

Structural, optical and electrical properties of ZnO:Al thin films for optoelectronic applications

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Abstract Undoped and aluminum-doped ZnO thin films are prepared by the sol–gel spin-coating process. Zinc acetate dihydrate, ethanol and mono-ethanolamine are used as precursor, solvent and stabilizer, respectively. The atomic percentage of dopant in solution were [Al/Zn]=1 %, 2 % and 3 %. The effect of Al doping on the optical and electrical properties of ZnO films was investigated by X-ray diffraction (XRD), Four-Point probe technique and UV–visible spectrophotometry. The results from the X-ray diffraction show that the pure ZnO thin films had a polycrystalline structure of the hexagonal Wurtzite Type. A minimum resistivity of $3.3 \times 10^{-3} \Omega \cdot \text{cm}$ was obtained for the film doped with 2 mol % Al. Optical transmissions reveal a good transmittance within the visible wavelength spectrum region for all of the films. The value of the band gap is enhanced from 3.21 eV (undoped ZnO) to 3.273 eV (Al/Zn=3 %), the increase in the band gap can be explained by the Burstein–Moss effect.

Keywords ZnO:Al · Sol–gel · XRD · Transmittance · Optical band gap · Electrical resistivity

1 Introduction

In recent years, ZnO thin films has reached an important place in new technologies, and shows a wide range of scientific and technological applications (El Hichou et al. 2002; Bahedi et al. 2007; Dabos-Seignon et al. 2007). ZnO thin film is used in the fabrication of solar cells (Lin

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et al. 2007), gas sensors (Lim et al. 2006) and catalysers (Miki-Yoshida et al. 2002). In the form of thin film, ZnO is a very promising alternative in flat display screens (Ghosh and Basu 1991) compared to tin-doped indium oxides (ITOs) which is a limited natural resource. When it is doped, ZnO film presents promising second-order nonlinear optical properties, which achieve the giant nonlinear optical effects about 50 pm/V (Ebothe et al. 2007). Many methods have been employed to prepare ZnO thin films like spray pyrolysis (Benny et al. 1999), molecular beam epitaxy (Feng et al. 2006), chemical vapor deposition (Funakubo et al. 1999), RF magnetron sputtering (Lai and Lee 2008) and sol–gel (Hwangbo et al. 2008). The latest method has the advantage to give a high surface morphology at lower crystallizing temperature. Doping is a very useful way for turning ZnO to an electronic material. Many dopants such as group I, V and rare earth elements have been used. Among those materials doping with Al elements can result in interesting structural, optical and electrical properties.

In this work, sol–gel technique was used to enhance the optoelectronic properties of ZnO thin films. $(\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})$ dopant have been used. The coating solutions were prepared using zinc acetate dihydrate as precursor, 2-methoxyethanol and mono-ethanolamine (MEA) as solvent and stabilizer, respectively. ZnO thin films were deposited on glass substrates by spin coating technique. Structural and optical properties of ZnO thin films were investigated. The effect of nature and doping concentration on optical and electrical properties were too studied.

2 Experimental details

Undoped and Al doped ZnO (AZO) thin films have been deposited by sol–gel associated with spin coating method onto glass substrates. Zinc acetate dihydrate, 2-methoxyethanol, and monoethanolamine (MEA) were used as starting precursor, solvent, and sol stabilizer, respectively. The molar ratio of dopant (aluminum nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in the first solution was varied to give a $[\text{Al}/\text{Zn}]$ ratio between 0 and 3 %. The molar ratio of $[\text{MEA}/\text{Zn}]$ to zinc acetate dihydrate was maintained at 1 and the concentration of zinc acetate was 0.75 M solutions were stirred at 60 °C for 2 h to yield a clear and homogeneous solution, which served as the coating solution after cooling to room temperature. The coating solution was dropped into a glass substrate, which was rotated at 3,000 rpm for 30 s. After depositing by spin coating, the film was dried at 200 °C for 10 min in a furnace to evaporate the solvent and remove organic residuals. The procedures from coating to drying were repeated five times. The films were then inserted into a tube furnace and annealed in air at 550 °C for 2 h.

For characterization we have used a high-resolution X-ray diffraction for XRD patterns in the θ – 2θ configuration with a copper anticathode ($\text{CuK}\alpha$, 1.54 Å). Sheet resistance was measured by the four point probe technique and the optical properties were monitored by transmittance using a Xe lamp in association with a 500 mm Yvon-Jobin HR460 spectrophotometer using a GaAs Photomultiplier tube detector optimized for the UV–VIS range (Table 1).

