Structural, Morphological and Optical Properties of Sol-Gel Spin Coated Al-doped Zinc Oxide Thin Films

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Abstract

A sol-gel spin coating method has been successfully used to synthesize Al-doped ZnO thin films. The XRD studies show synthesis of phase pure ZnO thin films with hexagonal wurtzite structure. The lattice parameters are a=3.2568Å and c=5.2108Å. Al-doping enhances the preferential growth along (002) direction. The lattice parameters decrease with increase in Al-doping concentration. SEM studies show that with Al-doping the growth of the films takes place with porous structure embedded with nanogranules overgrown on the folded structure. This indicates that Al-doping has an influence on the surface morphology of the films. AFM studies show that the maximum surface roughness of the film increases with Al-doping concentration. Optical study revealed that band gap of ZnO is 3.25 eV with direct band to band transitions and decreases with Al-doping concentration. The properties of ZnO thin films can be effectively tailored with Al-doping. These synthesized Al-doped ZnO thin films can be effectively used in photocatalysis and gas sensor applications.

1. Introduction

Transparent conducting oxide (TCO) films have been intensively investigated for their potential applications, such as flat-panel displays, liquid crystal displays, organic light-emitting diodes, thin-film transistors, and thin-film solar cells [1]. Among the various materials, zinc oxide is one of the technologically important transparent conducting materials. Compared to other II-VI group compounds, zinc oxide has a large band gap of 3.37 eV and rather large exciton binding energy, which makes the exciton state stable even at room temperature. The wide range of optical and electrical characteristics have made these films very adequate for several promising applications such as chemical sensors, piezoelectric transducers, transparent electrodes, light emitting diodes, laser diodes, ultra-violet photodetectors, varistors, SAW devices, gas sensors, etc [2-6]. The method and preparative conditions of ZnO nanoparticles are also very important to control the microstructure of the films and thus expected to influence the optical and electrical properties. Various techniques have been used to deposit pure and doped ZnO thin films on different substrates. These include spray pyrolysis [7], sol-gel [8, 9], RF sputtering [10, 11], SILAR [12], combustion [13] and chemical bath deposition [14]. Among these, the sol-gel technique has several advantages, such as deposition of high purity, homogeneous, cheaper, large-area films at relatively low temperatures [1].

The study of effect of dopants on optical properties of ZnO based nanostructures is very important for photonic applications. Compared to undoped semiconductors, doped materials offer the possibility of using the dopant to tune their optical and electronic properties. Therefore in addition

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to the existing advantages, which nanomaterials have offered in terms of controllable parameters such as size, shape and surface; dopants offer the additional flexibility for designing new functionalities and for altering their properties. Recent research reveals that ZnO films doped with Al, B, Ga, Mn and Cr show modifications in optical and electrical properties [11, 15, 16]. Tunable band gap can also be obtained by Al-doping in ZnO thin films. Especially, ZnO: Al thin films with highly *c*-axis oriented crystalline structure along [002] have potential device applications in broadband UV photo detector with high tunable wavelength resolution [17]. However, there are scarcely any reports on the effect of aluminum doping on the structure, morphology and optical properties of ZnO films prepared by the sol-gel spin coating technique. In this paper, we concentrate on the structural, morphological and optical properties of Al-doped ZnO thin films synthesized by sol-gel spin coating technique.

2. Experimental Details

Pure and aluminum doped ZnO thin films were deposited onto glass substrates by sol-gel spin coating method [9]. For deposition AR grade zinc acetate dehydrate, aluminum sulphate, 2-methoxethanol and monoethanolamine (MEA) were used as the starting materials. The sol was prepared by dissolution of zinc acetate dehydrate in 2-methoxethanol and monoethanolamine (MEA). $Al_2(SO_4)_3$ $16H_2O$ was dissolved in water and added to the host solution in the appropriate proportion. The prepared solution was stirred at 80°C for 20 minutes to get clear and homogeneous solution. The film was then deposited onto glass substrates by using spin coating unit (MILMAN-XT56), which was rotated at 3000 rpm for 2 minutes. After depositing by spin coating, the film was dried at 200°C for 10 minutes in a furnace to evaporate the solvent and remove organic residuals. The film was then annealed in air at 400°C for 4 h.

