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REGULAR ARTICLE

Properties of ZnO and Al Doped ZnO Thin Films Prepared by Spray Pyrolysis

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The Highly transparent and conducting aluminum doped zinc oxide thin films deposited on glass substrate held at 450°C using spray pyrolysis method. The structural analysis by X-rays diffraction showed that the films are of structure wurtzite with a preferential orientation according to the direction (002) for oxide zinc ZnO undoped, on the other that ZnO: Al has a direction (101). The crystallite size was varied from 34 to 36 nm with dopant concentration. The scanning electron microscopy results depicted that the microstructure of ZnO: Al films highly influenced by the aluminum doping. The measures optical showed that ZnO: Al layers have a transmission of about 85% and energy gap of 3.2 eV, 3.4 eV for ZnO:Al and ZnO respectively. The resistivity of the films decreased as increase the dopant concentration and it is 3×10^{-2} Ω cm for 1 at.% Al beyond which it increased.

Keywords: ZnO, ZnO:Al, Spray, Microstructural analyze, Electric and optical properties.

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1. INTRODUCTION

Due to the excellent electrical, optical and structural properties, Zinc oxide (ZnO) thin films have wide applications as ultraviolet (UV) sensors, photodetector sensor [1-2]. So far, the focus of most of the studies has been to extend their practical applications. The ZnO films showed a good chemical stability [3], what is important in the photodetection. I also believe that the structural defects of ZnO play a very important role in UV photosensitivity [4]. The ZnO is also used in radiation detection [5-8]. Generally, in undoped ZnO, the *n*-type conductivity has been attributed to hydrogen impurities, on the other hand, doping with Al increases the impurities in ZnO especially with the production methods. On the other hand, aluminum (Al) doping is a common method used to modify the conductivity type. There are different methods to prepare zinc oxide, such as RF magnetron sputtering [9], chemical vapor deposition [10], sol-gel [11] and spray pyrolysis [12-16] Among these methods, spray pyrolysis is better for large area thin film formation and easy doping. In this work, thin films of ZnO undoped and Al doped were prepared by spray pyrolysis onto glass substrates. The Microstructural, electrical and optical characterizations of thin films is studied.

2. EXPERIMENTAL PROCEDURE

Doped ZnO thin films have been deposited onto the glass substrates at 450 °C. 0.2 M solution of zinc acetate dehydrate (Zn (CH_3COO) 2-2H_2O) diluted in methanol was used for all the films, and aluminum chloride ($AlCl_3$), were added to starting solution as a dopant. The Al/Zn ratio were 0 to 2%. The starting solution was mixed thoroughly and final solution was sprayed. The nozzle substrate separation used was of 25 cm. During the spraying process, the substrates were heated by electrically heating plate. The flow of the solution was 2 ml/min and gaseous nitrogen was used as a carrier gas. Substrate temperature was controlled by means of thermocouple. After depositing the film, it was allowed to cool to room temperature. The films thickness was 0.5 μm, which was measured by Scanning electron micros-copy FEG, the Structural properties of the ZnO: Al thin films were performed through X-ray diffraction (XRD), using the Cu-Kα ($\lambda = 1.54056$ A°) radiation. The electrical sheet resistance of the ZnO: Al thin films was measured with the four-point, the measurement of transmittance taking air as the reference and ranging from 300 to 1100 nm was made by a UV-Visible spectrophotometer.

3. RESULT AND DISCUSSION

3.1 X-ray Diffraction

The X-rays pattern spectra of pure and ZnO: Al were displayed in Fig. 1. All the peaks of the thin films correspond to the peaks of standard ZnO (JCPDS N°:00-005-0664). The as-grown films were identified as polycrystalline ZnO with a hex-agonal crystal structure. For all the samples, (100), (101) and (002) diffraction peaks are observed in the XRD pattern, showing the growth of ZnO:Al crystallites along different directions. Strong preferential growth is observed along (002) plane indicating that the films ZnO pure are oriented along *c*-axis [10] and orientation

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for (101) for ZnO:Al 0.5, 1, 1.5 % and 2 % wt. The calculated structural parameters such as the grain size (D), the lattice parameters (a) and (c), the textural coefficient (TC) and the dislocation density (δ), reported previously, are gathered in Table 1.

