Optical Studies On Aluminum-Doped Zinc Oxide Thin Films Prepared By DC Sputtering Technique

M. M. Abd El-Raheem\textsuperscript{a,b}, Ateyyah M. Al-Baradi\textsuperscript{d}, A. M. A. Amry\textsuperscript{a,c}, F. Abd Elwahab\textsuperscript{a,b}, H. E. A. El-Sayed\textsuperscript{e}, S. A. Amin\textsuperscript{a,c}, H. H. AL-Off\textsuperscript{a}

\textsuperscript{a}Phys. Dept, Faculty of Science, Taif University, Taif 888, KSA
\textsuperscript{b}Phys. Dept, Faculty of Science, Sohag University, Sohag 82524, Egypt
\textsuperscript{c}Phys. Dept, Faculty of Science, Assiut University, Assiut 71516, Egypt
\textsuperscript{d}Phys. Dept, Faculty of Science, Aswan University, Aswan, Egypt
\textsuperscript{e}Phys. Dept, Faculty of Education, Ain Shams University, Roxy Square, Cairo, 11757, Egypt

1. Introduction

Formation and characterization of zinc oxide and doped zinc oxide via different techniques have attracted considerable attention due to their important applications in the development of materials science. ZnO has high transparency in the visible and near-ultraviolet spectral regions and a wide range of conductivity which can be changed under photo reduction/oxidation condition \[1\]. Pure ZnO thin films lack stability in terms of thermal aging in air and corrosive environment \[2\]. Thus, polycrystalline ZnO films have been doped with elements from group II and III metal ions such as In, Al, Ga, Cu Cd etc. to enhance their structural, optical and electrical properties \[3-8\]. Doping is required to get high transparency, stability and high conductivity. Aluminum doped ZnO thin films have high transmittance in the visible region, low resistivity, and the optical band gap can be controlled by using Al doping amount \[9\]. It has been reported that the optical band gap of ZnO is approximately 3.2 eV at room temperature \[4\], and for Al\(_2\)ZnO\(_4\) is in the range of 3.14 - 3.32 eV \[10\]. This wide band gap of Al\(_2\)ZnO\(_4\) semiconductors show optical transmission in the visible and near-infrared regions. This unique property has been widely studied for various practical applications such as solar cells \[11\] and flat panel display electrodes \[12\]. In addition, it is also find applications as surface acoustic devices, optical waveguide, gas sensors, and micro-machined actuators \[13-15\]. The physical properties of the films depend strongly on the deposition technique, the growth conditions and post deposition treatment. Several techniques have been used for preparing ZnO thin films such as sputtering \[16-17\], spray pyrolysis \[18\], pulsed laser ablation \[19\], reactive evaporation \[20\], chemical vapor deposition \[21\], solution growth \[22\], sol-gel \[23-24\], and cathodic vacuum arc techniques \[25\]. The simultaneous occurrence of high visible transparency and high electrical conductivity can be controlled through the material parameters like dielectric constant $\varepsilon'$, carrier concentration $N$ and mobility \[26-28\].

As far as the authors know that little attention has been paid to characterizing the structural and optical properties of Al\(_2\)ZnO\(_4\) thin films deposited at room temperature. So, in the present work, the structural and optical properties of Al\(_2\)ZnO\(_4\) thin films deposited using dc sputtering technique at substrate room temperature are studied.

