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On the Structural, Optical and Electrical Characterization of Zinc Oxide and Aluminium doped Zinc Oxide for Optoelectronic Applications

Research Article

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Abstract. Zinc Oxide (ZnO) and Aluminium doped Zinc Oxide (AZO) thin films are deposited on the glass slides by sol-gel spin coating technique. Zinc acetate dehydrate, 2 methoxyethanol, and diethanolamine are respectively used as a precursor, solvent, and stabilizer. Aluminium nitrate nonahydrate was used as the dopant source to obtain the atomic percentage of the dopant of 2%, 4%, 6% and 8%. The structural, optical, and electrical properties of the films were investigated using X-ray Diffraction (XRD), UV-visible spectrophotometry, and a Four-point probe technique respectively. The results from structural analyses show that the films are polycrystalline with a hexagonal wurtzite structure and a preferential orientation alongside the c-axis. The value obtained for the unit cell $a = 3.020$ Å and $c = 5.108$ Å are in line with the reported literature. The transmittance of the films was observed within the visible region of the spectrum and the optical bandgap of the un-doped ZnO was established to be around 4.11 eV. However, the optical bandgap of the AZO films (4 and 6 at %) marginally decreases with doping concentration, which may be ascribed to the shrinkage of band effect due to the increase in carrier concentration. The lowest resistivity of 3.53×10^{-3} Ω cm was observed for the doping concentration of 2% of Al. From the results, it was established that as the doping concentration increases, the thicknesses of the thin films were increased. Likewise, the increase in doping leads to a better uniformly distributed absorption spectra of the deposited AZO thin films.

Keywords. Sol-gel; Spin coating; AZO thin films; Film thickness; Optical properties

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1. Introduction

It is desirable for Transparent Conductive Oxides (TCOs) should have a wide bandgap (≥ 3.2 eV) such that most light from the solar spectrum can pass through the TCO films instead of being absorbed by them. The current industrial standard TCOs are primarily n-type semiconductors as p-type TCOs exhibit much lower carrier motility due to the large whole effective masses of these materials [10]. However, despite ITO's superior performance, indium is an expensive material and is harmful to both humans and the environment [5]. Also, the scarcity of indium is becoming a problem, therefore, alternative materials are urgently needed to replace ITO in its various applications. Hence, much attention is being paid to zinc oxide as a promising replacement of ITO due to its abundance and comparable material properties. ZnO can be synthesized easily in large quantities and the required materials are commonly available as inexpensive and stable with hydrogen plasma presence [15]. Snegal et al. reported several prospective applications of ZnO thin film such as making flat-panel liquid crystal displays, antibacterial agents, gas sensors, photo-catalysts, solar cells, and transparent conducting electrodes [18]. There are numerous methods in preparing Aluminium doped zinc oxide such as magnetron sputtering [11], pulsed laser deposition [13], sol-gel [20], SILAR [3]. The sol-gel technique by spin coating is regarded as popular methods among the aforementioned techniques due to its uncomplicatedness, safety, and cost-effectiveness. In this study, zinc oxide and aluminium doped zinc oxide thin films were synthesized using sol-gel spin coating methods and the influence of dopants on optoelectronics properties of the thin films were investigated.

2. Material and Methods

Zinc Oxide (ZnO) and Aluminium doped Zinc Oxide (AZO) thin films were prepared using a Sol-gel spin coating method. Zinc acetate dehydrate and Aluminium nitrate nonahydrate (dopant source) was dissolved into the 2-Methoxyethanol solution with the presence of Diethanolamine (DEA) as a stabilizer. The amount of Aluminium nitrate nonahydrate was controlled to obtained 0% (undoped), 2%, 4%, 6%, and 8% doping concentration in other to investigate the influence of aluminium concentrations on the characteristics of ZnO thin films. Keeping the solution was agitated for 2hours at 80 °C, and aged for 24 hours at room temperature before film deposition. At room temperature, ten (10) drops of the solution were spin-coated at 2000 rpm speed for the 60s. To disperse the film's solvent, preheated processes were done after each deposition at 150 °C for 5 minutes and were repeated 5 times to increase thin film thickness. The annealing was done at 500 °C for 1 hour in air ambient using a furnace for decomposition and oxidation of the precursor. To guarantee an impurity-free deposition of the AZO glass substrate (25.4 mm × 76.2 mm × 1.0 mm), subsequent cleaning procedure was carried out, the substrate was washed with detergent and distilled water and later rinsed using ethanol to avoid any oily attachments. The substrates were then put in the oven to dry before being used in sol-gel spin coating deposition. The thickness, structural, optical, and electrical properties of the films were analysed using a gravimetric, X-ray diffraction (XRD), UV-VIS spectrophotometry, and a Four-point probe technique respectively.