The lattice parameters (a) and (c) were deter-mined from the expression 1 according to (200) direction.

$$\frac{1}{d_{hkl}} = \sqrt{\frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}} \quad (1)$$

The grain size of crystallites was calculated using a well-known Scherrer's formula [12]:

$$D = \frac{(0.9\lambda)}{\beta \cos\theta_{(hkl)}} \quad (2)$$

Where D is the grain size of crystallite, λ (1.54059 A) the wavelength of X-rays used, β the broadening of diffraction line measured at half its maximum intensity in radians and θ is the angle of diffraction. The textural coefficient (TC) of the thin films is estimated using the Eq. 3:

$$TC_{hkl} = \frac{I_{hkl}}{\sum I^i_{hkl}} \quad (3)$$

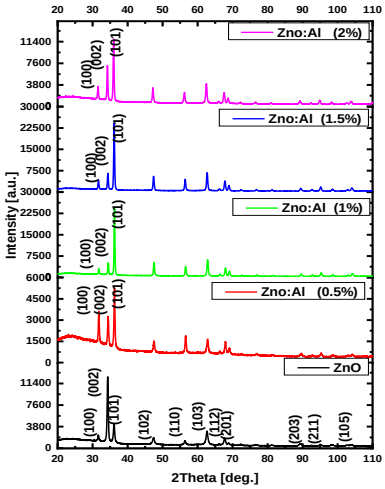

Fig. 1 – XRD patterns of ZnO and Al-doped ZnO films by spray pyrolysis deposition

The dislocation density (δ), defined as the length of dislocation lines per unit volume, are estimated using the Eq. 4:

$$\delta = \frac{1}{D^2} \quad (4)$$

The grain size is estimated at 36.09 and 36.21 nm according to (101) direction of undoped ZnO and ZnO: Al 1% respectively. Therefore, the crystallites are nanosized.

We noticed that the lattice parameters (a) and (c) changed with Al doping levels, in comparison with ZnO Standard (a = 3.2490 Å and c = 5.2050 Å (JCPDS N°:00-005-0664). The results were consistent with the improvement of the grain size and shape of the films depicted in the SEM images.

3.2 Surface Morphologies and EDX Analysis

Fig. 2 shows the scanning electron micrographs for ZnO films deposited at 450 °C with different concentrations Al. All micrographs show surface covered by uniformly grains distributed, with nanometric sizes [8]. It can also be noticed that the microstructure of the films is influenced by the variation in the Al doping concen-tration. For [Al/Zn] = 0 and 0.5 wt % ZnO: Al thin film, the surface is covered by plane hexagonal flake-like (Fig. 2 a-b), whereas for [Al/Zn] = 1, 1.5 and 2 wt % films (Fig. 2 c-d-e), the surface is covered by grains with elongated poles. This change was discovered by Larbah et all in his works [12]. This explanation was con-firmed by the change in orientation from 002 to 101. So, the hexagonal-shaped particles have an orientation of 002, and the other shape has an orientation of 101.

As an example, the film thickness (500 nm) of ZnO:Al 2 wt % thin film is observed by ESEM image in Fig. 2 f. The composition of ZnO and ZnO: Al is detected by EDS (Fig. 3). The 0.76 % at Al in pure ZnO is representing the Al concentration in the substrate. The difference between the concentration of Al in substrate and thin film represents 1.19 % at, so the Al content of the film is nearly the same as that in the solution.

3.3 Optical Properties

Fig. 4 presents the optical transmittance in the wavelength range (300-1100 nm) for the ZnO and ZnO:Al thin films deposited at T = 450°C. All thin films exhibit a high transmittance about (80 – 90) % in the visible. To determinate the gap energy of direct transition (E_g) of the ZnO thin films, optical method was used. The gap energy value is estimated using Tauc plot $(\alpha h\nu)^2$ against the photon energy for ZnO. The linear intercept at the ($h\nu$) axis gives the value of the direct band gap. The optical energy band gap of the films presents in Fig. 5. The band gap values were in the order of 3.29 eV for ZnO and 2.23 eV, 3.25 eV to 1 % and 2 % Al respected, these values of the optical gap are comparable with those found by A. Ashour and al. [17]. This reduction in gap with the rate of doping is primarily due to distortions caused in the network following the introduction of impurity (doping) and with the increase in concentration of the free electrons.

