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RESEARCH PAPER

Al Doped ZnO Thin Films; Preparation and Characterization

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ABSTRACT

ZnO is a promising material suitable for variety of novel electronic applications including sensors, transistors, and solar cells. Intrinsic ZnO film has inferiority in terms of electronic properties, which has prompted researches and investigations on doped ZnO films in order to improve its electronic properties. In this work, aluminum (Al) doped ZnO (AZO) with various concentrations and undoped ZnO films were coated on glass substrates by a sol–gel spin coating technique. The samples were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), Uv-Vis spectrometer and four point probe technique to investigate the structural, surface morphology, optical transmittance, and electronic properties of the thin films. The optical transmittances of these samples in the visible region are in the range of 85-95% and the SEM images showed the size of nanoparticles were decrease with doping. Also 2% Al doped ZnO thin films had a lowest resistivity of all the samples that prepared in this study.

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INTRODUCTION

Transparent conducting oxide (TCO) films have been widely used in the photovoltaic devices such as transparent electrode, organic solar cells(OSCs), flat panel display and organic light-emitting diodes (OLEDs)[1-3]. Among different TCO materials, indium tin oxide (ITO) is the most popular due to its prominent characteristics of the high optical transmittance, wide optical band gap, and high electrical conductivity[4]. However, some problems such as rarity, increasing price of the principal ingredient and instability in hydrogen plasma are the motivation for extending an alternative for ITO[5-7]. Hence, Zinc oxide (ZnO) thin films are one of the ideal troth as supersedence for ITO is owning to their high chemical permanence, wide direct band gap, its relatively low deposition temperature, low cost and non-toxicity[8-10]. pure ZnO films have poor properties, usually presents a low conductivity due to allow carrier concentration and doping with diverse dopants are usually necessary to improve these properties. Elements such as Boron(B), Indium(In), Silicon(Si), Aluminum(Al) and Gallium(Ga) have been applied in this regard[11-13]. Al doped ZnO (AZO) films have been researched in this study. The AZO thin films can be prepared by a variety of methods such as Chemical vapor deposition(CVD) [14], Magnetron sputtering[15], pulsed laser deposition(PLD)[16], spray pyrolysis[17], molecular beam epitaxy (MBE)[18] and sol–gel technique[19]. Among these techniques, sol-gel method absorbs much attention because sol-gel is a solution-based process with desirable features such as simple deposition appliance, low cost, easy regulate composition and dopants, and fabricating large area films at room temperature. In this article, Al-doped ZnO thin films from the sol with concentration of 0.1 M with different doping concentration are prepared by sol–gel method. The structure, electrical and optical properties are investigated.

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MATERIALS AND METHODS

The ZnO thin film was prepared using a sol-gel process. Zinc acetate dehydrate was first dissolved in 2propanol (iso propanol) and stirred at 70°C for 1 hour. Monoethanolamine (MEA) was then added to the solution as stabilizer (total concentration of the solution was 0.1 M). The mixed solution was stirred until becoming clear and homogeneous.

Before the coating process, the glass substrates were cleaned using distilled water and acetone in ultrasonic, and dried with argon nozzle. After the ageing process, the solution was dripped onto a glass substrate and spin-coated at 2500 RPM. Finally the samples were transferred to oven and annealed at 200 °C for 1h.

Al nitrate was dissolved in ethanol and were added into separate ZnO solutions drop by drop as doping material to obtain AZO. The total concentration of the solution was 0.1 M and aluminum concentrations were 0%, 0.5%, 1%, 2% and 4vt. %. The AZO thin films were prepared on glass substrates by spin coating at 2500 RPM. After spin coating, the film was annealed at 200°C for 1 h.

The surface morphologies of thin films were observed by a scanning electron microscope (SEM). The resistivity of the samples was measured by four-point probe. Optical transmission spectra were recorded by a UV-visible spectrometer in the wavelength range from 300 to 800 nm. The structural properties of the pure ZnO and AZO thin films were determined by the X-ray diffraction (XRD) system.

