The role of aluminum doping on structural and optical properties of ZnO thin films prepared by PLD

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Abstract.
In this work, pure and doped ZnO thin films with different Al wt% concentration were prepared using pulsed laser deposition technique on clean glass substrates at room temperature. Then investigate the effect of Al concentration on the structural and optical properties for the as deposited ZnO thin films. The structure of the prepared ZnO powder and thin films were examined by X-ray diffraction, whereas the optical properties of prepared thin films were characterized and investigated using UV-VIS-NIR spectrophotometer. The structure of powder and prepared pure and doped ZnO thin films were polycrystalline. Powder, pure and Al doped ZnO thin films were synthesized in hexagonal phase and the dominate orientation is (101). The crystallite size for (101) plane is increased with increasing Al wt%. The optical energy gap of doped ZnO thin film increased with increasing doping weight concentration. These make the prepared films as good candidate for gas sensor.

Keywords:

1. Introduction
Zinc Oxide (ZnO) films have become technologically important because of their range of electrical and optical properties, together with their high chemical and mechanical stabilities, which make them suitable for a variety of applications such as flat panel display electrodes, gas sensors and antibacterial agent [1,2]. ZnO is an n-type semiconductor from II-VI group having wurtzite crystal structure, with wide and direct band gap of 3.37 eV. It is generally used in optoelectronic devices especially for blue and UV emissions, like laser diodes [3, 4]. There are many elements doped with ZnO were used different techniques for various applications [5-8]. The doping of ZnO films with the group III components can increase the conductivity of the films, by comparison with other elements and aluminum is the best dopant [7, 9-12]. There are several techniques used for fabricating ZnO films, for example chemical vapour depositions [8], pulsed laser deposition, dc reactive sputtering [6], spray pyrolysis and sol–gel process [7, 13]. Among these techniques, PLD has unique advantages such as: stoichiometric deposition, easy control of experimental parameters and a naturally clean process. Through the preparation of ZnO thin films, the growth condition such as substrate type, deposition temperature, background gas pressure and laser energy density, have great influence on the crystal quality of ZnO film and cause a change in its structural and optical properties [14].
In this paper, pure and doped ZnO thin films with different Al concentration were grown using pulsed laser deposition technique from prepared powder, then study the role of Al wt% concentration on structural and optical properties of all prepared thin films.

2. Experimental Work

2.1 Sample preparation

The targets were composited of pure (ZnO) and doped (ZnO: Al) powder with high purity (99.999%). Different Al concentrations (3, 5, 7, 10) wt.% were mixed together and prepared by pressing them under 5 Ton for time of 10 minutes to form a target of 2.5 cm diameter. ZnO:Al thin films were prepared on clean substrate using pulsed laser deposition (PLD) method (Nd: YAG (Huafei Tongda Technology—DIAMOND-288 pattern EPLS) (SHG Q-switching beam) as shown in figure (1) which housing inside a vacuum chamber of 10-3Torr.

2.2 Sample Characterization

The optical measurements (transmittance and absorbance spectra) were recorded, in the wavelength range (190-1100) nm using UV-VIS-NIR spectrophotometer at room temperature. The XRD parameters of ZnO powder and films, transmittance and energy gap were calculated for ZnO thin films as a function of different Al concentrations.

3. Results and Discussion

The crystal structure and various structural parameters of the prepared powder, pure and Al doped ZnO thin films with different concentration (3, 5, 7, 10) wt% were analyzed from X-ray diffraction (XRD) patterns. Figure 2 display the X-ray diffraction patterns of ZnO powder. X-ray diffraction peaks showed that all samples had a polycrystalline structure. Eleven peaks were observed at 2θ = 31.77°, 2θ = 34.43°, 2θ = 36.26°, 2θ = 47.58°, 2θ = 56.62°, 2θ = 62.86°, 2θ = 66.40°, 2θ = 67.97°, 2θ = 69.10°, 2θ = 72.57° and 2θ = 76.98° corresponding to the wurtzite hexagonal phase of ZnO matching to the lattice planes of (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) plans respectively. These values are matched with values in the standard card number (96-901-1663), (96-901-1664) and (96-901-1665). The
dominate peak is for the plan (101) orientation. The average crystallite size (C.S Av) is 46.28 nm. Table (1) illustrates the X-ray parameters for the ZnO powder.