The thin films were then characterized through X-ray diffraction technique for its structural analysis. A Philips PW-3710 X-ray diffractometer with Cu K$_\alpha$ radiation (λ = 1.54056 Å) was used for this purpose. The range of 2θ angle was from 20° to 80°. The surface morphology of the thin films was observed on SEM (JEOL JSM 6360) operating at 20 kV. The topography of the films was recorded by an atomic force microscope (INNOVA 1B3BE). The UV-VIS spectrum of nanocrystalline zinc oxide thin films was recorded using Shimadzu UV-VIS-NIR spectrophotometer (UV-3600).

3. Results and Discussion

The deposited films are thin, uniform and strongly adhering to the glass substrate. The X-ray diffractograms of pure and doped ZnO thin films are shown in Fig. 1.
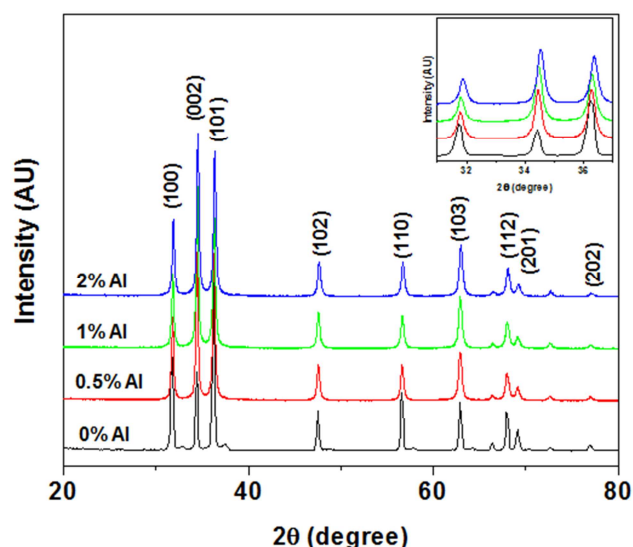

Fig. 1. X-ray diffractograms of Al-doped ZnO thin films.

The patterns were analyzed to get the information about crystal structure, lattice parameters and grain size. The d-values and intensities of the observed diffraction peaks match with the single crystalline form of the hexagonal ZnO (JCPD card no. 036-1451) indicating that synthesized sample is zinc oxide with hexagonal wurtzite structure. No separate aluminum phase is detected, however, the peak positions shifts towards higher 2θ values (Fig. 1 inset), which supports that Al ions are substituted at Zn sites entirely in the lattice of ZnO crystal. It is observed that for pure ZnO the strongest reflection is (101) plane. With Al-doping the intensity of (002) reflection gradually increases and becomes the strongest reflection. This suggests Al-doping enhances the preferential growth along (002) direction. Lattice parameters were then calculated from the d values and the values are listed in Table 1. The lattice parameters decrease with increase in Al-doping concentration. The decrease in lattice parameters can be attributed to the replacement of larger Zn^{2+} ion by smaller Al^{3+} ion [10]. The average crystallite size was determined by the Scherer's relation:

$$D = 0.89 \, \lambda \, / \beta \cos\theta \qquad (1)$$

where, D is the crystallite size, λ is wavelength of X-ray, β is full width at half maximum (FWHM) measured in radians and θ is the Bragg angle. The values of average crystallite size are listed in Table 1. The average crystallite size is in the range of 56-61 nm for all the samples.
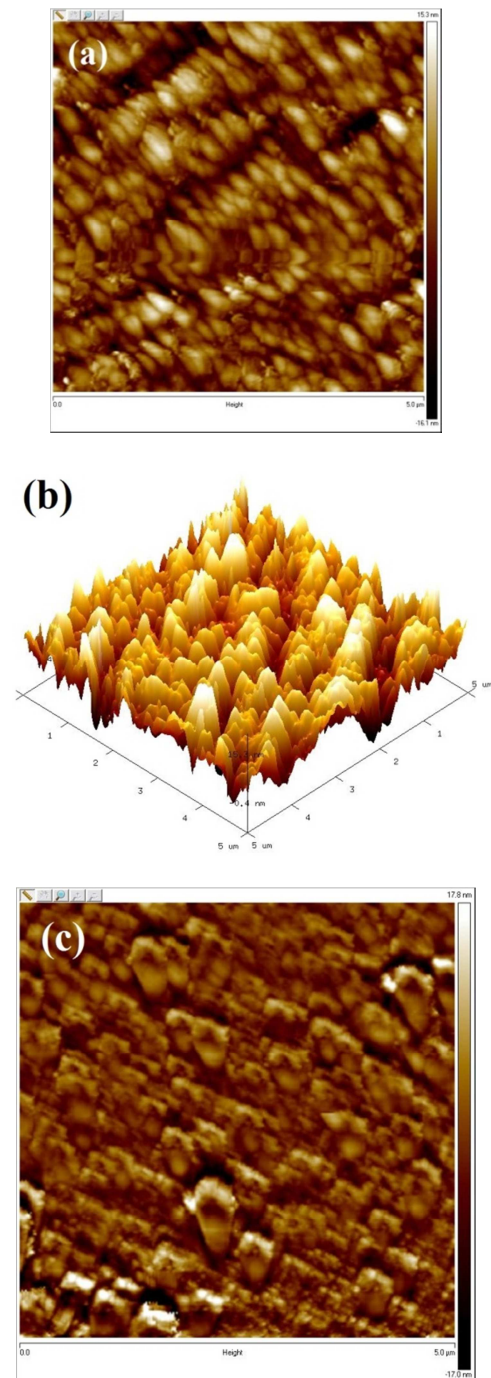
The surface morphology of the samples was studied with scanning electron microscope. The SEM images of pure and Al-doped thin films are shown in Fig. 2. For pure ZnO it is seen that the growth of the film takes place with folded structure increasing the open surface area of the film. With

Al-doping the growth of the films takes place with porous structure embedded with nanogranules overgrown on the folded structure. This indicates that Al-doping has an influence on the surface morphology of the films.
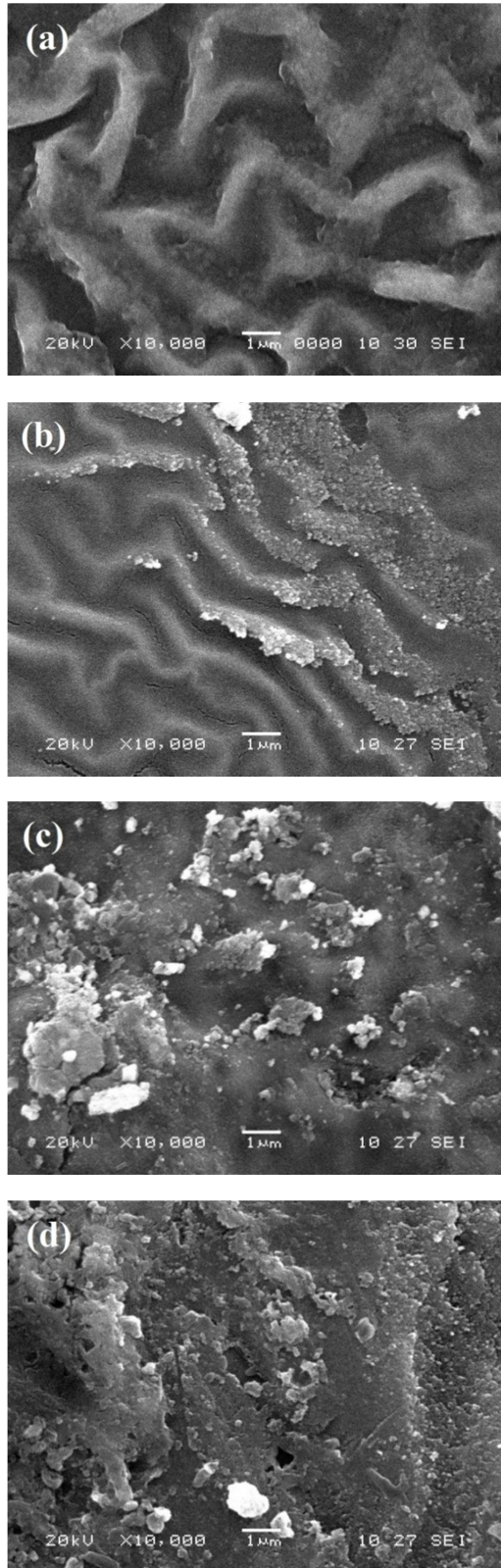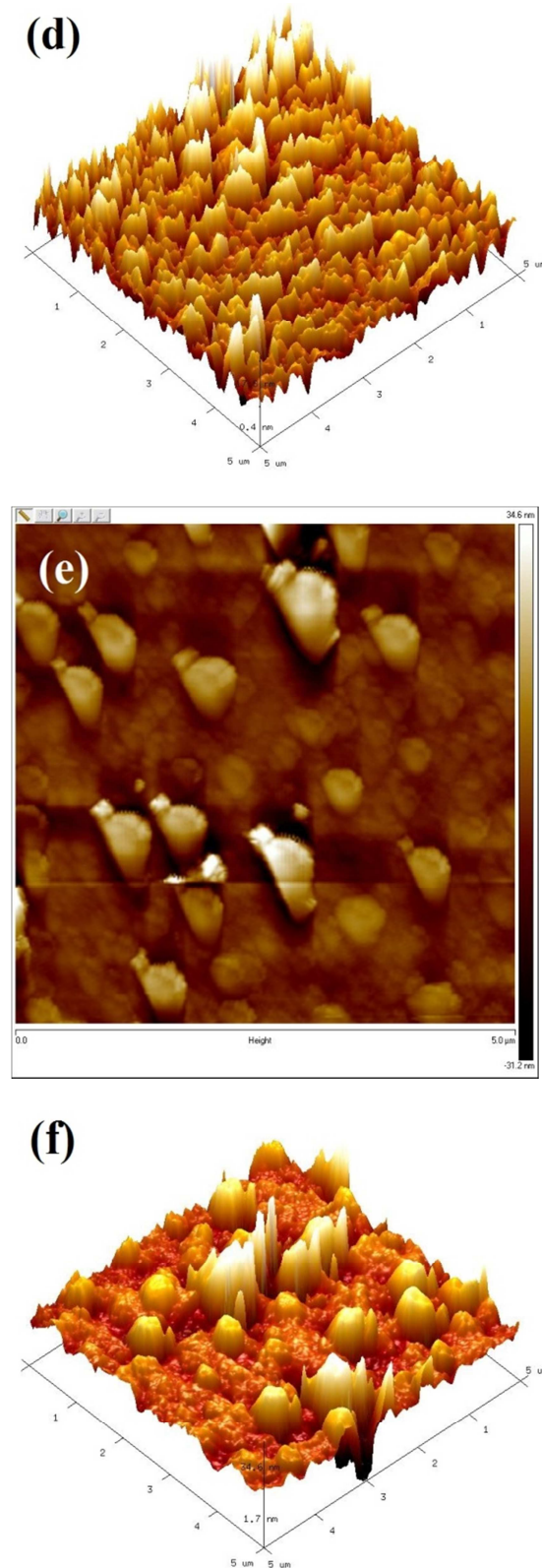