Theoretical Consideration

Thickness

Thin films thicknesses were measured using a gravimetric method as related in the equation below:

$$t = \frac{m}{\rho A}, \tag{2.1}$$

where m is the mass of the deposited film, ρ is the density and A is the area of the deposited films.

Optical

The optical transmittance (T) was calculated as related in equation (2.2):

$$A = \log\left(\frac{1}{T}\right), \tag{2.2}$$

where $T = \frac{I}{I_0}$, I is the transmitted light, and I_0 is the incident light [4, 9, 17]. Furlan *et al*. [7], given the relationship between the absorbance (A), transmittance (T) and reflectance (R) as it wassatisfying the conservation law of energy in the equation(2.3):

$$A + R + T = 1 \quad \text{or} \quad R = 1 - (A + T). \tag{2.3}$$

Also, Gittleman *et al*. [8], related the reflectance (R) with refractive index (n) as given by:

$$n = \frac{\left(1 + R^{\frac{1}{2}}\right)}{\left(1 - R^{\frac{1}{2}}\right)}. \tag{2.4}$$

Islam and Podder [12], employed Beer Lambert's formula to relate absorption coefficient (α) with absorbance and thickness thin films:

$$\alpha = 2.303\left(\frac{A}{d}\right). \tag{2.5}$$

The coefficient of extinction (K) was given by the relation below:

$$K = \frac{\alpha\lambda}{4\pi}, \tag{2.6}$$

where λ is the wavelength of radiation [9]. Near the absorption edge, absorption coefficient (α) is related to bandgap (Eg) by:

$$\alpha = \frac{A(hv - Eg)n}{hv}. \tag{2.7}$$

The bandgap was obtained from allowed direct transition by plotting $\alpha^2 hv^2$ against hv and extrapolating the graph to the point where $\alpha = 0$ is known as the energy bandgap. The optical conductivity is the optical response of a transparent solid. It is related to the absorption coefficient and the refractive index is given by:

$$\sigma = \frac{\alpha\eta c}{4\pi}. \tag{2.8}$$

Structural

The crystallites average size was calculated using the Scherer formula [16] given by:

$$D_{khl} = \frac{k\lambda}{\beta\cos\theta}. \tag{2.9}$$

3. Results and Discussion

Thin Films Thickness Determination

The samples AZO1, AZO2, AZO3, AZO4, and AZO5 have a varying film thickness of 42.52, 48.55, 44.23, 44.45, and 49.51 nm respectively due to increase in doping concentration as shown in Table 1. The chart of the thickness of each sample as shown in Figure 1(a). The chart shows the varying thickness of each sample when they were measured after deposition, as shown in the chart, AZO5 has a thickness of 49.51nm which is the highest thickness of the film.

Table 1. The samples thickness

Sample	AZO1	AZO2	AZO3	AZO4	AZO5
Thickness (nm)	42.52	48.55	44.23	46.45	49.51

Structural Properties

The x-ray diffraction pattern of 5 samples (annealing temperature = 500 °C) were shown in Figure 1(b). It depicts the intensity (in arbitrary unit) against 2θ (diffraction angle). It was observed from the figure, that the max. Intensity occurs at 20-30.619° which corresponds to the (002) plane. Other peaks occur at $2\theta = 25.728°$ and 41.808° which correspond to the, (100) and (101) planes, respectively. This behaviour proposes that the prepared ZnO thin film has a hexagonal configuration and is preferentially oriented along the c-axis normal to the substrate surface. The value obtained for the unit cell $a = 3.020$ Å and $c = 5.108$ Å are in consonant with those reported in the literature [19].