RESULTS AND DISCUSSION

Fig. 1 shows X-ray diffraction patterns of pure ZnO and AZO thin films. The diffraction peak of AZO at 2θ (°) 31.66°, 34.32°, 36.14°, 47.42°, 56.46°, 62.80° and 67.94° are indexed as (100), (002), (101), (102), (110), (103)and (112) planes. The lattice constants have been found to be a = 3.2539 A˚ and c = 5.2098 A˚ and are in accord with the standard data of JCPDS (card no. 36-1451). Compared with the diffraction peak of ZnO observed that the diffraction peaks of the Al-doped ZnO (AZO) show a small shift towards higher 2θ values. It was found that the sample has hexagonal structure. The grain size of ZnO and Al-doped ZnO films have been calculated using Scherer's equation:

$$D = \frac{k\gamma}{\beta cos\theta}$$

D is the grain size, k is a constant taken to be 0.94,γ is the wavelength of the X-ray radiation (XRD), β is the full width at half maximum (FWHM) and θ is the angle of diffraction. The grain size has been calculated about 14 nm for AZO, that is smaller than grain size for pure ZnO (about 24 nm). This can be attributed to the fact that dopant increments the nucleus number when it incorporates into the ZnO film[20].

The UV/vis transmittance spectra of sol-gel derived AZO thin films on glass substrates with different concentrations of Al and pure ZnO is showed in Fig.2. The average transmittance in the wavelength range of 300 to 800 nm was over 85% for ZnO thin film and over 90% for AZO thin films. According to the Fig.2 we can see that 2% AZO has highest transmittance. High transmittance might be due to the ameliorated surface morphology

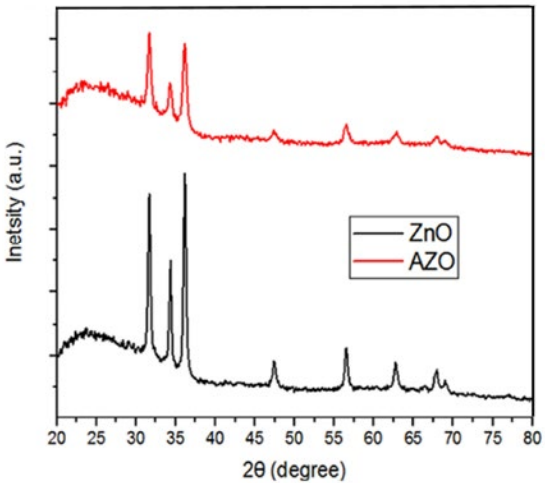

Fig. 1. XRD pattern of pure ZnO and AZO.

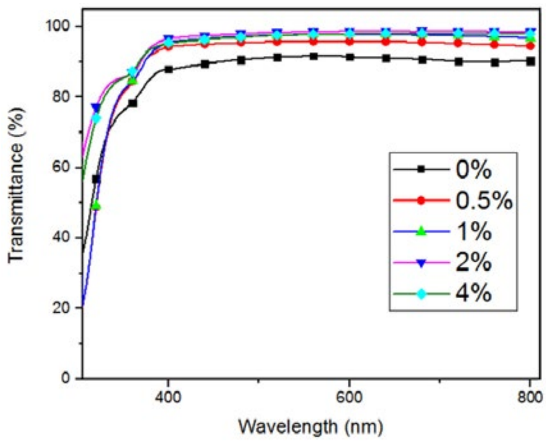

Fig. 2. UV/vis transmittance of 0 – 4 % Al doped ZnO thin films.

[21] and crystallinity of thin film[22]. Summarizing the above results, all the samples which were prepared here showed high transmittance in the visible wavelength, which made them proper for using in photovoltaic devices.

The energy band gap of ZnO thin films is calculated by using the Tauc formula:

$$(\alpha h\nu) = A\,(h\nu - E_g)^n$$

Where A is a constant, E_g is the band gap of the samples, $h\nu$ is the photon energy (h is Planck's constant), α is the absorption coefficient and exponent n depends on the type of transmissions. For direct allowed $n = 1/2$, indirect allowed transition $n = 2$ and for direct forbidden $n = 3/2$[23]. Here, the transmissions are direct so we take $n = 1/2$. The absorption coefficient was evaluated using the Beer-Lambert law:

$$\alpha = \left(\frac{1}{d}\right) \ln \left(\frac{1}{T}\right)$$

d and T are film thickness and transmittance respectively. Tauc's plot is sketched in Fig. 3. E_g for 0%, 0.5%, 1%, 2% and 4vt. % AZO thin films listed in Table 1. It can be clearly seen that 0.5% and 1% Al doped ZnO thin films showed a lower band gap than that of pure ZnO thin film and 2% and 4% AZO thin films showed a higher band gap than that of pure ZnO thin film. One possible reason for reduction in band gap is increasing in tensile strength that influences inter-atomic distance [24].

