophotometer (Jasko V-630) to study the optical properties.

3. Results and discussion

3.1. Structural properties

Fig. 1 exhibits the XRD diffraction spectra obtained in 5 wt% Cu doped ZnO thin films annealed at different annealing temperatures. As can be seen, three pronounced diffraction peaks corresponding to (100), (002) and (101) planes of the ZnO are present in all spectra. This result allows to assert that all films have a well polycrystalline nature and hexagonal wurtzite structure with preferential orientation (002). Increasing annealing temperature induces films crystallinity improvement. No diffraction peak related to Cu or CuO phases were observed.

The crystallite size may be estimated from the full width at half maximum (β) of (002) diffraction peak using Scherer's formula [24]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the X-ray wavelength, β is the full width at half maximum of the XRD peak, θ is the Bragg diffraction angle.

The XRD analysis (Table 1) revealed that the calculated grain size is between 21.65 and 36.47 nm. As shown in Fig. 2 the grain size increases linearly with increase in the annealing temperature. This is due to an increase of atoms mobility and crystallite cross linking to form larger grains.

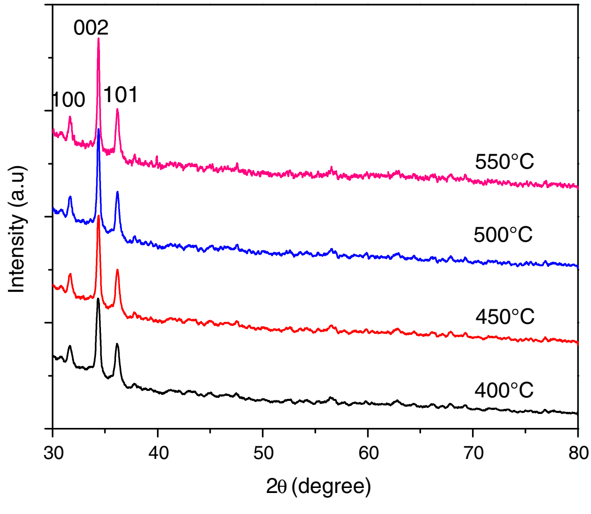

Fig. 1. XRD patterns of the Cu doped ZnO thin films annealed at different temperatures.

Table 1
The data evaluated form the XRD, AFM and UV–vis measurements of 5 wt% Cu doped ZnO thin films after annealing at different temperatures.

Annealing temperature (°C)	Position of (002) peak (°)	*B* of (002) peak (°)	Grain size (nm)	RMS roughness (nm)	Optical band gap (eV)
400	34.347	0.3890	21.65	5.3	3.36
450	34.362	0.3152	26.65	9.1	3.33
500	34.372	0.2725	31.5	13.7	3.31
550	34.386	0.2329	36.47	19.6	3.28

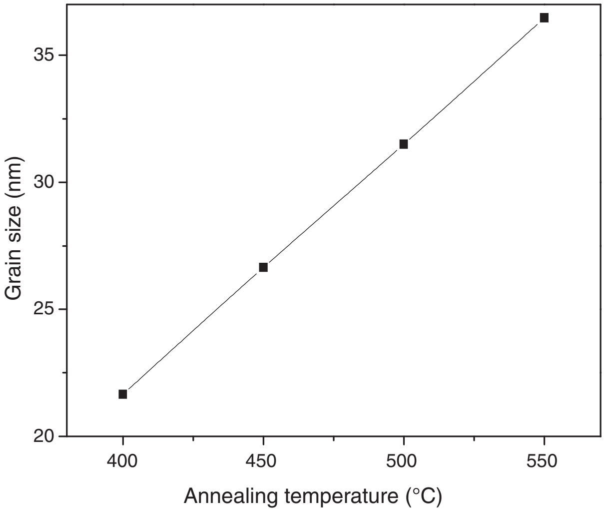

Fig. 2. Variation in grain size as a function of annealing temperature.

