

# Effect of aluminum doping on the structural, morphological, electrical and optical properties of ZnO thin films prepared by sol-gel dip coating

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Aluminum doped zinc oxide (AZO) thin films with 0-5 at.% aluminum content have been prepared by sol-gel dip coating technique. The thickness of the films has been measured using alpha step method. The structural and morphological properties have been studied, respectively, using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Higher intensity zinc oxide (ZnO) peak (002) has been observed in 1 at.% aluminum doped film with 450 °C of annealing temperature. The grains are more densely packed in the films doped in 1 at.% aluminum content. The grains have tendency to decrease in size as the aluminum content increases. Electrical resistivity measurement technique reveals that electrical resistance decreases with increase of film thickness. The lowest resistivity of the AZO thin film is  $3.2 \times 10^{-2} \Omega$ . Optical properties of AZO thin films are tested by UV-visible spectroscopy, while comparing with all the films 0.5 at.% aluminum doped film produces more than 90% of transmittance.

**Keywords:** AZO, Sol-gel, Transmittance

## 1 Introduction

Transparent conducting oxides (TCOs) based on zinc oxide (ZnO) is promising material for photovoltaic (PV) cells and various optoelectronic devices<sup>1</sup>. ZnO thin films have been widely used as transparent conductor, because the *n*-type ZnO thin films have a wide band gap semiconductor ( $E_g=3.2$  eV), and high transmission in the visible range, and ZnO thin films can take place of tin dioxide (SnO<sub>2</sub>) and indium tin oxide (ITO) because of their structural and optical properties and its excellent stability which has been mentioned widely<sup>2,3</sup>. ZnO thin films have been prepared with different process such as pulsed-laser deposition, chemical vapor deposition, spray pyrolysis and sol-gel process etc. among them, the sol-gel dip coating technique offers possibility of preparing a small to large area coating of ZnO thin films at low cost for technological applications<sup>4,7</sup>. The technology related to ZnO based TCOs with low resistivity and high transmittance by simple and low temperature deposition technique critically determine on whether the ZnO based TCOs were utilized in touch panels, liquid crystal displays (LCD) and other electronic devices<sup>8-11</sup>.

In several studies, the structural and optical properties of AZO thin films could be obviously

improved by optimized deposition conditions and controlled doping. The primary objective of this work is to investigate the influence of the preparation conditions on structural, electrical and optical properties of AZO films prepared by sol gel dip coating method. Alpha step method is used to measure the thickness of film. The structural characteristics have been studied using X-ray diffraction (XRD), the morphological features have been studied using scanning electron microscopy (SEM), and the optical properties are investigated by using UV-visible spectrometry (UV-Vis), respectively.

## 2 Experimental Details

Zinc acetate dihydrate (C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>Zn.2H<sub>2</sub>O) and diethanolamine (C<sub>4</sub>H<sub>11</sub>NO<sub>2</sub>) are used as a precursor material and the solvent, respectively. Diethanolamine (DEA) was first dissolved in isopropanol (iProH), zinc acetate dihydrate (ZnAc) was added under stirring, and heated under reflux for 1 h at 70 °C. Zinc acetate was dissolved in DEA by the molar ratio of 1 (DEA/Zn=1).

Doping of the solution was obtained by adding a 0.2 M solution of aluminum nitrate in ethanol. The molar ratio of dopant in the solution (Al/Zn), varies between 0.5% to 5%. Isopropanol was added to adjust the solution concentration to 0.5 Mol/L of ZnAc. The molar ratio of DEA to ZnAc was maintained 1 at. %. The solution was stirred at 70 °C for 2 h to yield a

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clear and homogeneous solution, which served as the coating solution after cooling to room temperature. The coating was usually made one or two days after the solution was prepared. Figure 1 shows the procedure for preparing the AZO films.

