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Preparation and Characterization of Ag-doped ZnO thin film deposited by sol-gel-based coating method

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Abstract

This work reports on the preparation of Ag-doped ZnO thin films deposited on glass substrate by sol-gel spin coating technique. Sol-gel spin coating is considered as a low cost and low-temperature processing for thin film fabrication technique that can be readily incorporated with variety of dopants. The ZnO thin films were fabricated using zinc acetate as a precursor via spin coating technique followed by annealing at 500°C for 2 h. The cathodic Ag dopant concentration was varied from 0 to 10 mol%. The influence of dopant concentration on structural, optical, and morphological were investigated by X-ray diffraction (XRD), ultraviolet-visible (UV-Vis) spectrophotometer, and field emission scanning electron microscope (FESEM). The XRD results revealed hexagonal wurtzite structure of the prepared films with no impurity phase. The transmittance spectra show high transmittance above 90% in visible region. The ZnO thin film exhibited significant red shift in its band gap when the incorporated Ag doping concentration increased.

Keywords: Thin film, Ag-doped ZnO, sol-gel method

1. Introduction

Zinc oxide (ZnO) is one of the most well-known semiconductor materials that can be used in many applications regarding its wide direct band gap (3.37 eV) and large exciton binding energy (60 meV) [1] for example transparent conductive coating [2], solar cells [3], light emitting diode [4], UV detector [5] and gas sensor [6]. Normally, ZnO is an intrinsic n-type semiconductor because of native defect such as oxygen vacancy and zinc interstitials. While the electronic devices need to use junction between p-type and n-type semiconductor. Making p-type ZnO is one of effective ways to enhance performance of the device that can improve carrier transport by interface modification at p-n junction. p-type ZnO can be achieved by doping with either group IA and IB elements such as Li, Na, Ag [7-9] for substituting into the Zn-site, and group-VA such as P and Sb [10, 11] on the O-site. However, Ag known as a group IB element could be considered to be one of good candidate acceptors to adjust electrical semiconducting property of ZnO from n-type to p-type. There are many processes to fabricate p-type ZnO including pulsed laser deposition (PLD) and hydrothermal process [12, 13]. Sol-gel spin coating technique is one of widely used processes to fabricate thin films because of significant advantages comparing with the other techniques such as low-cost system, low-cost precursor and simple deposition equipment.

In this work, we report the fabrication and characterization of Ag-doped ZnO thin films prepared by sol-gel spin coating technique on glass substrate with various doping concentrations. The effect of doping concentration on physical and optical properties of ZnO thin films were investigated.

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2. Experimental details

Ag-doped ZnO films were prepared by sol-gel spin coating technique onto glass substrate. First, the sol-gel was prepared starting from zinc acetate dihydrate as zinc precursor dissolved in absolute ethanol and 1 ml of diethanolamine. The mixture was stirred with magnetic stirrer until the sol-gel was clear followed by the addition silver acetate selected as the precursor of Ag. The doping concentration was varied from 0 to 10 mol%. After that, the mixture was stirred, heated at 75°C for 2 h and aged for 24 h. The glass substrates were cleaned by sonication in DI water, acetone, methanol and isopropanol for 10 min, respectively. The bare ZnO and doped ZnO thin films were spun at 2000 rpm for 30 s. Between spinning process the ZnO thin films were baked at 100°C then the coating was repeated 8 times. After the spinning process the deposited films were annealed at 500°C for 2 h in air.

The optical properties of the prepared films were investigated by Thermo Scientific Orion AquaMate 8000. The structural properties of all thin films were investigated by SmartLab X-ray diffractometer (XRD) while the surface morphology and thickness of the films were monitored by Hitachi S4700 field emission scanning electron microscope (FESEM).

3. Results and discussion

Figure 1 shows X-ray diffraction patterns of doped ZnO thin films with various doping concentrations. The diffraction patterns are nicely matched with hexagonal wurtzite zinc oxide phase (ICSD no. 157724) without any impurity phases. The XRD patterns of Ag-doped ZnO thin films exhibit slight decrease in peak intensity of three major peaks with increasing Ag doping content. Owing to relatively larger ionic radius of Ag^{+} (r=1.15 Å), Ag^{+} may partially substitute at Zn^{2+} (r=0.72 Å) site, inducing not only the expansion in unit cell but the stress in the prepared films, leading to the decrease in crystallinity.