Fig. 4 and Fig. 5 shows SEM micrograph of ZnO thin film and 2% AZO thin film respectively that prepared by sol-gel spin coating method. It can be seen the both samples composed of particles which were nearly 20-50 nm for pure ZnO thin film and 20-40 nm for 2% AZO thin film. It is evident that when dopant was added in ZnO solution the size of nanoparticles are decreased.

Electrical conductivity of each sample was determined by four-point probe. The measured conductivity of ZnO and 2% AZO thin films is 9×10^{-5} (S/cm) and 3×10^{-4}(S/cm) respectively. By adding impurities the resistance reduced. 2% Al doped ZnO thin films had a lowest resistivity of all the samples that prepared in this study. As reported in the literature, resistivity depends on carrier density and mobility [25]. With the interpolation

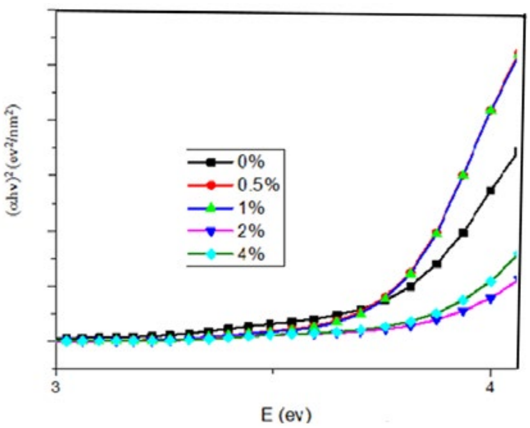

Fig. 3. Optical band gap of 0-4 % Al doped ZnO thin films.

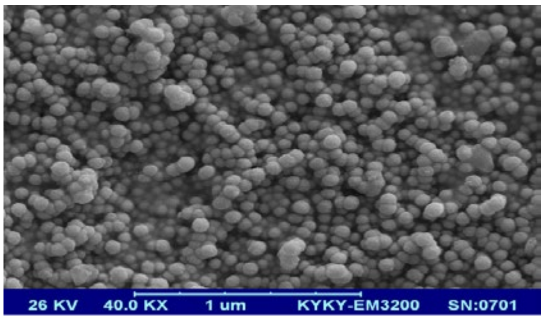

Fig. 4. SEM image of pure ZnO thin film.

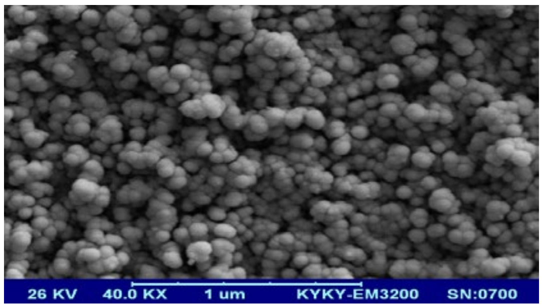

Fig. 5. SEM image of 2% Al doped ZnO thin film.

Table 1. Average transmittance and optical band gap of 0 – 4 % Al doped ZnO thin films.

Sample	Dopant concentration	Average transmittance	Band gap
1	0 %	86.46 %	3.47 eV
2	0.5 %	91.05 %	3.43 eV
3	1 %	92.71 %	3.44 eV
4	2 %	95.83 %	3.69 eV
5	4 %	94.89 %	3.64 eV

of Al content in Zn^{3+} with aluminum atom ionized in the form of Al^{3+} ion, free electron density increased that helping to better conductivity of Al doped ZnO thin films.

CONCLUSIONS

Surface morphology, electrical and optical properties of sol-gel derived AZO thin films in various doping concentration was investigated. All thin films were found to be good transparent in the 300 - 800 nm range of spectra that which made them suitable for use in electronic devices. AZO thin film showed higher transmittance in the range of 300 - 800 nm. The band gap of the sample was in the range of 3.43 - 3.69 eV. The X-ray diffraction peak showed that the AZO thin films have hexagonal structure. The grain size of ZnO and Al-doped ZnO films have been calculated using Scherer's equation and it's about 24nm for ZnO and about 14 nm for AZO thin films. Electrical conductivity of ZnO and AZO thin films that measured by four-point probe shows when dopant were added to ZnO the resistivity decreased. 2% Al doped ZnO thin films had a lowest resistivity of all the samples.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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