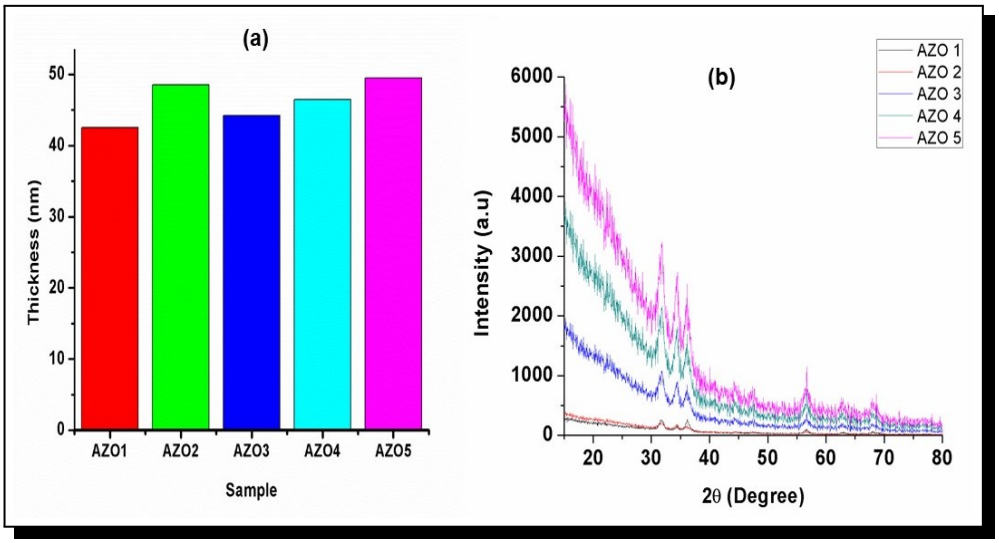

Figure 1. (a) The chart of the thickness of each sample, (b) XRD pattern of un-doped and Al-doped ZnO film

Optical Properties

The optical transmittance spectra with doping concentrations of ZnO thin films were shown in Figure 2(a). It was clear that all the samples have elevated transmittance in the visible

range (400-800 nm). Within the range from 300-400 nm doping has almost no effect on the transmittance. However, from 400-800 nm, it was observed that AZO5 with the highest doping concentration has the lowest transmittance. The highest transparency was obtained by 0 at % about 90% in the visible region of the wavelength. As the concentration increases, the transmittance was differing and 50% value of it was observed for doping concentrations of 8 at %. The decrease in the visible transmittance may be due to the crystal defect caused by the presence of Aluminium in the ZnO lattice.

The optical absorbance spectra of ZnO thin films were shown in Figure 2(b). In the VIS/NIR region, the spectra show low absorbance in the deposited ZnO thin film whereas; there is high absorbance in the UV region. However, an increase in Al-doping corresponds to a more uniform absorption spectra of the ZnO thin films. It was observed that as the doping concentration increases, the intensity of the UV peaks also decreases.

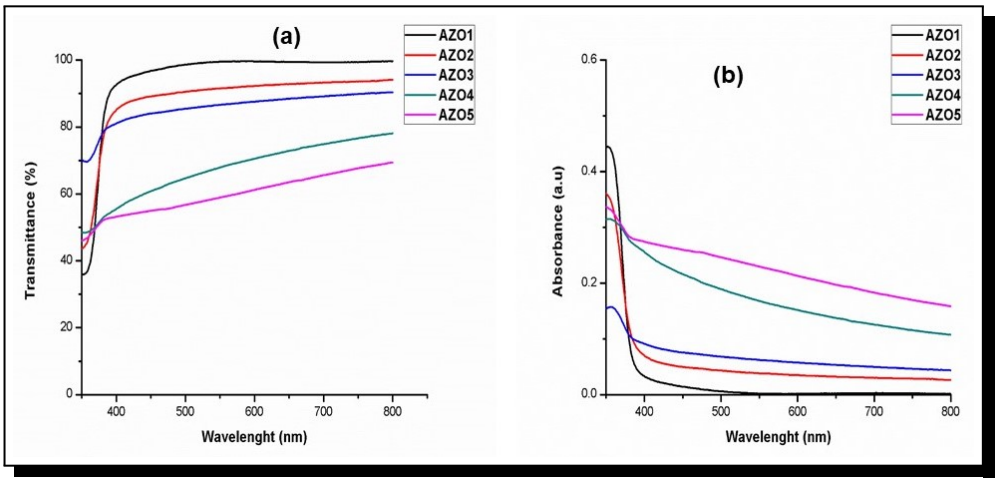

Figure 2. (a) The transmission spectra of doped ZnO thin films (b) The absorption spectra of ZnO thin films

In Figure 3(a), the absorption coefficient (α) of the deposited ZnO thin films was presented. The result shows that an increase in doping does not necessarily lead to an increase in the absorption coefficient because the sample with doping of 0 at % (AZO1) has the best absorption coefficient curve. Furthermore, the absorption coefficient is in the range of 10^4 to 10^5 cm, when hv>Eg [6]. The absorption coefficients in the UV-region were more than those in the visible region and decreased with Al-incorporation. Furthermore, there is a steady increase in the absorption coefficient as the photon energy increases further for all the samples.

The variation of extinction coefficient against wavelength of un-doped and aluminium-doped zinc oxide thin films as shown in Figure 3(b). The extinction coefficient (k) is high in the wavelength 550-800 nm and low in the range of 300-450 nm wavelength.