2. Experimental

The Al doped ZnO thin films were deposited on a pre-cleaned glass substrate using UNIVEX 350 SPUTTERING UNIT with DC POWER MODEL Turbo drive TD20 classic (Leybold) and rate thickness monitor model INFICON AQM-160. The Al\(_2\)ZnO\(_4\) target, from Cathey was used as a sputtering source. The weight ratio of Al\(_2\)O\(_3\) to ZnO (both were 99.99% pure) was 20%. The high vacuum of the chamber was better than 2x10\(^{-6}\) Torr and sputtering was carried out in 98% argon + 2% oxygen atmosphere, both of the gas has a purity of 99.99 and of pressure $10^{-6}$ Torr.
of 2x10^{-2} torr. The target substrate distance was 10 cm with an angle 65°. The substrate temperature was kept at 25 °C during deposition. The structural characteristics of Al2ZnO4 thin films was investigated by X-ray diffraction pattern. Philips X-ray diffractometer X' Pert was used for the measurements which utilized monochromatic CuKα=1.5406 Å radiation operated at 40 kV and 25 mA. The diffraction patterns were recorded automatically with scanning speed of 2deg/min. The optical transmittance and absorbance of the films were measured in the wavelength range of 200-1200 nm at normal incidence using double beam spectrophotometer (JASCO model V-670 UV-VIS-NIR).

3. Theory and Calculation

The study of the fundamental absorption edge provides useful complementary information concerning energy band structure and the type of transition of the charge carriers. The absorption coefficient $\alpha$ of the films was determined using the formula [29]:

$$\alpha = \frac{1}{d} \ln \left( \frac{(1-R)^2}{T} \right)$$

(1)

where $T$ and $R$ are the transmittance and reflectance of the films respectively and $d$ is the film thickness.

The allowed indirect optical energy gap $E_{op}$ was estimated from optical measurements using the following expression [30]:

$$(ah\nu)^{1/2} = A(h\nu - E_{op})$$

(2)

where $h\nu$ is the photon energy, $A$ is a constant characteristic parameter independent of photon energy, and $h$ is Planck’s constant. $E_{op}$ values were obtained by extrapolating the linear portion of the plots of $(ah\nu)^{1/2}$ versus $h\nu$ to $(ah\nu)^{1/2} = 0.0$.

The refractive index $n$ was calculated from the following equation:

$$n = \frac{1}{1-R} \pm \sqrt{\left[ \frac{R}{R-1} \right]^2 - (1+k^2)^2}$$

(3)

where $k = \alpha \lambda / 4\pi$ is the absorption index, and $\lambda$ is the incident wavelength. Besides, for spectra including fringes, the refractive index, n was calculated from the transmission spectra using Swanepoel’s method [21,22] using the envelope method suggested by Manifacier et al [23]. The envelope connecting the interference maxima and minima are considered to be continuous functions of the wavelength. Therefore, for each maximum of the transmittance curves, TM, a corresponding minimum, Tm, may be determined at the same wavelength, $\lambda$. The refractive index of Al2SnO4 thin films, n, as a function of wavelength $\lambda$; can be calculated using the following equation [21-24]:

$$n = \sqrt{N + \sqrt{N^2 - s^2}}$$

(3')

where $N$ and $s$ are given by:

$$N = \frac{1}{2} \left[ \frac{T_m - M_{lo}}{T_m T_n} \right]$$

$$s = \frac{2 \times (T_m - M_{lo})}{T_m T_n}$$

(4)

The refractive index of the substrate $s$ could be calculated from the following formula:

$$s = \frac{1}{T_s} + \left( \frac{1}{T_s} - 1 \right)$$

(5)

where $T_s$ is the transmission of the substrate.

The relation between the real dielectric constant $\varepsilon'$ and the wavelength, $\lambda$, in the normal dispersion region is given by [31, 32]:

$$\varepsilon' = n^2 - k^2 = \varepsilon_\infty - \frac{e^2}{4\pi^2 c^2 \varepsilon_\infty} \frac{N}{m^*} \lambda^2$$

(6)

where $\varepsilon_\infty$ is the residual dielectric constant, $c$ is the light velocity, $N$ is the free carrier concentration, $m^*$ is the electron effective mass), $e$ is the electronic charge and $\varepsilon_\infty$ is the permittivity of free space. The plasma frequency is in the form:

$$\omega_p^2 = \left( \frac{Ne^2}{\varepsilon_\infty \varepsilon_\infty m^*} \right)^{1/2}$$

(7)