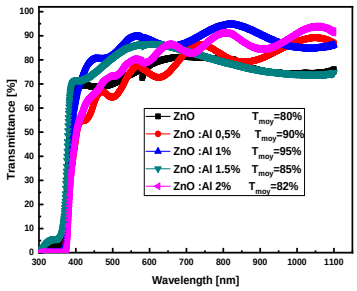

Fig. 4 – Transmittance spectra of ZnO as function of [Al]/[Zn] %

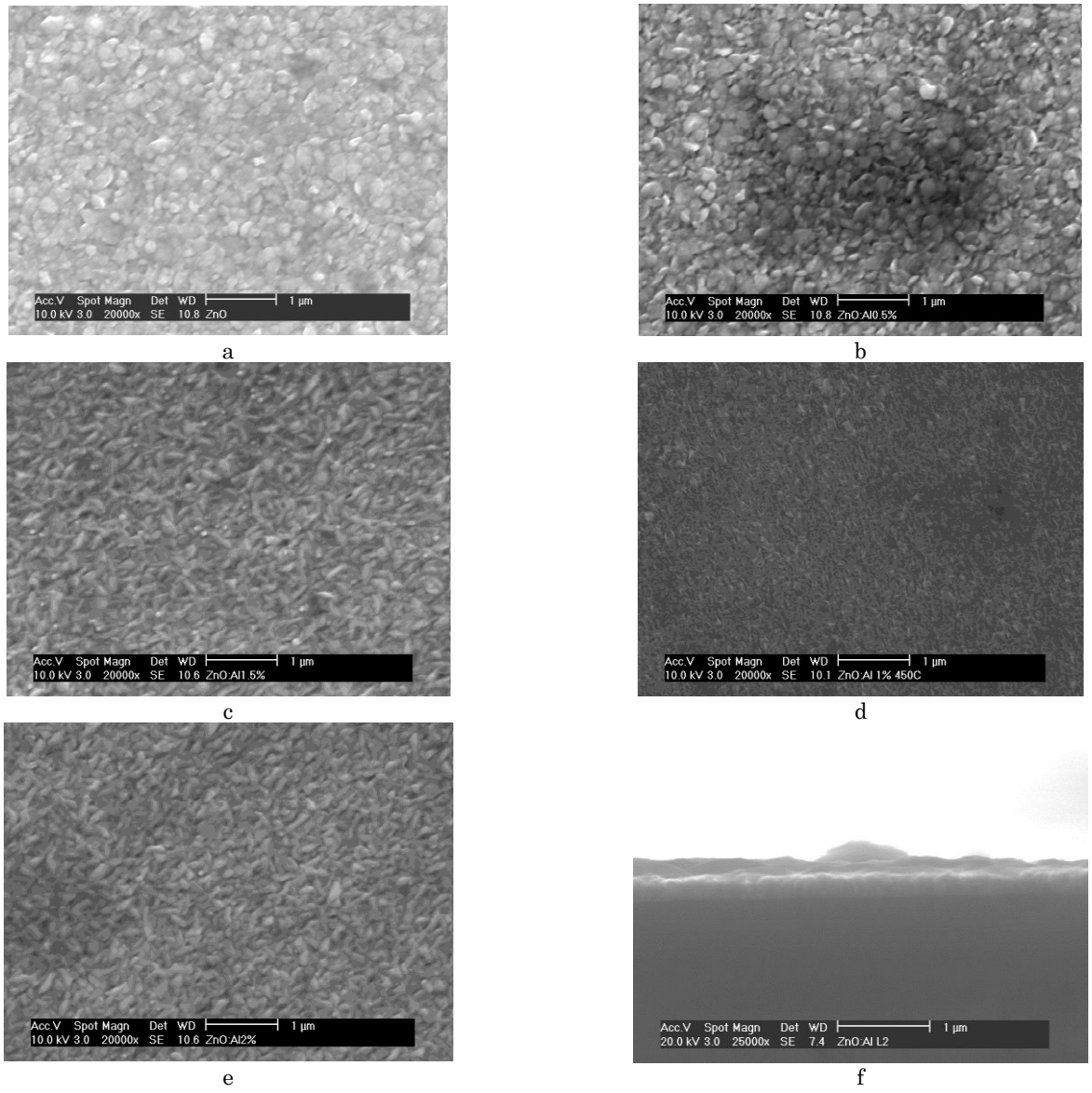

Fig. 2 – SEM photographs of the surfaces of a) ZnO, b-c-d-e) ZnO:Al films with different concentration and f)thickness of ZnO:Al 2 % thin film

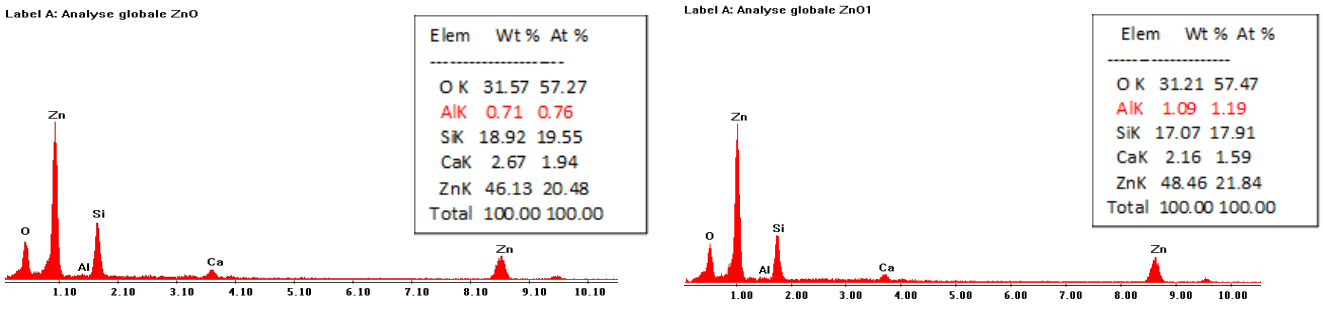

Fig. 3 – Energy dispersive X-ray spectrum (EDS) of ZnO and ZnO: Al (1 %)

Table 1 – Structural parameters of Al-doped ZnO thin film

	Planes	2Th [°]	FWHM [°]	Crystallite size *D* [nm]	TC	*a* [Å]	*c* [Å]
ZnO pure	(100)	31.685	0.297	31.61	0.08	3.258	5.229
	(002)	34.277	0.372	34.29	0.50		