3 Results and discussion

3.1 X-ray diffraction

The crystal structure and orientation of ZnO thin film have been investigated by X-ray diffraction (XRD) method. The XRD pattern of the film is shown in Fig. 1. The XRD result suggests that the ZnO thin film has the polycrystalline structure. The film was crystallized

Table 1 Crystallite size calculated from XRD

2θ (deg)	Miller indice (hkl)	Crystallite size (nm)
34.44	002	78,94

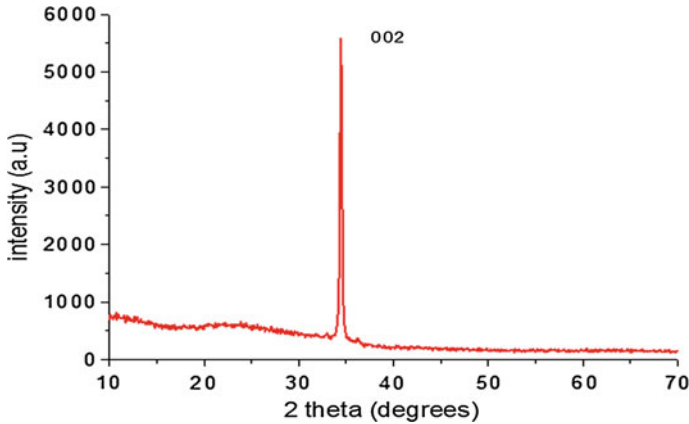


Fig. 1 X-ray diffraction pattern of the ZnO thin film

with the hexagonal wurtzite structure (Sun et al. 2005) and a strong preferred orientation (5,574 au) along the direction (002) which is located at 2θ = 34.44 along the c axis with lattice parameters a = 0.3258 nm and c = 0.5225 nm, very close to the theoretical values a = 0.3256 nm and c = 0.5237 nm (Minami et al. 1999).

The lattice constants -a- and -c- of the Wurtzite structure of ZnO can be calculated using the relations.

$$c = \frac{\lambda}{\sin \theta} \quad a = \sqrt{\frac{1}{3}} \frac{\lambda}{\sin \theta} \quad D_{hkl} = 0.94 \frac{\lambda_{hkl}}{\beta_{hkl} \cos(\theta_{hkl})}$$

D_{hkl} is the crystallite diameter, λ the wavelength, θ the Bragg angle, β_{hkl} the full-width at half-maximum (FWHM) of the peak (Shah and Asiri 2009).

3.2 Electrical properties

Besides the optical properties, the electrical properties are also an important aspect of the performance of AZO thin films. The effects of doping aluminum concentration on the electrical resistivity of the ZnO thin films are presented in Fig. 2.

Figure 2 shows the evolution of the electrical resistivity of ZnO:Al films depending on the doping level (Al). It is observed that the resistivity of the samples decreases 90.4 × 10⁻⁴Ω·cm (undoped ZnO) with increasing doping percentage and reached its lowest value 3.3 × 10⁻³Ω·cm for doping Al 2%, then it increases to 3.7 × 10⁻⁴Ω·cm (3% Al). This decrease in resistivity with increasing doping concentration is due to the increased number of charge carriers (electrons) from donors Al³⁺ ions incorporated in the interstitial or substitutional sites of Zn²⁺ cations (Li et al. 2009).

On the other hand, the electrical resistivity increases beyond 2% Al may be due to the appearance of Al₂O₃ phase gives rise to the formation of an alloy instead of a doping (An et al. 2008). This drastic reduction in mobility can be explained by the segregation of dopants at the grain boundaries. It seems that the micro-mechanism of the influence of doping is quite

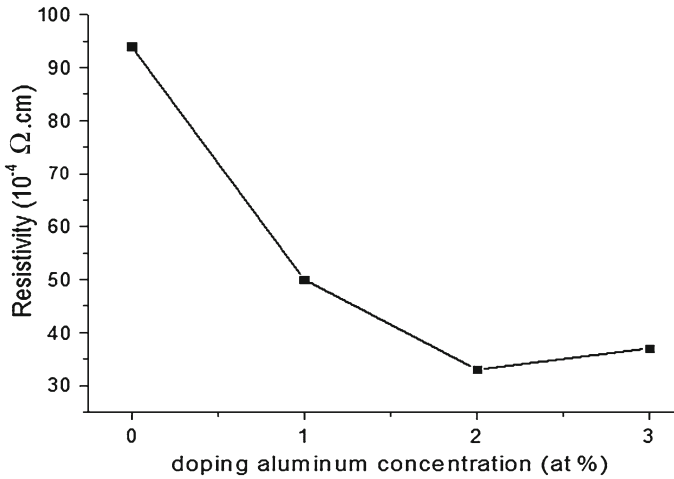


Fig. 2 Sheet resistance of undoped and Al doped ZnO films at various (at %)