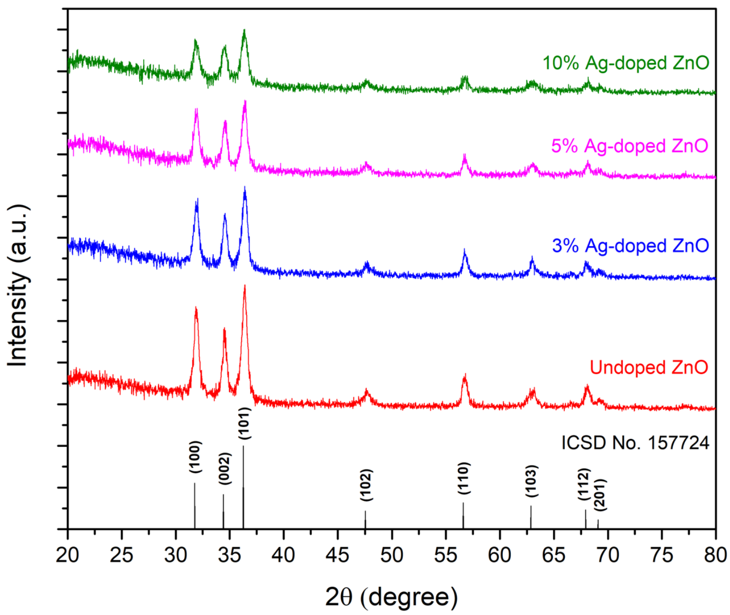

Fig. 1. XRD pattern of Ag-doped ZnO thin films with various doping concentrations.

Table 1. Average crystalline size of undoped and Ag-doped ZnO thin films.

Samples	**Average crystalline size (nm)**
Undoped ZnO	15.68
3% Ag-doped ZnO	15.35
5% Ag-doped ZnO	14.99
10% Ag-doped ZnO	13.38

The crystalline size of samples were calculated by Scherrer's equation using 3 main peaks of ZnO at 31, 34 and 36 degree correspond with (100), (002) and (101), respectively. The Scherrer's equation is expressed in equation (2).

$$D = \frac{K\lambda}{\beta cos\theta} \tag{2}$$

Where, D is crystallite size, K is Scherrer's constant, λ is X-ray wavelength and β is full width at half maximum (FWHM). The average crystallite size of ZnO of the undoped and Ag-doped ZnO films is shown in Table 1. The calculation exhibits slight decrease of crystalline size corresponding with the decreasing its peak intensity.

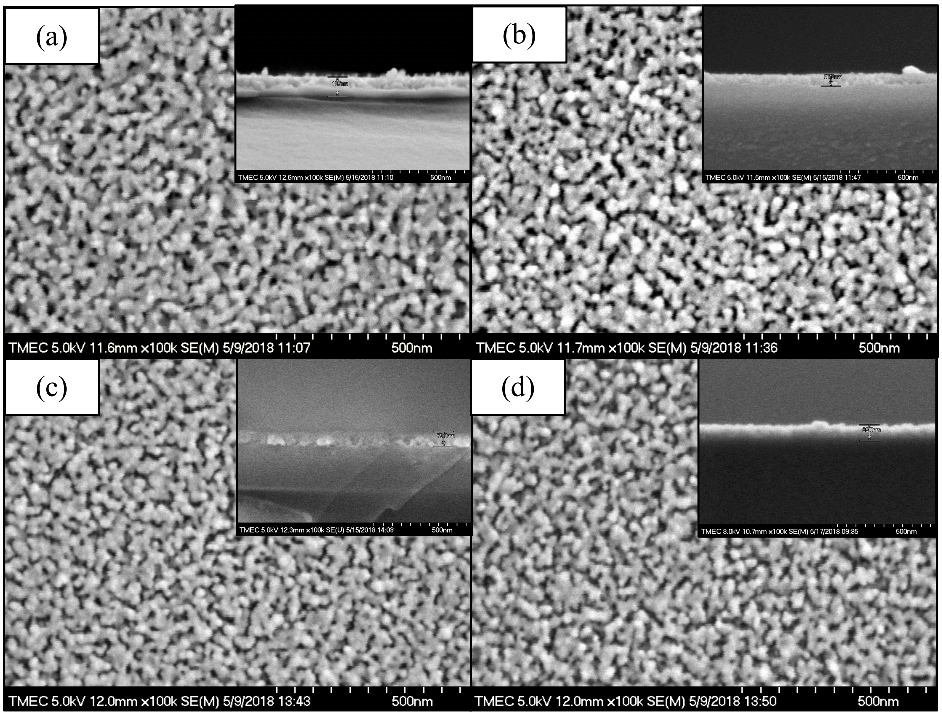

Fig. 2. Surface morphologies and cross section images of (a) Undoped ZnO, (b) 3% Ag-doped ZnO, (c) 5% Ag-doped ZnO, (d) 10% Ag- doped ZnO.

