The Effect of Aluminum Dopant on some physical Properties of Zinc Oxide Thin Films Via Chemical Spray Pyrolysis
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Abstract:
Zinc oxide has been synthesized by using Chemical spray pyrolysis (CSP) method with different Al concentration (0, 2 and 4) at%. XRD styles reveal that these films are polycrystalline hexagonal wurtzite structure, crystallite size was varied from 13.30 nm to 14.34 nm as Aluminum concentration increase. The AFM images displays uniform, crack free and average particle size was in the range (84.27-72.18) nm. Transmittance spectra have an average about 85%. The bandgap is moved to lower energy as Al doping increase.

Keywords: CSP, ZnO: Al thin films, structural and Optical properties.

Introduction
Zinc oxide (ZnO) has gained significant attention as an n-type semiconductor due to its unique characteristics, including a direct band gap of 3.37 eV, high electron mobility, and a substantial exciton binding energy of approximately 60 meV [1]. In order to enhance its physical properties, various metals such as Indium (In), Aluminum (Al), Gallium (Ga), Copper (Cu), and Cadmium (Cd) have been introduced as dopants into ZnO [2-7]. The doping will lead to small lattice deformation and the latter will make it less reactive and more resistive to oxidation [9]. ZnO films are produced utilizing different techniques like SG [10], magnetron sputtering [11], RF sputtering [12], chemical deposition [13], PLD [14], Solid-phase reaction [15], MBE [16], electrodeposition [17], thermal decomposition [18], and CSP [19]. CSP is employed in many applications due to its simplicity and cost-effective. This study seeks to contribute to the existing body of knowledge by focusing on the deposition of ZnO films and exploring the impact of aluminum (Al) additives on specific physical properties. In doing so, we aim to build upon and complement prior research in this field, drawing insights from previous studies conducted on ZnO doped with various metals, and
elucidating how our findings align with or expand upon the current understanding of this promising semiconductor material.

**Experimental**

Thin films of Undoped ZnO and ZnO: Al is deposited by CSP. A solution containing 0.05 M of zinc acetate dihydrate (ZnO (CH$_3$COO)$_2$·2H$_2$O)) was prepared and mixed with 100 mL of deionized water to create the desired solution. A dopant solution was prepared by dissolving 0.1 M of aluminum nitrate nonahydrate (Al(NO$_3$)$_2$·3H$_2$O) in deionized water, resulting in dopant concentrations of 2% and 4% volumetrically. For the deposition process, a sprayer with a base-to-sprayer distance of 29 cm was utilized. The spraying time was set to 8 seconds, and there was a 2-minute time interval between successive sprays. The transport gas used was air, pressurized at 10$^5$ Pa. The thickness of the samples was determined using the weighting method, yielding a thickness of 330 ± 20 nm. To assess the structural properties, X-ray diffractometry was employed. The surface characteristics of the deposited films were investigated using an AA3000 Scanning Probe Microscope (AFM). Additionally, the transmittance spectra were recorded using a UV-Visible spectrophotometer.

**Results and discussions**

**Structural properties**

The XRD patterns are compared with standard ICDD card no. 36-1451. Figure 1 displays the XRD diffraction of the intended films prepared by the CSP technique. In all samples, hexagonal (wurtzite) was observed with predominant peak along [100]. The films offer sundry diffraction peaks at 2θ = 36.80˚, 56.35˚ and 63.250˚ with orientation of (002), (110) and (103) planes respectively. The position of (100) peak is shifted slightly with increasing concentration Al doping. The observation suggests that an excess of dopant can lead to the impairment of the ZnO film's crystal structure. This phenomenon could be attributed to the relatively smaller ionic radius of Al³⁺ (0.054 nm) compared to Zn²⁺ (0.074 nm), which aligns with Vegard's law [20, 21].

The crystallite size (denoted as D) is determined utilizing Debye-Scherrer's formula [22].

$$D = \frac{k\lambda}{\beta \cos \theta} \quad -1$$

where θ is Bragg angle, β is the FWHM and λ is the wavelength of X-ray used and the shape factor k=0.9.
The lattice strain ($\varepsilon$) was gained by the relation given beneath [22].

$$\varepsilon = \frac{\beta \cos \theta}{4} - 2$$

The dislocation densities ($\delta$) was gained by the relation given beneath [22].

$$\delta = \frac{1}{D^2} - 3$$

$D$ shoe increment with increment the concentration of doping, whilst $\varepsilon$ and $\delta$ are decreased with doping. Table.1 summarizes effects of variation in concentration of doping on the structure parameters $S_{\text{para}}$. Fig.2 shows the structure parameters $S_{\text{para}}$ of ZnO thin films with dopant in Al different concentration.

![XRD styles of the grown films.](image-url)
### Table 1. Spara of grown films.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$2\theta$ (°)</th>
<th>(hkl) Plane</th>
<th>FWHM (°)</th>
<th>crystallite size (nm)</th>
<th>Dislocations density ($\times 10^{15}$ lines/m$^2$)</th>
<th>Strain ($\times 10^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped ZnO</td>
<td>36.35</td>
<td>101</td>
<td>0.68</td>
<td>12.30</td>
<td>6.60</td>
<td>2.81</td>
</tr>
<tr>
<td>ZnO: 2 % Al</td>
<td>36.31</td>
<td>101</td>
<td>0.63</td>
<td>13.27</td>
<td>5.67</td>
<td>2.61</td>
</tr>
<tr>
<td>ZnO: 4 % Al</td>
<td>36.27</td>
<td>101</td>
<td>0.58</td>
<td>14.34</td>
<td>4.86</td>
<td>2.41</td>
</tr>
</tbody>
</table>

**Fig. 2.** X-ray parameter of Undoped and ZnO: Al films.
AFM Analysis

Figure 3 shows 78nm × 78 nm AFM images obtained for the deposited films. ZnO film shows a homogeneous distribution of grains, but the doped films have a greater vertical Particle size in comparison with Undoped ZnO. The surface roughness (rms) is presented in Table 2. There is a decrement in rms via increment of Al content. The kinetic mechanism in charge of this, showing a decrease in surface diffusion [23,24].