![X-ray patterns of ZnO powder.](image)

**Table 1.** XRD parameters for ZnO powder.

| 2θ_{Exp} (Deg.) | d_{Exp} (Å) | d_{Std} (Å) | FWHM (Deg.) | C.S (nm) | C.S_{Av} (nm) | hkl | Phase | Card No. ASTM |
|----------------|-------------|-------------|--------------|----------|----------------|-----|--------|---------------|
| 31.7757        | 2.8138      | 2.8137      | 0.2103       | 39.3     | 46.28          | (100)| Hex.   | 96-901-1663   |
| 34.4393        | 2.6021      | 2.6035      | 0.1752       | 47.5     | (002)          |     | ZnO    |               |
| 36.2617        | 2.4754      | 2.4754      | 0.2103       | 39.8     | (101)          |     |        |               |
| 47.5818        | 1.9095      | 1.9110      | 0.2454       | 35.4     | (102)          |     |        |               |
| 56.6238        | 1.6242      | 1.6245      | 0.2103       | 42.9     | (110)          |     |        |               |
| 62.8621        | 1.4772      | 1.4772      | 0.2102       | 44.3     | (103)          |     |        |               |
| 66.4019        | 1.4067      | 1.4069      | 0.1753       | 54.2     | (200)          |     |        |               |
| 67.9790        | 1.3779      | 1.3782      | 0.2103       | 45.6     | (112)          |     |        |               |
| 69.1005        | 1.3582      | 1.3582      | 0.2103       | 45.9     | (201)          |     |        |               |
| 72.5701        | 1.0316      | 1.3017      | 0.1752       | 56.3     | (004)          |     |        | 96-901-1664   |
| 76.9860        | 1.2376      | 1.2377      | 0.1753       | 57.9     | (202)          |     |        | 96-901-1665   |

Figure 3 display the X-ray diffraction patterns of pure and doped ZnO thin film with different concentration of Al metal. Nine peaks were observed at 2θ=31.77°, 2θ=34.41°, 2θ=36.23°, 2θ=47.51°, 2θ =56.54°, 2θ =62.80°, 2θ =66.27°, 2θ =67.87° and 2θ= 68.98° corresponding to (100), (002), (101), (102), (110), (103), (200), (112) and (201) plans for ZnO thin films respectively. These values are matched with values in the standard card number (96-901-1663). Two peaks were disappeared for (004) and (202) orientation as compared with that was shown in figure (2) for ZnO powder. The samples which
investigated were prepared at room temperature without any treatment, so, the samples have polycrystalline structure.

The prepared films exhibit a dominant peak corresponding to the (101) plan of ZnO. Presence of various peaks corresponding to plans (100), (002), (101), (102), (110), (103), (200), (112) and (201) suggests polycrystalline nature of the prepared thin film. One can observe that phases for all peaks were hexagonal.

Another noticeable remark is that the angle value is slightly shifted towards lower angle when ZnO thin film doped with Al for (101) orientation which is due to stresses within the lattice caused by doping and crystalline defects [15]. This indicates that the lattice parameters of the Al doped ZnO films are larger than that of pure ZnO thin films (Table 3). Such an increment in lattice parameter can be attributed to the different ionic radius of Al3+ (0.053 nm) comparing to that of Zn2+ (0.074 nm)[16]. The variation in lattice parameter signifies the incorporation of Al3+ due to doping also introduces stress in the film. Substitution replacement of smaller size Al3+ was resulted in a tensile stress [17, 18].

The average value of crystallites size (C.S) was measured by using Scherrer equation [19]:

\[ C.S = \frac{k\lambda}{\beta \cos \theta} \]  

In this relation, k is the shape factor having value 0.94, \( \lambda \) is wavelength of the Cu Ka (1.5414 Å), \( \beta \) is full width of half maximum (FWHM) in radian and \( \theta \) is the Bragg’s angle in degree.