Figure 4(a) shows the UV-visible diffuse reflectance spectroscopy was used to investigate the optical properties of ZnO and spectroscopy measurements were continued at room temperature in the wavelength range 300-800 nm. Diffuse reflectance spectra of un-doped ZnO and AZO thin film with different Al concentration (2-8 at %) were also measured. In general, the reflectance

increases with an increase in Aluminium concentrations because the sample with doping of 8 at % has the highest reflectance curve.

Table 2. Optical band gap for un-doped and AZO thin films

Sample	AZO1	AZO2	AZO3	AZO4	AZO5
Energy band gap (eV)	4.11	4.13	4.06	4.09	4.14

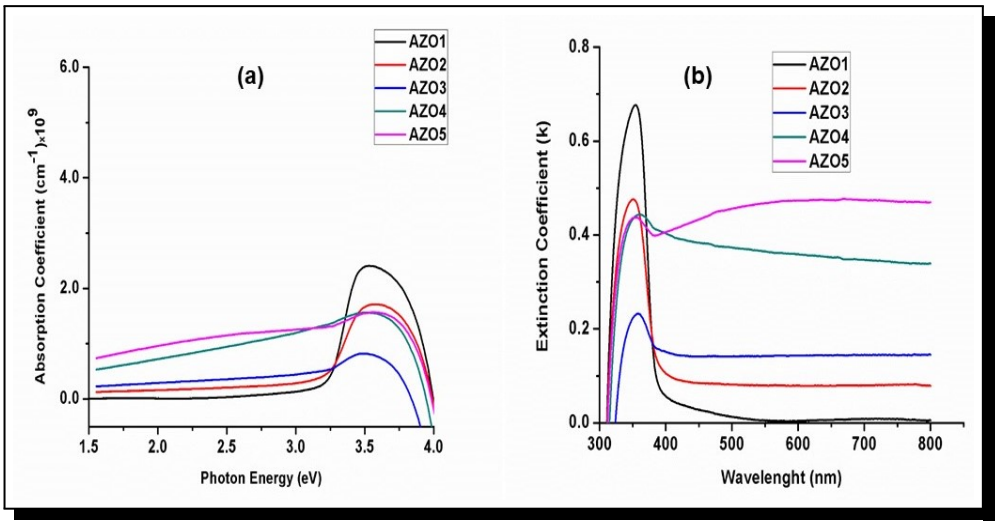

Figure 3. (a) The variation of absorptioncoefficient (α) against photon energy (eV), (b) The extinction coefficient of the thin films

In Table 2, the dissimilarity of the optical band gap values for un-doped and Al-doped ZnO films were shown. Figure 4(b), shows the plots of $(\alpha\ \mathrm{hv})^2$ against the Photon Energy of AZO thin films with dopants. The bandgap of the un-doped ZnO thin films was found to be about 4.11 eV. The bandgap of the AZO thin films (4 and 6 at %) marginally decreases with the presence of Aluminium, while bandgaps of the AZO thin films (2 and 8 at %) were increased accordingly, which agreed with the literature. The marginal decrease in the optical bandgap of the stock ticker AZO films (4 and 6 at %), may be ascribed to the shrinkage of band effect due to the increase in carrier concentration.

The variations of optical conductivity with the incident photon energy were illustrated in Figure 5(a). The behaviour of the optical conductivity of all the samples followed a similar pattern as is observed from the graph. It showed that conductivity increased to a peak at 3.40 eV, and AZO 1 having the highest peak. This behaviour is caused by the dependency of optical conductivity on the nature of the refractive index and absorption coefficient which are greatest at the UV region and diminishes as the wavelength increases [1].