### 3 Results and Discussion

#### 3.1 X-ray diffraction analysis

The X-ray diffraction analysis (XRD) was used to investigate the physicochemical process involved in the sol-gel deposition of ZnO. The XRD patterns of these films with different aluminum contents are shown in Fig. 2. The ZnO (002) XRD peak is the only peak observed for all the aluminum doped films, irrespective of the aluminum content, which indicates that preferred orientation of the crystals is present

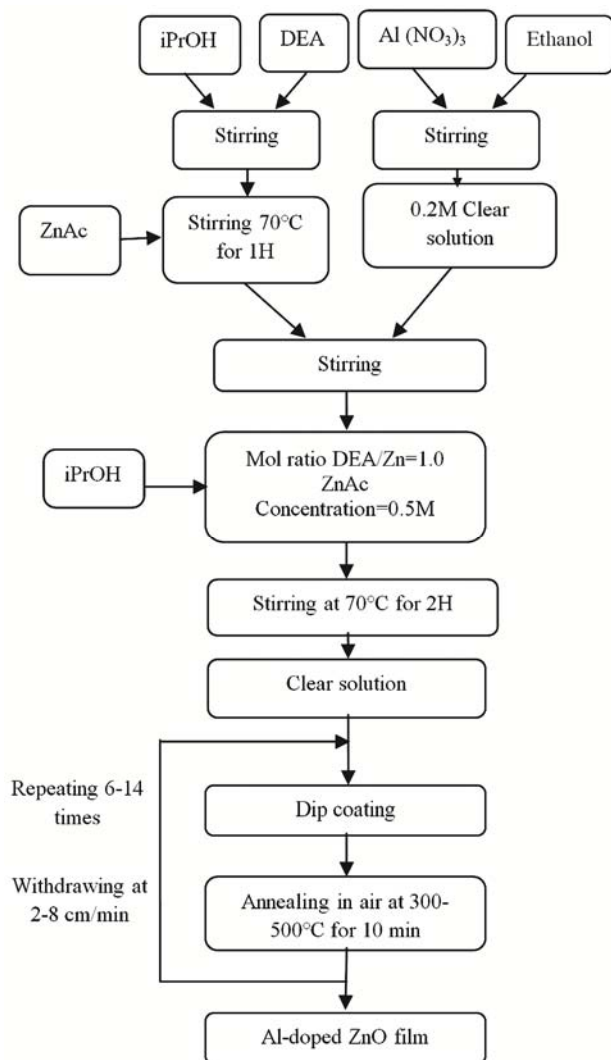


Fig. 1 — Flowchart showing the procedure for preparing the aluminum doped ZnO thin films

with the *c*-axis perpendicular to the substrate surface. Higher intensities of the (002) peak are observed in a limited aluminum concentration range of 0.25 to 1.0 at.%. Film containing 1.0 at.% Al has the highest (002) diffraction peak intensity. The peak intensity of those films decreased with doping concentrations increasing more than 1.0 at.%, which indicates that an increase in doping concentration deteriorates the crystallinity of films, which may be due to the formulation of stress induced by ion size difference between zinc and aluminum and the segregation of aluminum in grain boundaries for high doping concentrations. Figure 3 shows the XRD patterns of

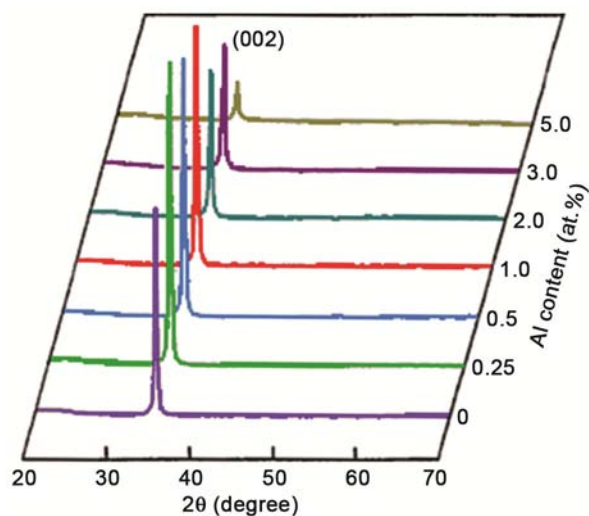


Fig. 2 — XRD patterns of the aluminum doped ZnO films with different aluminum contents

