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Structural, optical and photocurrent properties of undoped and Al-doped ZnO thin films deposited by sol–gel spin coating technique

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ABSTRACT

Undoped and Al-doped ZnO thin films have been deposited onto glass substrates by the sol–gel spin coating method and their structural and optical properties have been investigated. The XRD results showed that all films were crystallized under hexagonal wurtzite structure and presented a preferential orientation along the *c*-axis where the maximum crystallite size was found to be 25 nm for undoped film. The average transmittance of all films is over 95% in the visible region and the band gap energy increases from 3.25 to 3.29 eV with the increase of Al concentration. In addition to the vibrational modes from undoped ZnO, longitudinal optical (LO) mode in the Raman spectra was enhanced by the Al doping. Photoluminescence of the films showed an ultraviolet (UV) and defect related visible emissions like violet, blue and green. 3% Al doped ZnO film shows the best photocurrent properties.

1. Introduction

ZnO is a II-VI semiconductor with a wide and direct bad gap, large exciton binding energy, high transmittance in the visible region, high chemical and thermal stability, and non-toxic nature. Because of their excellent electrical and optical properties, ZnO has attracted great attention in recent years due to its potential applications in optoelectronic and transparent electronic devices [1,2]. ZnO can be doped with a wide variety of ions to meet the demands of several application fields. Among the various dopants, Al has been found to be an efficient n-type dopant for realizing high quality samples with enhanced band gap, higher conductivity, ultraviolet/blue light emission and good optical transmittance [3]. ZnO:Al thin film is also an attractive candidate for ultraviolet (UV) photoconductive sensor applications [4]. Several techniques have been used for fabrications of ZnO thin films such as radio frequency magnetron sputtering, spray pyrolysis, electrochemical deposition and sol–gel processing. Among these techniques, sol–gel [5] attracted increased interests for obtaining thin films because of its great advantages: simplicity, low cost, large area substrate coating and easy to realize doping incorporation. In this study, undoped and aluminum doped ZnO (ZnO:Al) thin films have been deposited on glass substrates by the sol–gel spin coating process and the effects of Al doping on the structural, optical and photocurrent properties of the films have been investigated.

2. Experimental details

Undoped and Al-doped ZnO thin films have been deposited by the sol–gel spin coating method onto glass substrates. As a starting material and dopant source, zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] and aluminum chloride hexahydrate [$AlCl_3 \cdot 6H_2O$] were used. Isopropanol and monoethanolamine (MEA) were used as a solvent and stabilizer, respectively. The molar ratio of MEA to metal ions was maintained at 1.0 and the concentration of metal ions is 0.6 mol L^{-1}. The Al dopant level was defined by the Al/(Al+Zn) ratio; it varied from 0% to 7 mol%. The solutions were stirred at 65 °C for 2 h to yield a clear and homogeneous solution and then the solutions were aged for 24 h at room temperature. The glass substrates were cleaned in ethanol and acetone for 10 min each by using an ultrasonic cleaner and then cleaned with deionized water and dried. The coating solution was dropped onto a glass substrate, which was rotated at 3000 rpm for 30 s by using a spin coater. After the deposition by spin coating, the film was preheated at 300 °C for 10 min in a furnace to evaporate the solvent and remove organic residuals. After the spin coating and

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preheating procedures have been repeated several times, the films were annealed at 500 °C for 1.5 h under air ambiance.

The crystal structure of thin films was performed by X-ray diffraction using a diffractometer (Bruker D8 Advance) with Cu Kα line (λ=0.154 nm). The surface morphology of the films was observed using scanning electron microscopy (JEOL JSM-5800 LV). The optical transmission spectra were investigated by UV–vis (UV-3101 PC – Shimadzu) in the wavelength region of 300–800 nm. Room temperature photoluminescence measurements were carried out using a spectrofluorometer (Perkin Elmer LS 50B) using an excitation wavelength of 250 nm. Raman spectra of the films were investigated using a wavelength of 514 nm laser excitation. The photocurrent was measured at 1 V by illuminating the film with light of wavelength 366 nm from a ultraviolet (UV) lamp.

3. Results and discussion

3.1. Structural and morphological properties of the undoped and Al doped ZnO thin films

Fig. 1 shows the XRD patterns of the undoped and Al-doped ZnO thin films. The results indicate that all samples are polycrystalline hexagonal wurtzite structure (JCPDS 36-1451), and no other crystalline phase was found. The intensity of the diffraction peaks decreased with increasing Al content, indicating that the film crystallinity is deteriorated. This is due to the formation of stress caused by the introduction of the dopant and the segregation of dopant in grain boundaries at high doping concentration [5,6]. The preferential orientation was determined using a texture coefficient TC(*hkl*) [4]. A sample with randomly oriented crystallite presents TC(*hkl*)=1, while values higher than 1 indicate the abundance of crystallites in a given (*hkl*) direction. After the calculation of texture coefficients, it is seen that the highest TC values are in the (002) plane for all the films, which indicates that the films grew preferentially in the *c*-axis orientation. The crystallite size of the films was estimated by the Scherrer formula [6]: $D=K\lambda/\beta\cos\theta$, where D is the crystallite size, K is a constant of 0.9, λ is the X-ray wavelength, β is the full width at half maximum, and θ is the diffraction angle. The (002) peaks were used to estimate the crystallite size. Increasing the Al-doping amount induced to decrease the average grain size from 25 nm (ZnO pure) to 17 nm (ZnO doped with 7% Al), because of the substitution of smaller Al atoms at Zn site in the lattice of ZnO [5,7].