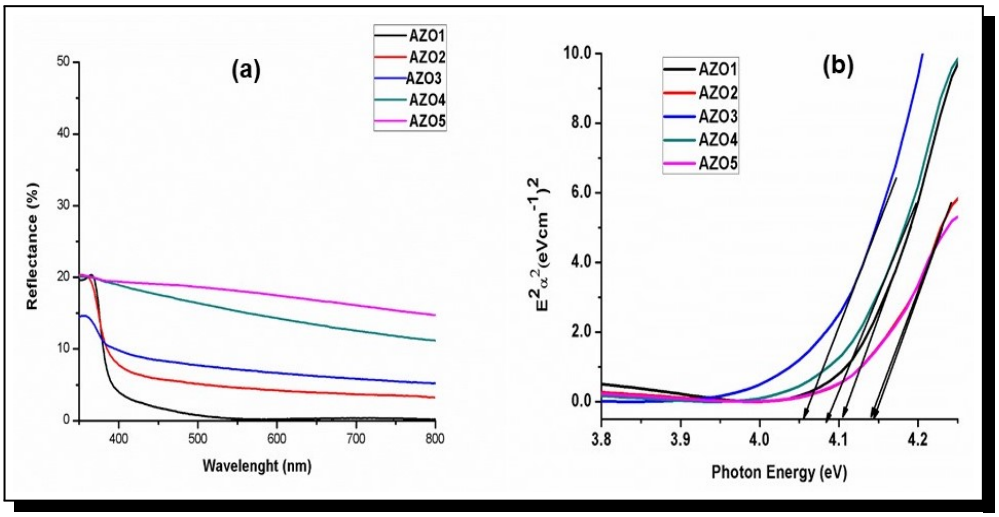

Figure 4. (a) The variation of reflectance against wavelength of the AZO thin films, (b) Plots of $(\alpha\ \mathrm{hv})^2$ against photon energy of the AZO thin films

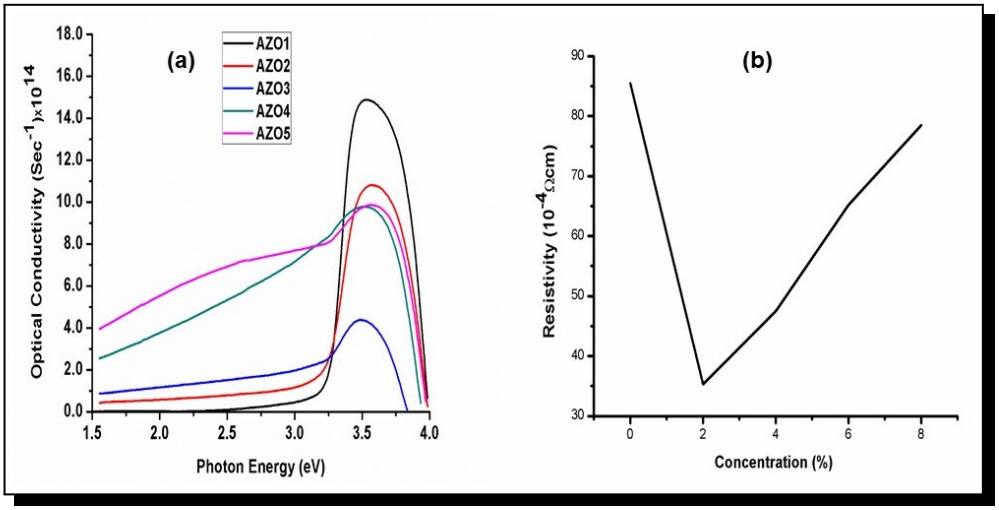

Figure 5. (a) Optical conductivity Variation against photon energy, (b) Sheet resistant of the AZO films with concentration

The influence of Aluminium doping concentrations on the electrical properties of AZO thin films was shown in Figure 5(b). It was found that the electrical resistivity of the films decreases as the doping concentration increases in percentage, $85.5 \times 10^{-4}\ \Omega\,\mathrm{cm}$ for undoped ZnO and reached the lowest values of resistivity $35.3 \times 10^{-4}\ \Omega\,\mathrm{cm}$ for doping concentration of 2%. This may be due to the presence of Al^{3+} ions which might have increased charge carriers in the interstitial or substitutional sites of Zn^{2+} cations [14]. However, the resistivity increases to 47.5, 65.2 and $78.5 \times 10^{-4}\ \Omega\,\mathrm{cm}$ for doping concentrations of 4%, 6%, and 8%, respectively. The electrical resistivity increases above the doping concentration of 2%, maybe due to the appearance of Al_2O_3 phase gives rise to the formation of an alloy instead of doping [2].

4. Conclusion

The Opto-electrical properties of Zinc Oxide (ZnO) and Aluminium doped Zinc Oxide (AZO) has been successfully studied by sol-gel spin coating techniques. It was found out that all the deposited AZO thin films have a polycrystalline structure, with a preferred c-axis orientation and XRD spectra showed the hexagonal wurtzite structure of ZnO. The optical properties revealed that they all have high transmittance and low transmittance in the 400-700 nm ranges of wavelength and near the fundamental absorption region respectively. Also, the thin films deposited show the high absorbance in the UV region and low absorbance in the VIS/NIR region. Meanwhile, there is a steady proliferation in the absorption coefficient with the increase in photon energy. However, the energy band gaps of the AZO films are fairly constant despite the varying in the doping concentration. The thicknesses of the AZO thin films were increasing with the increase in doping concentrations. The electrical resistivity of AZO films hinge on the level of doping concentration and the transmittance spectra showed high transparency of ZnO:Al thin films about 90%.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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