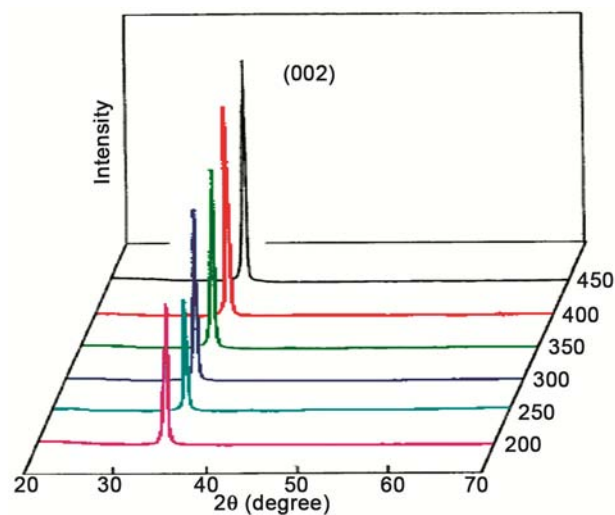


Fig. 3 — XRD patterns of the aluminum doped ZnO films (1.0 at.% of aluminum) prepared for various annealing temperatures

these 1.0 at.% aluminum doped films prepared with different annealing temperatures. All the films show a preferential crystal orientation, and the intensity of the ZnO (002) peak increases as the annealing temperature increases, up to 450 °C, and show a maximum at that temperature, which indicates the highest degree of crystalline orientation attained by annealing the gel films at 450 °C.

### 3.2 Morphological analysis

The morphological feature was studied by scanning electron microscope. Figure 4(a-d) shows SEM micrographs of the different aluminum contents. The grains have a tendency to decrease in size as the aluminum content increase, as shown by the surface morphology. The SEM images show that the surface morphology of the films is strongly dependent on the concentration of aluminum. Uneven surface and dense microstructure are observed in Fig. 4 for the un-doped ZnO film. The 0.5 at.% doped film exhibits a porous microstructure and the spherical crystalline size is approximately 38 nm. When the doping concentration is 1.0 at.%, particle size decreases and the film becomes denser. The surface morphology of 5.0 at.% doped film is similar to that of 1 at.% doped film. The change in ionic radius<sup>12</sup> is in between zinc (0.074 nm) and aluminum (0.057 nm). The grains are more densely packed in the films with higher aluminum contents. The surface micrograph reveals a lower porosity for films with higher aluminum content, which is the consistent with this observation.

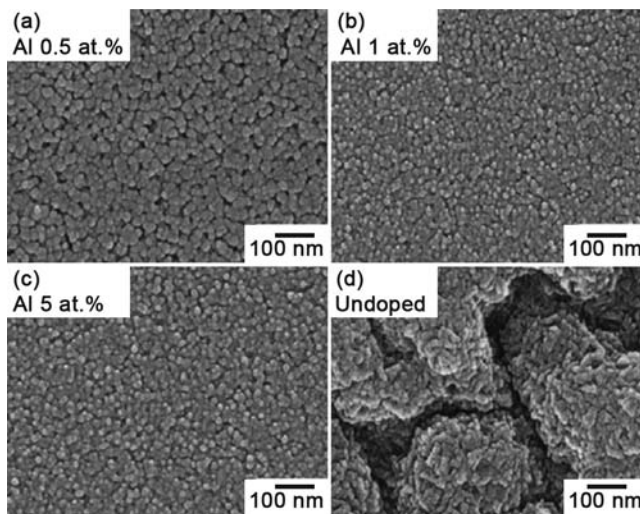


Fig. 4 — SEM images of doped and un-doped ZnO thin films with different aluminum contents, (a) 0.5 at.% AZO, (b) 1 at.% AZO, (c) 5 at.% AZO and (d) un-doped ZnO

### 3.3 Electrical properties

The electrical properties are also important aspects of the performance of the AZO thin films. The effect of doping aluminum concentration and annealing temperature on the un-doped and doped thin films are presented in Figs 5 and 6. The electrical conductivity of ZnO is directly related to the number of electrons, electrons formed by the ionization of the interstitial zinc atom and the oxygen vacancies<sup>13</sup>. It can be seen from Fig. 5 that the electrical resistivity of the doped films is lower than that of the un-doped films. The lowest electrical resistivity value of 1 at.% aluminum doped film is  $3.2 \times 10^{-2} \Omega\text{-cm}$ . However the increase of the electrical resistivity of doped films with increasing doping concentration may be due to a decrease in mobility of the carriers caused by the segregation of the dopant at