Fig.3. AFM of Undoped and ZnO: Al films.
Table 2. AFM parameter measurement of Undoped and ZnO: Al films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Average Particle size (nm)</th>
<th>$R_a$ (nm)</th>
<th>R. M. S. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped ZnO</td>
<td>84.27</td>
<td>6.82</td>
<td>9.82</td>
</tr>
<tr>
<td>ZnO: 2% Al</td>
<td>76.35</td>
<td>4.37</td>
<td>6.29</td>
</tr>
<tr>
<td>ZnO: 4% Al</td>
<td>72.18</td>
<td>3.64</td>
<td>4.28</td>
</tr>
</tbody>
</table>

**Optical analysis**

The transmittance (T), is gained by,

$$T\% = \frac{I}{I_o} \times 100$$

where $I$ is light intensity after it push through the sample and $I_o$ is the premier light intensity.

Apologies for any confusion earlier. The correct relationship between absorbance (A) and transmittance (T) is given by the Beer-Lambert Law:

$$A = -\log_{10} \left( \frac{I}{I_o} \right)$$

Fig. 4. Offers T of deposited films. T is transparent with transmission override 80–90 % in the visible area. The optical transmittance decrease with increase doping in Al, which might be due to low, impurities and lattice defects [25].
Fig. 4. Transmittance of Undoped and ZnO: Al films.

The absorption coefficient $\alpha$ was determined using the relation [26]:

$$\alpha = \ln \left( \frac{1/T}{t} \right)$$

where $t$ is film thickness. Fig. 5. Illustrate the relation between $T$ and $\lambda$. 
Fig. 5. $\alpha$ of Undoped and ZnO: Al films with different dopant.

$\alpha$ and photon energy ($h\nu$) can be written as [27]:

$$\alpha h\nu = B (h\nu - E_g)^r$$

where $E_g$ is the on-band gap and $B$ is constant, and the exponent ($r$) = 1/2 for direct transition.

Band gap decreases with Al content. This implies that the addition of Al enhances the structure of the sample as expected. As dopants can introduce additional energy levels within the band structure, effectively shifting the band edges and reducing the band gap. However, this variation of energy gap (from 3.34 to 3.26 eV) is really small because a small amount of Al is added. By adding a trace amount of Al, expected the conductivity of ZnO can be improved without [28]. The value of energy gap of ZnO film agrees with norm value of (3.2 to 3.3) eV.
The refractive index (n) is gained from the reflectance (R) employing the relation [29]:

\[ R = \frac{(n - 1)^2}{(n + 1)^2} \]

The extinction coefficient k is gained from the relation [30]:

\[ k = \frac{a\lambda}{4\pi} \]

The values of (n, k) versus wavelength are offered in Figs. (7, 8). n decreases from 3.54 to 3.25 from 420 nm to 550 nm, This decrease in n can be attributed to the dispersion of light, where shorter wavelengths are more strongly affected by the material's electronic structure. Beyond 550 nm, you mentioned that n becomes almost constant with the decrement of photon energy (hv). This behavior suggests that in this wavelength range, the electronic structure of the material is less influenced by changes in photon energy. K decreases with the increase of doping which might be due to low...
band tailing effect and defects, indicating that the material becomes more transparent or exhibits less light absorption [31].

Fig. 7. k of grown films
Conclusion

Undoped ZnO and ZnO: Al nanostructured thin films were synthesized by CSP method. The X-ray diffraction analysis of both undoped ZnO and ZnO:Al nanostructured thin films confirmed the presence of a polycrystalline hexagonal structure. The crystallite size ranged from 12.3 nm to 14.34 nm. This suggests that the films exhibited well-defined crystalline characteristics. Atomic Force Microscopy (AFM) investigations revealed that the addition of aluminum (Al) dopant led to a decrease in surface roughness compared to undoped ZnO films. Additionally, the particle size of the films was found to be in the range of 84.27 nm to 72.18 nm. These results suggest that the introduction of Al dopants contributes to smoother film surfaces and smaller particle sizes.

An important finding was the high transmittance observed in all thin films. This high transmittance indicates that both undoped ZnO and Al-doped ZnO films are suitable for use in electronic devices, particularly in applications where transparency is essential, such as displays and photovoltaic devices. The determined band gap values for the films ranged from 3.34 eV to 3.26 eV. This suggests that Al doping had a slight impact on the band gap of ZnO.
The variation in band gap values may be attributed to the different Al doping levels or the crystallite size variations observed in the films.

References

تأثير التنشوب بالألمنيوم على بعض الخواص الفيزيائية لأغشية أوكسيد الزئبق الرقيقة المحضرة

بطرية الترسيب الكيميائي الحراري

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منطقة الرابطة

الكلمات المفتاحية: الترسيب الكيميائي الحراري ، اغشية ZnO: Al، الخصائص التركيبية والبصرية.