	(101)	36.106	0.334	36.09	0.35		
ZnO 0.5%Al	(100)	31.774	0.300	31.72	0.14	3.249	5.203
	(002)	34.443	0.305	34.42	0.19		
	(101)	36.196	0.297	36.22	0.30		
ZnO 1 % Al	(100)	31.693	0.260	31.74	0.06	3.380	5.204
	(002)	34.438	0.297	34.44	0.09		
	(101)	36.192	0.297	36.21	0.47		
ZnO 1.5% Al	(100)	31.541	0.260	31.53	0.10	3.272	5.238
	(002)	34.209	0.297	34.20	0.20		
	(101)	36.039	0.3348	36.00	0.34		
ZnO 2 % Al	(100)	31.696	0.2604	31.66	0.13	3.25706	5.22636
	(002)	34.288	0.6696	34.30	0.16		
	(101)	36.118	0.3348	36.07	0.35		

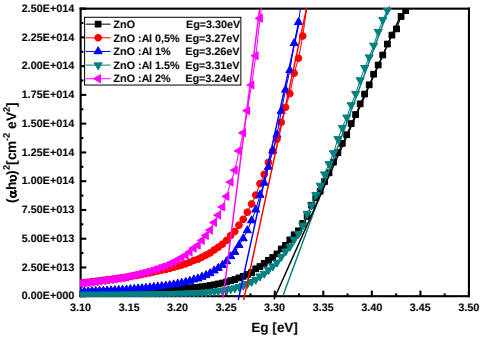

Fig. 5 – A Tauc plot for pure and Al-doped ZnO thin films as a function of photon energy