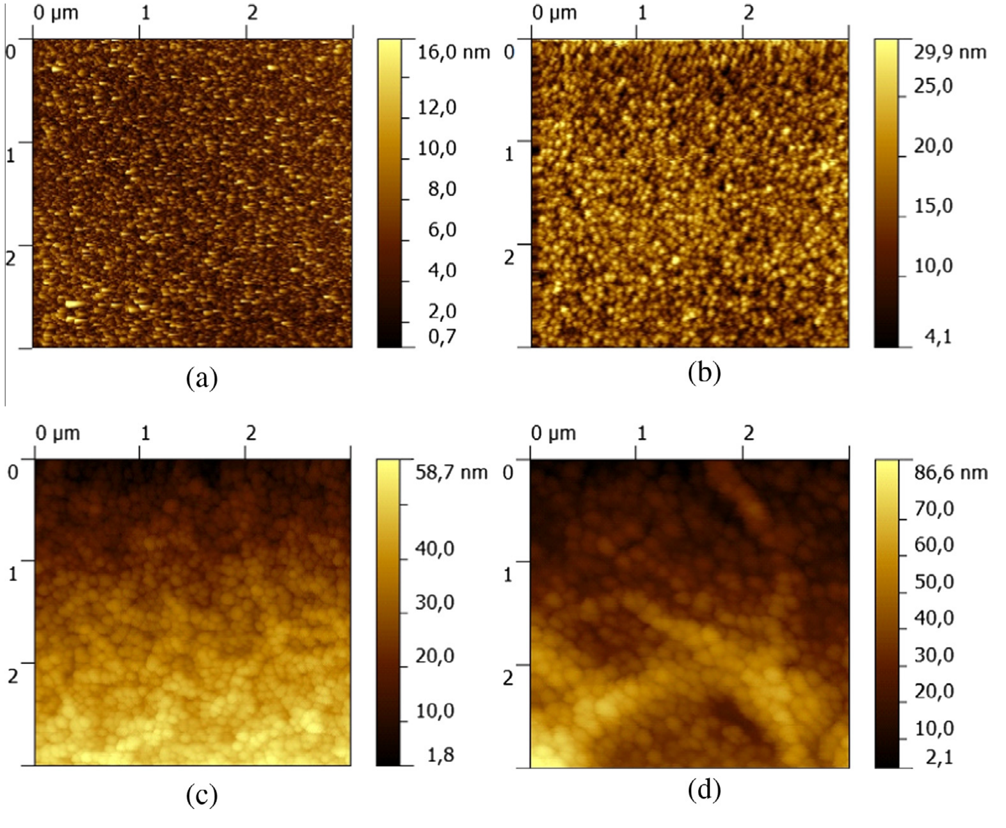

Fig. 3. Two dimensional surface morphology images of the 5 wt% Cu doped ZnO thin films annealed at different temperatures: (a) 400 °C, (b) 450 °C, (c) 500 °C and (d) 550 °C.

3.2. Surface morphology

Fig. 3 shows the images of the surface morphology of the 5 wt% Cu doped ZnO sample annealed at different temperatures. As can be seen, all films surface were continuous, highly dense and without any cracks. The topographical analysis (Table 1) showed that the root mean square (RMS) films surface roughness increases from 5.3 nm to 19.6 nm with increasing annealing temperature from 400 °C to 550 °C. This is due to the growth of grain size which resulted in an increase in surface roughness [25].

3.3. Optical properties

The optical transmission spectra of 5 wt% Cu doped ZnO thin films as a function of the annealing temperatures were measured in the range of 300–1100 nm as shown in Fig. 4. This figure shows that

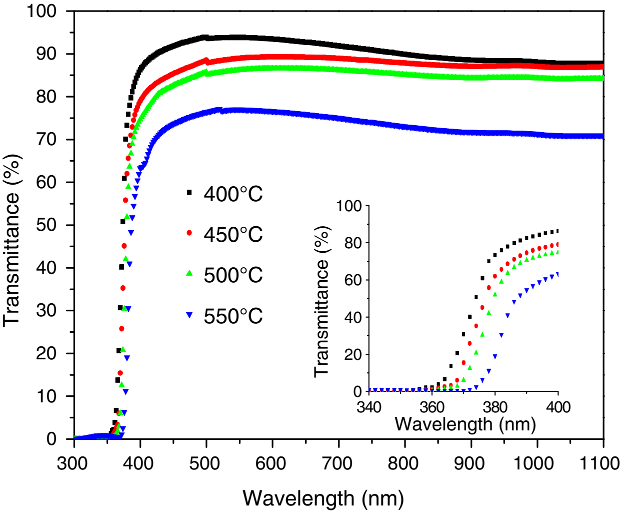

Fig. 4. Transmittance spectra of the Cu doped ZnO thin films; inset shows enlarged spectra of the films with absorption edges from 340 nm to 400 nm.