Table 2 illustrates the values of Bragg’s diffraction angles (2θ), full width of half maximum (FWHM), inter-planer distance (dhkl), the crystallite size (C.S), and the corresponding Miller indices of the standard cards (hkl) for pure and doped ZnO with different Al concentrations.

The full width of the peaks changed due to the change in strain applied on lattice due to the particle size change (eq.1). The crystallite size at (101) orientation is increased with increasing Al, whereas the average crystallite size value varied unsystematic with increasing Al wt% concentration from 0 to 10.
Figure 3. X-ray patterns of pure ZnO films and doped ZnO thin film with different Al wt% concentrations (a) 0,(b) 3,(c)5,(d)7,(e)10.

Table 2 XRD parameter for pure and doped ZnO thin film with different Al wt% concentrations (3, 5, 7 and 10).
| Al wt% | 2θ (Deg.) | d_{hkl} Exp. (Å) | d_{hkl} Std. (Å) | FWHM (Deg.) | C.S (nm) | C.S_{(hkl)} (nm) | (hkl) | Phase | C.S | Card No. | ASTM |
|--------|-----------|-----------------|-----------------|-------------|---------|-----------------|-------|-------|-----|----------|-------|
| 0      | 47.5110   | 1.9122          | 1.9110          | 0.2127      | 40.8    | (102)           |       | Hex.  |     | 96-901-1665 |       |
|        | 56.5400   | 1.6264          | 1.6245          | 0.1415      | 63.8    | (110)           |       | Hex.  |     | 96-901-1665 |       |
|        | 62.8020   | 1.4784          | 1.4772          | 0.1825      | 51.0    | (103)           |       | Hex.  |     | 96-901-1663 |       |
|        | 66.2760   | 1.4091          | 1.4069          | 0.2004      | 47.4    | (200)           |       | Hex.  |     | 96-901-1663 |       |
|        | 67.8720   | 1.3798          | 1.3782          | 0.2216      | 43.2    | (112)           |       | Hex.  |     | 96-901-1663 |       |
|        | 68.9830   | 1.3603          | 1.3582          | 0.1745      | 55.3    | (201)           |       | Hex.  |     | 96-901-1663 |       |
|        | 31.7350   | 2.8137          | 2.8137          | 0.1629      | 50.7    | (100)           |       | Hex.  |     | 96-901-1663 |       |
|        | 34.4190   | 2.6035          | 2.6035          | 0.1698      | 49.0    | (002)           |       | Hex.  |     | 96-901-1663 |       |
|        | 36.2390   | 2.4768          | 2.4754          | 0.1686      | 49.6    | (101)           |       | Hex.  |     | 96-901-1663 |       |
|        | 47.5110   | 1.9122          | 1.9110          | 0.2127      | 40.8    | (102)           |       | Hex.  |     | 96-901-1665 |       |
|        | 56.5400   | 1.6264          | 1.6245          | 0.1415      | 63.8    | (110)           |       | Hex.  |     | 96-901-1665 |       |
|        | 62.8020   | 1.4784          | 1.4772          | 0.1825      | 51.0    | (103)           |       | Hex.  |     | 96-901-1663 |       |
|        | 66.2760   | 1.4091          | 1.4069          | 0.2004      | 47.4    | (200)           |       | Hex.  |     | 96-901-1663 |       |
|        | 67.8720   | 1.3798          | 1.3782          | 0.2216      | 43.2    | (112)           |       | Hex.  |     | 96-901-1663 |       |
|        | 68.9830   | 1.3603          | 1.3582          | 0.1745      | 55.3    | (201)           |       | Hex.  |     | 96-901-1663 |       |
|        | 31.7350   | 2.8137          | 2.8137          | 0.1629      | 50.7    | (100)           |       | Hex.  |     | 96-901-1663 |       |
|        | 34.4190   | 2.6035          | 2.6035          | 0.1698      | 49.0    | (002)           |       | Hex.  |     | 96-901-1663 |       |
|        | 36.2390   | 2.4768          | 2.4754          | 0.1686      | 49.6    | (101)           |       | Hex.  |     | 96-901-1663 |       |
Table 3 and figures 4 (a and b) show the variation of lattice constants for hexagonal pure and doped ZnO thin films. The lattice constant (a) reduced to a minimum value of 3.2533 Å with increase of Al to 3% for the prepared thin films and then increase by increasing Al up to 7% after that it remain constant. On the other hand, it’s observed that the lattice constant (c) has adverse behavior with this parameter, i.e., it increases with increasing Al concentration and the maximum value of lattice constant (c) is 5.2216 Å at 7% Al then it decreases to 5.2185 nm at 10%.