For one kind of free carrier the relaxation time $\tau$ can be determined by plotting $\varepsilon'$ versus $\lambda^2$ and calculating the slope and intercept of the straight line using the following equation:

$$\varepsilon' = 2nk = \frac{\varepsilon_\infty \omega_p^2}{4\pi^2 c^2 \tau} \lambda^2$$

(8)

where $\varepsilon'$ is the imaginary part of the complex dielectric function. It is worth mentioning that the real part generally related to dispersion, while the imaginary part provides a measure to the dissipative rate of the wave in the medium [33]

The dispersion data of the refractive index has been analyzed on the basis of the Wample and DiDomenico (WD) model which is based on the single oscillator formulae [34-37]:

$$(n^2 - 1)^{-1} = \frac{E_o}{E_d} - \frac{1}{E_a E_d} (h\nu)^2$$

(9)

where $E_o$ is the oscillator energy and $E_d$ is the dispersion energy which is a measure of the strength of interband optical transition. The values of $E_o$ and $E_d$ can be directly determined by plotting $(n^2 - 1)^{-1}$ against $(h\nu)^2$ .

The amount of tailing can be estimated to a first approximation by plotting the absorption edge data in terms of an equation originally given by Urbach [38], which has been applied to many glassy materials. The exponential depends on the absorption coefficient, ($\alpha$) and photon energy ($h\nu$). It has been found that $h\nu$
holds over several decades for a glassy material and takes the formula \[ \alpha = \alpha_o e^{E_u} \] (10)

where $\alpha_o$ is a constant and $E_u$ is interpreted as the width of the tail of the localized state (Urbach tails) in the forbidden band gap.

3. Results and discussion

3.1 Structural investigations

The X-ray diffraction patterns of Al$_2$ZnO$_4$ thin films of thicknesses 100, 200, 400, 600, and 800 nm were investigated at Fig.(1), revealing a crystalline nature with (004) plane preferred orientation at $2\theta =72.5^\circ$, followed by amorphous background as seen in Fig. (1-a). This plane (004) has been detected at $2\theta =72.5^\circ$ by Joeng et al [39]. The intensity of the peak representing the preferred plane was found to increase with increasing the thickness of the films as revealed in Fig.(1-a). This can be interpreted as due to an improvement of the crystallinity of the films. In addition, Fig.(1-b) showed that the intensity of the peaks increases with increasing the rate of the gas at $2\theta =72.5^\circ$ also.

![Figure 1-a](image)

Figure 1-a X-ray diffraction for as-prepared Al$_2$ZnO$_4$ thin films of different thicknesses.