3.2. Optical properties

The optical transmittance spectra of thin films in the wavelength range 300–800 nm at room temperature are shown in Fig. 2. All films have an average transmittance over 95% in the visible region. Further, a blue shift of the absorption edges can be observed in the doped thin films. For evaluating the band gap (E_g), we employed an $(\alpha h\nu)=C(h\nu-E_g)^{1/2}$ [6] relationship, where α is the absorption coefficient, C is a constant and $h\nu$ is the photo energy. The absorption coefficient α of the films was calculated from the transmittance using the equation $\alpha=(-1/d)\ln T$, where T is the transmittance and d is the film thickness. The band gap was determined by extrapolating the linear region of $(\alpha h\nu)^2$ versus the photo energy. As shown in the inset in Fig. 2, the optical band gap energy increases from 3.25 to 3.29 eV with increasing Al concentration; the increase in the band gap can be explained by the

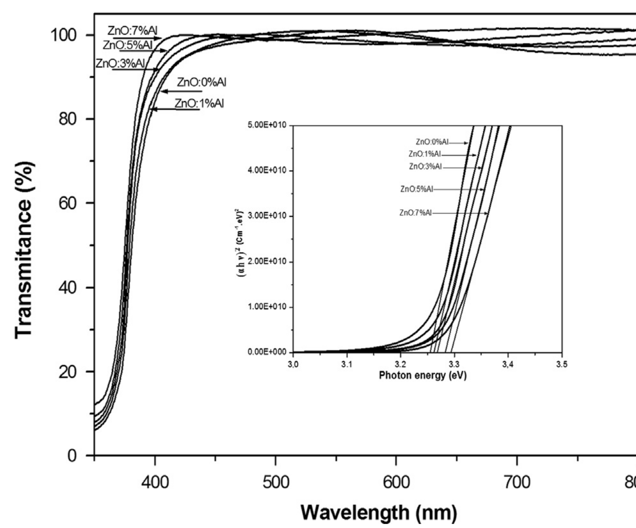

Fig. 2. Transmittance spectra of undoped and Al-doped ZnO thin films and their band-gaps.

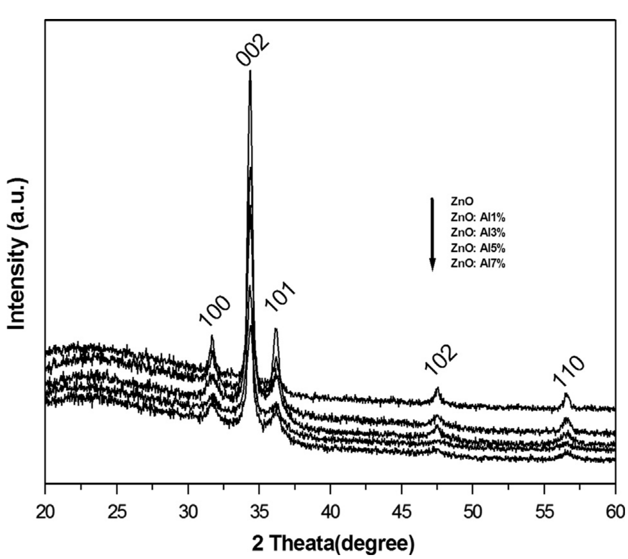

Fig. 1. XRD patterns of undoped and Al-doped ZnO thin films.

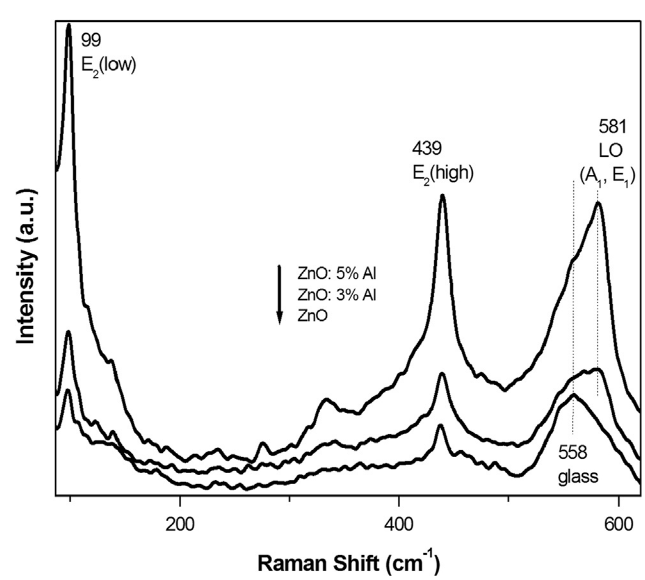

Fig. 3. Raman spectra of undoped and Al-doped ZnO thin films.