Table 3. Lattice constants for pure and Al doped ZnO thin films at different concentrations.

| Al wt % | a (Å) | c (Å) | Average C.S (nm) |
|---------|-------|-------|------------------|
| 0       | 3.2542 | 5.2071 | 50.1            |
| 3       | 3.2533 | 5.2127 | 73.4            |
| 5       | 3.2551 | 5.2185 | 48.9            |
| 7       | 3.2559 | 5.2216 | 60.6            |
| 10      | 3.2559 | 5.2185 | 54.3            |

Figure 4. Variation of lattice constants vs Al wt% concentration for pure and doped ZnO thin films (a) a and (b) c.

Figure (5) shows the transmittance (T) spectrum for pure and doped ZnO thin films through which study the effect of the Al on their optical properties. It can be observed that the optical transmittance is increased suddenly at wavelength more than 130 nm then become nearly constant at wavelength ≥180 nm, while having low values at short wavelength because only photons with energy equal to or greater than the energy difference between the valence and conduction bands interact with valence electrons creating a pair of electron-hole. It is also observed that the transmittance has maximum value for ZnO doped with 7% Al concentration, whereas the minimum value is at ZnO doped with 3%. Another noticeable remark is that the value of T decreases with other Al doping (5 and 10) %. This may be due to the change in the crystallization rate or because of the change in the value of the energy gap.
The amount of energy gap is one of the most important parameters that determine thin films applications. The direct optical gap of the samples was calculated using the Tauc formula [20], where the optical energy gap was calculated from the graphing between $(\alpha h\nu)^2$ as a function of the photon energy $(h\nu)$.

Determining the energy gap $(E_g)$ from the tangent intersects point of the linear region with the x-axis according to equation [20]:

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

where $\alpha$ is absorption coefficient and $B$ is factor inversely proportional to amorphousity.

Figures 6 (a-e) show the change in the value of the direct optical energy gap with the various Al wt% concentrations in zinc oxide. On can observe there are two energies gap which is confirming the polycrystalline structure of prepared films.

These figures show that increasing the Al concentration (0,3,5,7 and 10 wt%) has increased its transparency and energy gap values $(E_g2)$ (3.35, 3.70, 3.87 and 3.98) eV respectively. Whereas the lower energy gap $(E_g1)$ is varied (2.0, 2.3, 2.0, 3.1 and 2.78) eV with increasing Al concentration from 0 to 10% respectively. The low values of the band gap $(E_g1)$ may be due to the existence of tail states within the band gap and the absorption edge is not sharp. There are several factors that change the value of the optical band gap, such as the difference in distance between the atoms due to lattice distortion. The difference in the values of the energy gap from the standard values is due to preparation conditions.
Figure 6. $(\alpha h\nu)^2$ versus $(h\nu)$ for doped ZnO thin films at different Al wt% concentration (a) pure (b) 3 (c) 5 (d) 7 (e) 10.

4. Conclusions
The results of examination of as deposited ZnO thin films prepared on glass substrates at different Al wt% concentration using PLD technique are summarized as following:
Powder, pure and Al doped ZnO thin films were synthesized a polycrystalline structures with hexagonal phase. The best sample crystallinity appeared for (101) orientation for pure and doped ZnO thin films. The crystallite size for all prepared thin films at (101) orientation is increased with increasing Al concentration, whereas the average crystallite size value varied unsystematic with increasing Al concentration from 0 to 10%. The increasing Al concentration in ZnO thin films leads to increase transparency and in turn increase energy gap with values more than standard value for bulk samples.

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