The effect of sol aging time on Structural and Optical properties of sol gel ZnO doped Al

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Abstract. Currently the doped or undoped ZnO semiconductor is of great importance in the field of electronic and optoelectronic devices such as transparent conductors and optical windows of solar cells based on silicon. ZnO thin films are produced by several techniques such as sol–gel method which is a chemical technique usually dependent on solution conditions. However, the sol gel aging time is an important parameter, which can have a significant impact on the properties of thin films. In this work we studied the effect of aging times (0h, 24h, 48h, 72h, 1 week) of the precursor solution on the structural and optical properties of ZnO doped Al (3 at.%). Thin films prepared by spin coating on glass substrates were investigated. The X-ray diffraction (XRD) analysis shows that the ZnO doped Al (3 at.%) exhibit the hexagonal wurtzite structure with a preferential orientation along (002) direction. The shift of (002) peaks towards higher diffraction angles is observed with sol aging time and also, a variation of crystallite sizes and thickness of thin films are shown with increasing sol aging time. All films present an average optical transmittance around 90% in the visible range with some interference fringes indicating a relative smoothness of films. We note an increasing in transmittance level with sol aging time from 0h to 48h. We can conclude that the aging times of the precursor solution influences the structural and optical properties of studied thin films.

1. Introduction
In recent years, undoped and doped Zinc oxide (ZnO) thin films received extensive attention due to their excellent optical and electrical properties [1-2]. Doped ZnO thin films are investigated as converter of photons for conductive photovoltaic solar cell window layers [3] and as optoelectronic devices in the UV range [4,5]. This importance came from its high direct band gap (\(E_g = 3.37\) eV) at room temperature and an exciton bending energy of 60 meV [6]. Several techniques were used to synthesize undoped and doped ZnO thin films, such as metalorganic chemical vapor deposition (MOCVD) [7], sputtering [8], pulsed laser deposition [9], spray pyrolysis [10,11 ] and sol-gel method [12,13,14].

In this work we have studied the effect of sol aging times (0h, 24h, 48h, 72h and 1 week) on structural and optical properties of Al doped ZnO at 3% deposited on glass substrates by the sol gel process using the spin coating method. The crystallinity of the undoped and AZO thin films was measured by...
an X-ray diffractometer X’Pert Pro equipped with a CuKα source (λ= 1.5406 Å) and optical transmittance measurements were carried out using a LAMBDA 900 UV-VIS-IR spectrophotometer.

2. Experimental Method
The spin coating method was used to prepare ZnO and AZO thin films on glass substrates. The solution of undoped ZnO and AZO aged at different times were prepared. For synthesis, we have employed zinc acetate dihydrate [Zn(CH3CO2)2.2H2O], absolute ethanol [C2H6O], ethanolamine [MEA,C2H7NO] and aluminum nitrate nanohydrate [Al(NO3)3.9H2O], respectively as a precursor of zinc, solvent, stabilizer and source of dopant. Firstly, the zinc acetate dihydrate was dissolved in mixture of ethanol and ethanolamine MEA solution. The zinc acetate concentration in solution was kept to 0.5M and the molar ratio of MEA/Zinc was maintained to 1.0. Aluminum nitrate nanohydrate was added at the solution with Al/Zn concentration of 3%. The finale solution was refluxed in magnetic stirrer for 1h at 80°C until clear and homogeneous solution was obtained. The procedure to fabricate the AZO thin films is similar to the process used for elaboration of undoped ZnO thin films as described in our previous work [15]. The flow chart of deposition process is shown in Figure 1.

![Flowchart of deposition process](image)

Figure 1. Procedure for preparing spin coated AZO thin films.

3. Results and Discussion

3.1. Structural properties
Figure 2 shows X-ray diffraction patterns of ZnO doped Al thin films with different aging times (0h, 24h, 48h, 72h and 1 week) of the precursor solution. The analysis of the peaks intensity shows that all films are polycrystalline with a hexagonal wurtzite structure with preferential growth along the c-axis direction. We note an increasing in the (002) peak intensity when the precursor solution aging rised of 0h to 48h and then decreased for 72h and 1 week. This means a smoothness growth at 48h sol aging and indicating an optimum sol aging time condition. A gradual shift in (002) peak was observed toward higher angles with increasing sol aging time, 2θ= 34.31° for 0 h and reached at 2θ= 34.46° for
1 week aged sol. The shift of the peak (002) to the wide angle is due to the incorporation of Al in the matrix of ZnO as reported by Shahzad et al. [16].

The crystallite size (D) was estimated using the (002) diffraction peak from the XRD data in accordance to the Debye-Scherer’s formula [17].

\[
D = \frac{0.9 \lambda}{\beta \cos(\theta)}
\]

(1)

where \( \beta \) is the full width half maximum (FWHM) of the diffraction peak measured in radians, \( \lambda \) (1.5406 Å) is the wavelength of the X-ray, and \( \theta \) is the Bragg’s diffraction angle of (002) plane. An average crystallite size value corresponding to ZnO and AZO films deposited at different aging times is presented in Table 1. For the aging time 48h the crystallite size for ZnO and AZO decreases of 35.214nm to 17.235nm respectively, we explain this change by substitution of Zn sites by Al dopant of weak ionic ray and low structure degradation as shown by DRX spectra and observed by other authors [16]. For AZO thin films, the crystallite size increases with time aging due to the viscosity ascent of precursor solution as illustrated in figure 3.