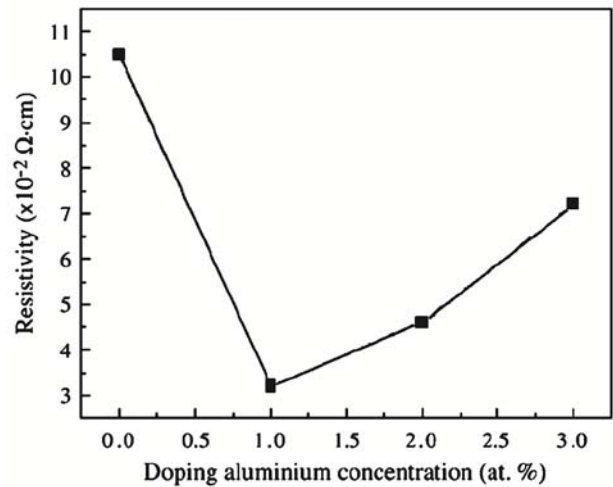


Fig. 5 — Effect of aluminum doping in electrical resistivity

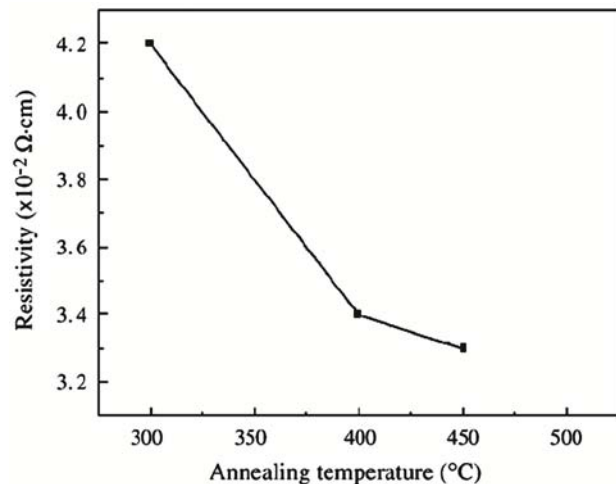


Fig. 6 — Effect of aluminum doping in electrical resistivity due to annealing temperature

the grain boundary. Doped aluminum is acting as an electrical dopant at initial doping concentration but as an impurity at higher doping concentrations, the later films having the lowest electrical resistivity values. Additionally, it has been shown that the electrical resistivity values of doped films is inversely proportional to the prevalence of the (002) orientation of film<sup>14</sup>. As mentioned above, the electrical resistivity of the films decreases with the increase of the (002) preferred orientation of the film, which is influenced by the annealing temperature. Figure 6 shows the effect of annealing temperature on the electrical resistivity. The electrical resistivity of the films is decreased gradually with the increase of annealing temperature, which may be attributed to the fact that the grain boundaries and the crystal lattice deficiencies of the film are decreased with increasing of annealing temperature, resulting in an increase of the mobility of the carriers.

### 3.4 Optical properties

The optical properties are investigated by UV-visible spectrophotometry. Figure 7 indicates that the transmittance of the doped and un-doped ZnO films is always higher than 80% and the transmittance of the doped ZnO films is higher than that of the un-doped films. Moreover, the transmittance of doped film with 0.5 at.% Al is nearly 90% for wavelengths over 400 nm, and is higher than that of the doped film with 1 at.% and 5 at.%. This may be due to the fact that the film with 0.5 at.% doping presents more voids than the films with 1 and 5 at.% doping. This may lead to a decrease in optical scattering<sup>15</sup>. According to Fig. 8, when the thickness of the AZO films is increased from 400 nm to 1600 nm, the transmittance of the AZO films decreases gradually. As the annealing temperature increases from 200 °C to 450 °C, the transmittance of the AZO films increases. The transmittance of the AZO films annealed at 450 °C is higher than 90% for wavelength over 400 nm.

### 4 Conclusions

Aluminum doped zinc oxide (AZO) thin films were prepared by a sol-gel dip coating technique and the films were annealed in air followed by cooled to the ambient atmosphere. Films were annealed to tune and enhance the desired properties. The X-ray diffraction technique reveals that, the higher intensity of the (002) peaks are observed in a limited aluminum concentration range of 0.5 at.% to 1 at.%. When the annealing temperature was increased from 200-450 °C, the films were oriented more preferentially along