Fig. 2. SEM images of ZnO thin films with (a) 0% Al, (b) 0.5% Al, (c) 1% Al and 2% Al.

Atomic force microscopy was used to record the topography of the Al-doped ZnO thin films. Fig. 3 shows the surface topography of pure and doped ZnO films observed by AFM in two dimensional and three dimensional views. The surface roughness of the film over a $5\mu m \times 5\mu m$ area was measured. Two dimensional view shows that the ZnO film surface is covered uniformly by fine grains. The three dimensional view shows that the growth of film takes place with closely placed sharp peaks and valleys. The values of maximum surface roughness are listed in Table 1. The maximum surface roughness of the film increases with Al-doping concentration.

(d)

Fig. 4. Optical absorption spectra of ZnO: Al thin films.

A sharp ultraviolet absorption edge at approximately 390nm is observed for pure ZnO and absorption edge shifts to 440nm as Al-doping concentration increases. The spectra was studied to evaluate the absorption coefficient (α) energy gap (E_g) and nature of transition involved. In general, the absorption coefficient (α), energy gap (E_g), and photon energy ($h\nu$) are related as [18, 19]:

$$\alpha h\nu = A\,(h\nu - E_g)^{n/2} \qquad (2)$$

Assuming the mode of transition to be of the direct allowed type (n = 1), the band gap energies have been calculated from the variation of $(\alpha h\nu)^2$ versus $h\nu$. Fig. 5 shows the variation of $(\alpha h\nu)^2$ versus $h\nu$ which shows straight line behavior on the higher energy side that confirm direct type of transitions involved in these films. The values of band gap energy for all the composition are listed in Table 1.