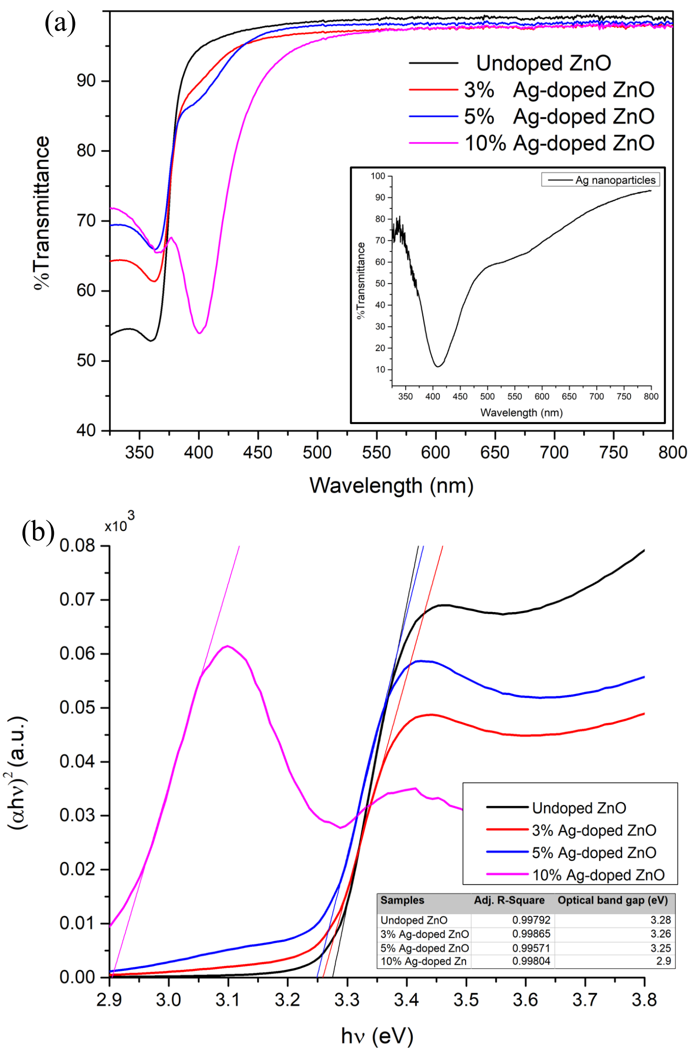

Fig. 3. Undoped and Ag-doped ZnO thin films with various doping concentration (a) Transmittance spectra, (b) Tauc plot.

The morphologies of undoped and Ag-doped ZnO thin films with various doping concentrations are illustrated in Fig. 2(a)-2(d). These results exhibit the composition of ZnO nanoparticles with average size diameter 20 nm on the undoped films. For the Ag-doped ZnO, the average size diameter is almost in the same value of the undoped ZnO. The inset of Fig. 2 exhibits cross section of undoped and Ag-doped ZnO. The results reveal quite uniform film with average thickness of 70-100 nm. base on sol-gel process the morphologies of the sample are porous film due to the decomposition of acetate group during annealing process.

The Figure 3 (a) illustrates the transmittance spectra of undoped and Ag-doped ZnO thin films indicating high transparency (>90%) in visible region of the prepared films. For Ag-doped ZnO thin films, the corresponding spectra illustrate the observable absorption band in the wavelength region of 375-425 nm with absorption peak at ~400 nm. This additional feature could be originated from surface plasmon resonance phenomena of the incorporated Ag nanoparticle [14]. In order to confirm this phenomenon, the transmission spectrum of bare silver nanoparticles (<100 nm) dispersed in ethylene glycol is shown in the inset of Fig. 3(a), showing prominent absorption band positioned at 410 nm. As doping concentration was increased to 10% the absorption edge exhibited the significant red-shift to 425 nm reflecting the reduction of optical band gap due to the shift of Fermi level to the conduction band of ZnO matrix induced by Ag dopant acting as a donor atom [15]. The optical band gaps of all samples can be interpreted from transmittance spectra using Tauc's equation expressed in equation (2).

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2} \qquad (2)$$

Where, α is absorption coefficient, $h\nu$ is photon energy, A is constant and Eg is optical band gap. As seen in Fig. 3(b), the corresponding band gap of undoped ZnO thin film is approximately 3.28 eV. As compared to undoped ZnO, Ag-doped ZnO exhibits slightly decreasing band gap of 30 meV. These values of the optical band gap are comparable to previous work reported by Karyaoui *et al.* [16] who prepared Ag-doped ZnO by spray chemical route. At 10% Ag-doping content, the optical band gap of the sample is approximately 2.9 eV. This phenomenon due to the silver nanoparticle in the film corresponding with the transmittance.

4. Conclusion

In conclusion, this work reports the Ag-doped ZnO thin films synthesized by sol-gel spin coating technique with various doping concentration. The XRD result shows that all prepared films possess ZnO hexagonal wurtzite structure with no impurity phase. The transmittance spectra show that all samples have high transmittance above 90% in visible region. For 10% Ag-doped ZnO, the result shows the red shift of absorption edge of the transmittance spectra. Ag-doped films shows lower optical band gap than undoped ZnO.

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