3-2 Optical characterization

Effect of thickness of Al$_2$ZnO$_4$ thin films on the optical properties

Figure (2) depicts the changes of the transmittance $T(\%)$ with the incident wavelength. Through the range of the applied wavelength from 280 to 700 nm, there were peaks belonging to the films of thicknesses 200, 300, 400, 500, 600, and 800 nm in the visible range of wavelength. It is noticed that the peaks of the transmittance were shifted toward the longer wavelength with increasing the thickness of the film. The spectra belonging to the films thicker than 200 nm reveal interference fringes in the wavelength regions from 500 nm up, this confirmed an excellent quality and homogeneity of the film. It is observed also that the number of fringes increases as the film thickness increases. Besides, the maximum values of the transmittance increased with increasing the film thickness as seen in Fig.(2), the highest value was found to be 90% for the films of thickness 500, 600, and 800 nm respectively. Furthermore, strong absorption was observed at photon energies 4.21, 4.14, 4.01, 3.95, 3.89, 3.77, and 3.71 eV for the films of thickness 100, 200, 300, 400, 500, 600, and 800 nm respectively, where interference effects are suppressed almost completely due to a well defined band edge.
For obtaining the optical energy gap, the plots of $(a h \nu)^b$ vs. $h \nu$ were drawn for $b = 1/2$, 2, 3/2, and 3. The best value of $b$ found to be 1/2 indicating allowed indirect optical energy gap $E_{op}$. Values of $E_{op}$ was estimated by extrapolating the linear portion of the plots $(a h \nu)^{1/2}$ versus $h \nu$ to $(a h \nu)^{1/2} = 0.0$ as shown in Fig.(3). The estimated values of the optical energy gap found to decrease with increasing the thickness of the films, their values were 4.20, 4.15, 4.08, 3.90, 3.85, 3.72 eV for the thicknesses, 100, 200, 300, 400, 500, 600, and 800 nm respectively. This can be attributed to changes of atomic distances and grain size and structural defects in the films [40]. Also, there is a possibility of structural defects in the films due to their preparation at room temperature; this could give rise to the allowed localized states near the conduction band in the forbidden region [41]. In case of thick films, these allowed states may merge with the conduction band resulting in the reduction of the band. The results are in a good agreement with literatures [42-46]. The width of the band tails of the localized states (Urbach tails) $E_u$ were estimated from the slope of the plots of $\ln(\alpha)$ vs. $h \nu$ as shown in Fig.(4). The values of $E_u$ were found to increase with increasing the thickness of the films; they were 0.29, 0.37, 0.38, 0.34, 0.39, 0.45, 0.47 eV for the thickness 100, 200, 300, 400, 500, 600, and 800 nm respectively. These results of the Urbach tails confirm those of the optical energy gap [47]. Figure (5) depicts the change of the refractive index for the as-prepared $\text{Al}_2\text{ZnO}_4$ thin films of thicknesses 100, 400, 600, and 800 nm. It is clear that the refractive index decreases with increasing the wavelength indicating normal dispersion in the visible range. In addition, the refractive index increases with increasing the thickness of the film, this may be due to changing the film thickness could change the density and/or the polarizability of the material of the thin films.
The optical conductivity $\sigma_{op}$ is considered to be a very important tool for studying the electronic states in materials [48]. The optical conductivity of different thickness is calculated by [49, 50];

$$\sigma = \frac{\alpha n c}{4\pi}$$  \hspace{1cm} (11)

Where $\alpha$ is the absorption coefficient, $n$ is the refractive index and $c$ is the velocity of light. Figure (6) shows the variation of the optical conductivity with changing the photon wavelength. It is clear from Fig.(6) that the optical conductivity increases with increasing the film thickness which could be attributed to the increase in the refractive index and the density of localized states in the forbidden gap due to the appearance of new defects states [47].

The effect of the rate of flow of argon+oxygen mixture gas on the optical behavior of Al$_2$ZnO$_4$ of 300 nm thick showed that, the maximum values of the transmittance were shifted toward longer wavelength of the photons as the rate of flow increased as shown in Fig.(8). Besides, slight increase of the maximum value of the transmittance took place with increasing the rate of flow, where they had the values 90, 90, 90, 93, and 93% for the rates, 5, 10, 15, 20, and 30 sccm respectively as seen in Fig.(8).

Using DiDomenico dispersion relationship, the single oscillator energy $E_o$ and dispersion energy $E_d$ can be calculated from the slope and intercept of the plot $(n^2-1)^{-1}$ versus $(h\nu)^2$ as seen in Fig.(7). The values of single oscillator energy found to be 2.29, 2.81, and 2.46 eV for the films of 400, 600, 800 nm respectively. The dispersion energy found to be 3.51, 4.26, and 5.92 eV for the films of 400, 600, 800 nm respectively.
The optical energy gap found to have a slight decrease with increasing the rate of flow, where it had the values 3.70, 3.70, 3.66, 3.6 for 10, 15, 20 eV and 30 sccm respectively as seen in Fig.(9).

The calculated values of Urbach from Fig.(10) were 0.26, 0.34, 0.40, 0.42 eV for the flow rates 10, 15, 20 and 30 sccm respectively. It is clear that Urbach tails increased with increasing the rate of flow.

![Transmittance spectra of as-prepared Al₂ZnO₄ thin films deposited under different rate of flow.](image1)

Figure 8 Transmittance spectra of as-prepared Al₂ZnO₄ thin films deposited under different rate of flow.