(e)

(f)

Fig. 5. Variation of $(\alpha h\nu)^2$ vs. $h\nu$ for the determination band gap.
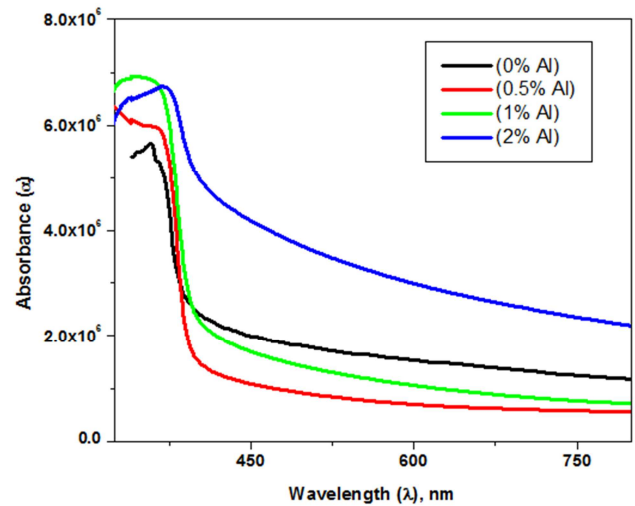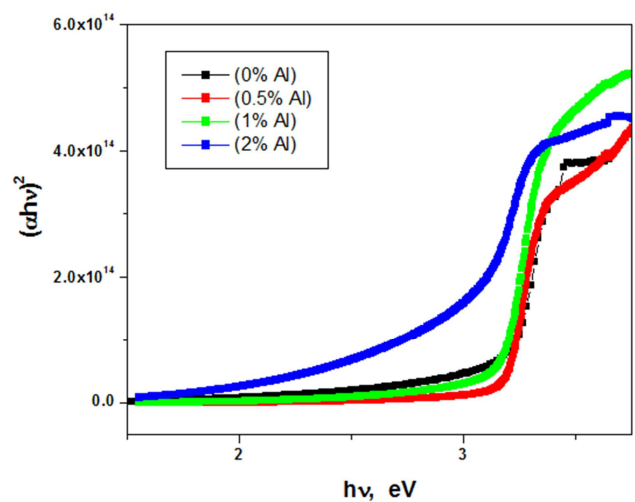
Fig. 3. AFM images of ZnO thin films: (a & b) 0.5% Al, (c & d) 1% Al and (e & f) 2% Al.

The optical absorption spectra of Al-doped ZnO thin films recorded over the wavelength range 300-900 nm at room temperature is shown in Fig. 4.

The band gap (E_g) of the pure ZnO thin film is 3.25eV. The observed band gap energy is in good agreement with the

reported values. However, it is observed that the band gap of ZnO thin films decreases with increase in Al-doping concentration. In general, band gap of Al-doped ZnO thin films increases with doping concentration. Many reports are available on blue shift of the absorption edge and increase in the band gap wherein they have attributed this to the Burstein-Moss shift [20, 21]. The observed decrease in the band gap in the present case can be attributed to creation of new donor levels below the conduction band. Similar results are also observed by Rahman et al for Al-doped ZnO thin films and Ubale et al for Mn doped ZnO thin films and [15, 17].

Table 1. Structural and optical analysis of ZnO: Al thin films.

Al-doping Concentration (Wt%)	Lattice Parameters		Grain Size (nm)	Surface Roughness (nm)	Band Gap (eV)
	a (Å)	c (Å)			
0	3.2568	5.2108	58.8	---	3.25
0.5	3.2503	5.2079	60.9	35	3.16
1	3.2483	5.2020	56.8	65.9	3.12
2	3.2413	5.1947	58.8	96.5	2.98

4. Conclusions

A sol-gel spin coating method has been successfully used to synthesize Al-doped ZnO thin films. The XRD studies show synthesis of phase pure ZnO thin films with hexagonal wurtzite structure. The lattice parameters are a=3.2568Å and c=5.2108Å. Al-doping enhances the preferential growth along (002) direction. The lattice parameters decrease with increase in Al-doping concentration. SEM studies show that with Al-doping the growth of the films takes place with porous structure embedded with nanogranules overgrown on the folded structure.

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Acknowledgement

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