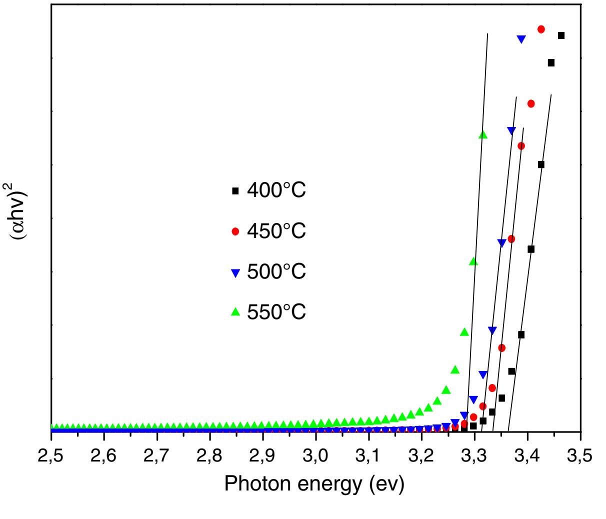

Fig. 5. Curves of $(\alpha h\upsilon)^2$ versus photon energy for the Cu doped ZnO thin films.

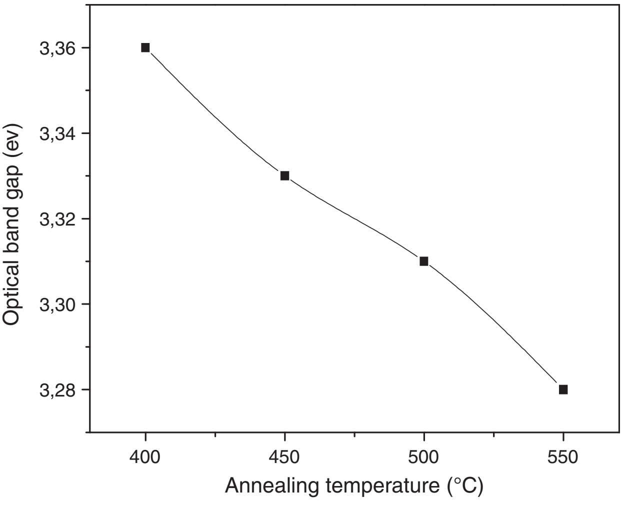

Fig. 6. Variation in the optical band gap of Cu-doped ZnO thin films as a function of annealing temperature.

all the films exhibit high transmittance in the visible region with a sharp absorption edge at about 370 nm. The average transmittance of the films decreased from 93% to 78% when the annealing temperature was increased from 400 °C to 550 °C. This behavior can be related to the increased surface roughness, which dispersed light and causes its diffusion in random directions, resulting in transmittance decrease [26].

The optical band gap of the 5 wt% Cu doped ZnO thin films annealed at different temperatures was estimated by employing the Tauc equation [27]:

$$(\alpha h\upsilon) = B(h\upsilon - E_g)^{1/2}$$

where B is a constant, $h\upsilon$ is the photon energy and E_g is the optical band gap.

Fig. 5 shows $(\alpha h\upsilon)^2$ variation as a function of photon energy $(h\upsilon)$. The optical gap can be estimated from the extrapolation of the linear part of the curve $(\alpha h\upsilon)^2$ on the axis abscissa $(h\upsilon)$. The evolution of the optical gap of as a function of the annealing temperatures is reported in Fig. 6. As can be seen, the optical gap decreases from 3.36 eV to 3.28 eV with the increasing the annealing temperature of 400–550 °C. This reduction of the gap with the annealing temperature is mainly due to the growth of the grain size.

4. Conclusions

In this work, the 5 wt% Cu doped ZnO thin films were prepared by sol gel dip coating method on glass substrates, the effect of annealing temperature on the structural, morphological and optical properties of these samples were investigated. The X-ray diffraction reveals that all films had a polycrystalline nature and hexagonal wurtzite structure with preferential orientation (002), which gradually improves with increasing the annealing temperature. The grain size increases from 21.65 nm to 36.47 nm when the annealing temperature was increased from 400 °C to 550 °C. The AFM study revealed that surface roughness of 5 wt% Cu doped ZnO thin films was increased with annealing temperature. The prepared films exhibited high transmission which is greater than (>78%) in the visible region and the optical gap of ZnO thin film decreased from 3.36 eV to 3.28 eV with increasing the annealing temperature.

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