Figure (11) explain the behavior of the refractive index of Al₂ZnO₄ thin films with respect to the incident photon wavelength. It is obvious that the refractive index spectra confirm the normal dispersion. The single oscillator energy and the dispersion energy were calculated from the slope and intercept of the relation \((n^2-1)^{1/2}\) versus \(hv\) as shown in Fig.(12). The calculated values of the single oscillator energy were 1.63, 1.59, 1.58, 1.49 and 1.43 eV for the flow rates 10, 15, 20, 25 and 30 sccm respectively. The calculated dispersion energy were 2.80, 2.84, 2.86, 2.95, 3.12 eV for the rate of flow 10, 15, 20 25 and 30 sccm respectively.

![Plots of Ln(α) vs. photon energy for as-prepared Al₂ZnO₄ thin films deposited under different rate of flow.](image2)

Figure 10 Plots of Ln(α) vs. photon energy for as-prepared Al₂ZnO₄ thin films deposited under different rate of flow.

![Dispersion relation of the refractive index n for the as-prepared Al₂ZnO₄ thin films deposited at different rate of flow.](image3)

Figure 11 Dispersion relation of the refractive index n for the as-prepared Al₂ZnO₄ thin films deposited at different rate of flow.
The change of the optical conductivity with photon wavelength showed that the optical conductivity decreased with increasing the photon wavelength as seen in Fig. (13).

Table 1: Changing optical parameters with respect to thickness of Al$_2$ZnO$_4$ thin films and rate of flow.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$T$ (%)</th>
<th>$E_{op}$ (eV)</th>
<th>$E_u$ (eV)</th>
<th>$E_o$ (eV)</th>
<th>$E_d$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>82</td>
<td>4.20</td>
<td>0.29</td>
<td>3.41</td>
<td>2.93</td>
</tr>
<tr>
<td>200</td>
<td>83</td>
<td>4.15</td>
<td>0.37</td>
<td>3.23</td>
<td>3.08</td>
</tr>
<tr>
<td>300</td>
<td>89</td>
<td>4.08</td>
<td>0.38</td>
<td>3.14</td>
<td>3.27</td>
</tr>
<tr>
<td>400</td>
<td>83</td>
<td>3.90</td>
<td>0.34</td>
<td>2.99</td>
<td>3.51</td>
</tr>
<tr>
<td>500</td>
<td>90</td>
<td>3.85</td>
<td>0.39</td>
<td>2.91</td>
<td>4.04</td>
</tr>
<tr>
<td>600</td>
<td>90</td>
<td>3.80</td>
<td>0.45</td>
<td>2.81</td>
<td>4.36</td>
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<tr>
<td>800</td>
<td>90</td>
<td>3.72</td>
<td>0.47</td>
<td>2.46</td>
<td>5.92</td>
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</table>

<table>
<thead>
<tr>
<th>Rate (sccm)</th>
<th>$T$ (%)</th>
<th>$E_{op}$ (eV)</th>
<th>$E_u$ (eV)</th>
<th>$E_o$ (eV)</th>
<th>$E_d$ (eV)</th>
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<tr>
<td>10</td>
<td>90</td>
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<td>93</td>
<td>----------</td>
<td>----------</td>
<td>1.43</td>
<td>3.12</td>
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</table>

It is clear from table 1 that increasing both the thickness of the films and the rate of flow were accompanied with increasing the maximum values of the transmittance, Urbach tails. Besides, increasing both the film thickness and rate of flow resulted in decreasing the optical energy gap. On the other hand, increasing the rate of flow was accompanied with decreasing dispersion energy.

4 Conclusion

The optical constants of Al$_2$ZnO$_4$ thin films prepared using dc sputtering technique showed that, the optical energy gap $E_{op}$ and single oscillator energy $E_o$ decreased with increasing the film thickness. Whereas, Urbach tails $E_u$, dispersion energy $E_d$ increase with the thickness of the film. The electrical resistivity found to increase with increasing the film thickness, whereas, the carrier concentration found to decrease with increasing the film thickness.

References

[38] F. Urbach, Phys. Rev. 92 (1953) 1324