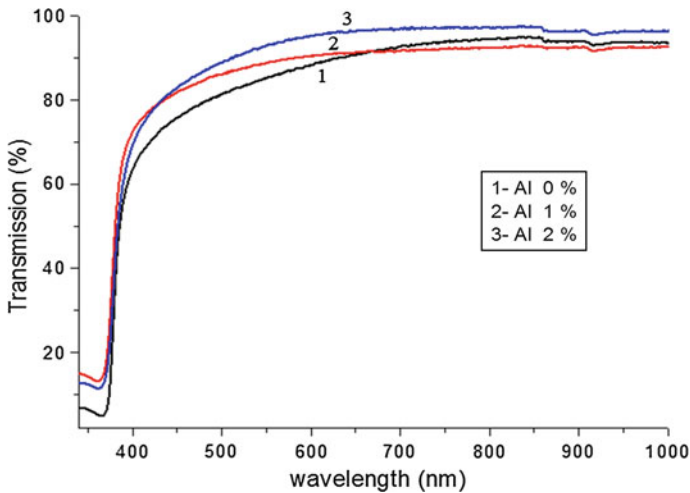


Fig. 3 Transmission and reflection spectra of AZO thin films deposited on glass substrates, for different values of concentration of aluminum dopant

complicated. Thus, we can conclude that beyond a doping concentration of 2% Al, there is a segregation of dopant atoms in non-crystalline regions that produces disturbances in the network. These defects act as diffusion centers giving rise to different diffusion mechanisms resulting in a sharp decrease in mobility and hence an increase in resistivity.

3.3 Optical properties

The transmittance of the deposited films with different Al content was measured at room temperature and the resulting transmittance spectra was shown in Fig. 3. It may be seen that all the films are highly transparent over the visible and near infrared regions from 350 to 800 nm.

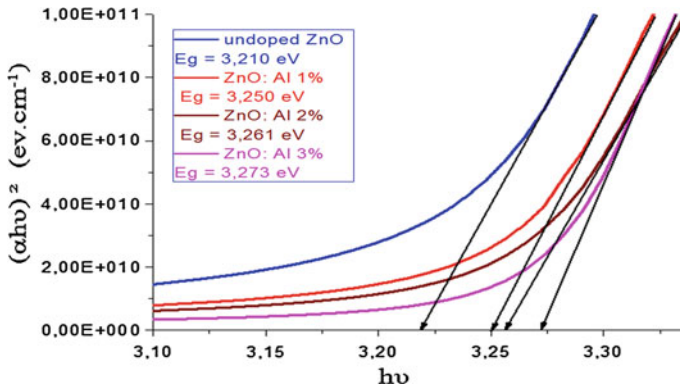


Fig. 4 Plot of $(\alpha h\nu)^2$ and energy of the incident photon for films prepared at different aluminum doping concentration in the starting solution

The effect of Al doping on optical properties of ZnO films has been studied. In the present work, the average transmittance of all the deposited films varies from 80 to 90 % in the wavelength range from 350 to 800 nm. These results clearly show that this material can be used as a transparent oxide in solar cells.

From the transmission curve as a function of the wavelength we can represent the variation of $(\alpha h\nu)^2$ with $(h\nu)$ for calculated the band gap E_g , from the following equation (Daneshtar et al. 2003).

$$(\alpha h\nu)^2 = B(h\nu - E_g) = f(h\nu),$$

where $h\nu$ is the energy of incident photons, E_g the optical gap and B is a constant.

Figure 4 shows the energy gaps for undoped ZnO and doped with a (1, 2, 3 %) aluminum. An obvious increase is observed for the values of the energy gap with the increase in the concentration of aluminum. This increase is explained by the preposition that the ZnO:Al films are semiconductors in which the Fermi level lies in the conductive band which means that the levels at the bottom of the conductivity band are occupied by electrons and the shielding of electronic traveling to these levels is termed the Burstein–Moss effect (Moss 1954).

4 Conclusions

X-ray diffraction studies showed that the films are polycrystalline and the peaks fit well to the hexagonal wurtzite structure with a preferred orientation along the (002) direction which is located at $2\theta = 34.44$ along the c axis.

The effects of different aluminum concentrations on the electrical resistivity and optical transparency of the films were studied.

The electrical resistivity of ZnO:Al films depending on the doping level (Al). It is observed that the resistivity of the samples decreases with increasing doping percentage and reached its lowest value $3.3 \times 10^{-3} \Omega \cdot \text{cm}$ for doping Al 2 %.

The optical properties we can see the transmission increases with the increase in concentration of doping aluminum, the highest transmission is observed at (2 %) doping.

Optical transmissions reveal a good transmittance within the visible wavelength spectrum region for all of the films. The value of the band gap is enhanced from 3.21 eV (undoped ZnO) to 3.273 eV (ZnO:Al 3 %). The increase in the band gap can be explained by the Burstein–Moss effect.

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