Figure 2. XRD spectrum of undoped ZnO and AZO thin films at different aging time

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Figure 3. Viscosity of AZO thin films at different aging times
The average uniform strain ($\varepsilon$) in the AZO films along c-axis was calculated by using biaxial strain model [18]:

$$\varepsilon = \frac{C_{\text{film}} - C_{\text{bulk}}}{C_{\text{bulk}}} \quad (2)$$

where $C_{\text{bulk}}$ (5.20661 as JCPDS 36–1451) is the lattice constant of undoped bulk ZnO for hexagonal structure and $C_{\text{film}}$ is the lattice one of AZO elaborated films. The $C_{\text{film}}$ was calculated using the DRX data by the relation:

$$C_{\text{film}} = \frac{\lambda}{\sin(\theta_{002})} \quad (3)$$

For the calculated strain values we note that the aged sample at 48h presents the minimum strain which indicates a good crystallinity as identified by XRD.

**Table 1.** Various structural parameters of AZO thin films, and the $\varepsilon$ strain

| Sol aging time (h) | Crystallite size (nm) | (002) peak position $2\theta$ (deg) | FWHM (deg) | Lattice constant $c$ (Å) | Strain $\varepsilon$ |
|-------------------|-----------------------|------------------------------------|------------|--------------------------|---------------------|
| Undoped film (48h)| 35,214                | 34,4567                            | 0.1181     | 5,208                    | -1.0564E-4          |
| 0                 | 14,767                | 34.3152                            | 0.5628     | 5.223                    | 0.00315             |
| 24                | 14,768                | 34.3300                            | 0.5628     | 5.220                    | 0.00257             |
| 48                | 17,235                | 34.4630                            | 0.4824     | 5.200                    | -0.00127            |
| 72                | 20,6815               | 34.4453                            | 0.4020     | 5.203                    | -6.934E-4           |
| 168               | 21,016                | 34.4508                            | 0.3956     | 5.206                    | -1.172E-4           |

### 3.2. Optical Properties

Figure 4 shows the plots of optical transmittance and absorption coefficient spectra of the AZO thin films at different sol aging times. It was showed that the films present an averaged optical transmittance around 85% in the wavelength range of 400–800 nm with some interference fringes. No variation of optical transmittance is observed with prolonged sol aging time.

![Figure 4. Optical Transmittance and Absorption coefficient plots of Al doped ZnO at different sol aging times](image-url)
It was observed in figure 5 that at 48h aging time, the transmittance decreased from 95% to about 87% from un-doped ZnO film to doped ZnO at 3%. This effect can be due to the degradation of the crystallinity of doped films as observed in XRD spectra (there is more scattering of light and this decreases the transmittance).

![Image of Optical Transmittance for ZnO and AZO thin films at 48h]

**Figure 5.** Optical Transmittance for ZnO and AZO thin films at 48h

The optical band gap \( E_g \) of the films are calculated using the Tauc relationship \([19]\):

\[
(\alpha h\nu)^2 = B(h\nu - E_g)
\]

(4)

where \( B \) is an independent energy constant, \( h\nu \) is the photon energy and \( \alpha \) is the absorption coefficient. The Tauc’s plot \((\alpha h\nu)^2\) versus \( h\nu \) is shown in Figure 6. The optical band gap \( E_g \) for AZO thin films was estimated by extrapolating the linear portion of the each curve with the \((h\nu)\)-axis. In the lower energy range \( \alpha \) varies exponentially with photon energy and follows the Urbach formula \([20]\):

\[
\alpha(h\nu) = \alpha_0 \exp(h\nu / E_u)
\]

(5)

where \( \alpha_0 \) is a constant and \( E_u \) is the Urbach energy that is the width of the tailing in the bandgap. Inside Figure 6, we have presented, the plot of \( \ln \alpha \) versus the photon energy \( h\nu \) for Al doped ZnO thin films at different sol aging times.

![Image of \((\alpha h\nu)^2\) and \(\ln(\alpha)\) vs photon energy of AZO thin films at different sol aging time]

**Figure 6.** The Plots of \((\alpha h\nu)^2\) and \(\ln(\alpha)\) vs photon energy of AZO thin films at different sol aging time
Table 2 gives the band gap $E_g$, the Urbach $E_u$ energies and the estimated thickness of the films which was estimated using the transmittance spectra fringes.

Table 2. The optical parameters of undoped and doped Al(3%at) ZnO thin films.

| Sol aging time (h) | Thickness (nm) | $E_g$ (eV) | $E_u$ (eV) |
|-------------------|----------------|-----------|------------|
| Undope film (48h) | 204,526        | 3.2837    | 0.065      |
| 0                 | 198,862        | 3.2609    | 0.103      |
| 24                | 202,614        | 3.2663    | 0.099      |
| 48                | 200,774        | 3.2636    | 0.105      |
| 72                | 193,696        | 3.2645    | 0.103      |
| 168               | 208,323        | 3.2600    | 0.114      |

Table 2 shows decreasing of the optical band gap $E_g$ for doped AZO films compared to undoped ZnO thin films aged at 48h. Also it can be seen that AZO at 48h produce an Urbach band tail width around 0.105 eV higher value of about 0.065 eV observed for undoped ZnO films, which indicate an increase of defects level in the band gap. No significantly variation of optical band gap, thickness and Urbach energy with sol aging time was observed, as showed by [12].

4. Conclusion
The effects of sol aging time on structural and optical properties of sol gel ZnO doped Al thin films deposited by sping coating on glass substrate were investigated. The results show that the undoped and Al doped ZnO thin films were polycrystalline and present a hexagonal wurtzite structure with a preferential orientation (002) along c-axis. The results indicated a smoothness growth at 48h sol aging exhibiting an optimum sol aging time condition. The films were highly transparent in the visible range. We note no significantly effect on optical properties with sol aging time.
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