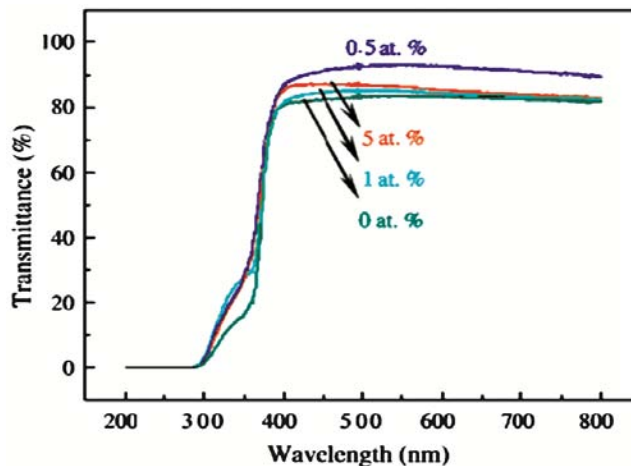


Fig. 7 — Optical transmittance of the un-doped and Al doped ZnO thin films

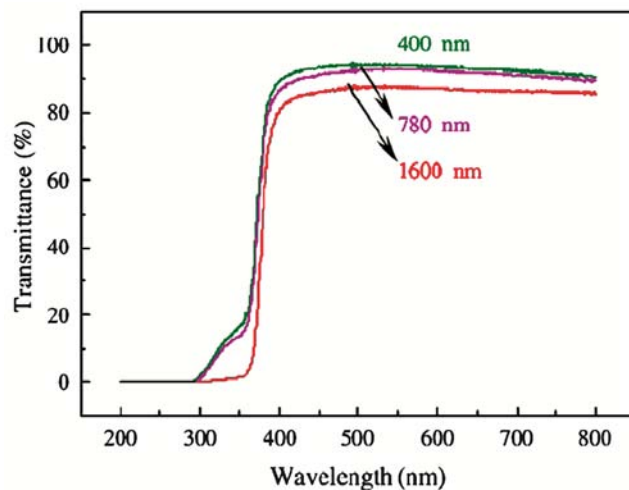


Fig. 8 — Optical transmittance of the 0.5 at.% Al doped ZnO thin films for various film thicknesses

the (002) direction, the grain size of the films increased. According to the SEM results 0.5 at.% aluminum doped film exhibits a porous microstructure and the spherical crystalline particle size is approximately 38 nm. The lowest resistivity of  $3.2 \times 10^{-2} \Omega \text{cm}$  is obtained for 1 at.% aluminum doped films. It is observed from the results of UV visible spectroscopy that all the aluminum doped zinc oxide thin films have the optical transparency of greater than 80%. The transparency of 0.5 at.% aluminum doped films has more than 90% transmittance over visible region and also it reveals that, when the thickness of AZO films is increased from 400 nm to 1600 nm, the optical transmittance of the films has decreased gradually.

**References**

- 1 Tadatsugu M, *Semicond Sci Technol*, 20 (2005) 35.
- 2 Look D C, *Mater Sci Eng B*, 80 (2001) 383.
- 3 Shan F K & Yu Y S, *J Eur Ceram Soc*, 24 (2004) 1869.
- 4 Zu P, *Solid State Commun*, 103 (1997) 459.
- 5 Cossement D & Streydio J M, *J Cryst Growth*, 72 (1985) 57.
- 6 Nishino J, *J Mater Sci Lett*, 16 (1997) 629.
- 7 Gupta V & Mansingh A, *J Appl Phys*, 80 (1996) 1063.
- 8 Suche M, Christoulakis S, Katsarakis N, Kitsopoulos T & Kiriakidis G, *Thin Solid Films*, 515 (2007) 6562.
- 9 Klein Lisa C, *Sol-Gel Technology for Thin Films, Fibers, Performs, Electronics and Specialty Shapes*, (New Jersey (US): Noyes Publications) edited by Lisa C Klein, 382, 1988.
- 10 Jeong S H, Park B N, Yoo D G & Boo J H, *J Korean Phys Soc*, 50 (2007) 622.
- 11 Stadler A, *Materials*, 5 (2012) 661.
- 12 Nunes P, Fortunato E, Tonello P, Braz F F, Yilarinho P & Martins R, *Vacuum*, 64 (2002) 281.
- 13 Sukkar M H & Tuller H L, *Adv Ceram*, 7 (1984) 71.
- 14 Lee J H & Park B O, *Thin Solid Films*, 288 (1996) 112.
- 15 Kozuka H & Yoko T, *J Am Ceram Soc*, 81 (1998) 1622.