3.4 Electrical Studies

The electrical resistivity ρ of pure and Al-doped ZnO was shown in Fig. 6. The resistivity has been found to vary from 0.03 to 64 Ω·cm, the minimum value of 3×10^{-2} Ω·cm for the films ZnO 1 %Al. This is due because Al, which occupied lattice sites of zinc, resulting in more free charges It is found that the mobility and the carrier concentration n increase with the Al concentration. When a small amount of Al was introduced into ZnO films, the Al was ionized into Al^{3+} and substituted for Zn^{2+}. Also, a larger grains size induced a reduction in the film resistivity. Our results corroborate with those found in literature, for the ZnO: Al layers prepared at 450 °C, M. de la L. Olvera et al. have found the resistivity of 3×10^{-2} Ω·cm [18]. The thermoelectric determination of the type of conductivity of the film by the technique of the heated electrode enabled us to confirm that our film has a conductivity of the type N [19] for ZnO and ZnO:Al.

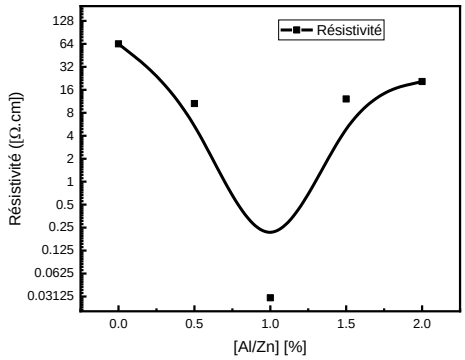

Fig. 6 – Variation of film resistivity (ρ) of ZnO pure and ZnO:Al with different concentration

4. CONCLUSION

We studied the structural, optical, and electrical properties of ZnO: Al thin films with thicknesses ranging from 600 nm for applications solar cell applications. The XRD results showed that the increasing Al concentration resulted in a predominant peak change from (100) to (002). The average optical transmittance was greater than 85 % in the visible range with an absorption edge shift due to the Burstein-Moss shift. The lowest resistivity was 3×10^{-2} (Ω cm) with an Al content of 1 wt. % in the 500 nm thick ZnO:Al.

REFERENCES

1. S.K. Mishra, U.K. Tripathi, R. Kumar, R.K. Shukla, *Mater. Lett.* **308**, Part B, 131242 (2022).
2. K. Liu, M. Sakurai, M. Aono, *Sensors* **10** No 9, 8604 (2010).
3. Y. Larbah, M. Adnane, T. Sahraoui, *Mater. Sci.-Poland*, **33** No 3, 491 (2015).
4. S. Mondal, S. Ghosh, D. Basak, *Mater. Res. Bull.* **144** 111490

(2021).
5. S. Pramanik, S. Mukherjee, S. Dey, S. Mukherjee, S. Das, T. Ghosh, P.K. Kuiri, *J. Lumin.* **251**, 119156 (2022).
6. S. Alamdari, M.H.M. Ara, M.J. Tafreshi, *Opt. Laser Technol.* **151**, 107990 (2022).
7. S. Sahi, W. Chen, *Radiation Measurements* **59**, 139 (2013).
8. A.F. Aldosary, M.A. Shar, H.R. AlQahtani, *Measurement: Sensors* **24**, 100600 (2022).
9. M. Bouderbala, S. Hamzaoui, A.B. Stambouli, H. Bouziane, *Appl. Energy* **64** No 1-4, 89 (1999).
10. X.J. Qin, L. Zhao, G.J. Shao, N. Wang, *Thin Solid Films* **542**, 144 (2013).
11. B. Rahal, B. Boudine, Y. Larbah, L. Guerbous, M. Sebais, O. Halimi, M. Siad, *J. Optik* **169**, 303 (2018).
12. Y. Larbah, M. Adnane, B. Rahal, *Semiconductors* **54**, 1439 (2020).
13. Y. Larbah, M. Adnane, A. Djelloul, M. Melouki, *J. Nano-Electron. Phys.* **7** No 3, 03013 (2015).
14. Y. Larbah, B. Rahal, M. Adnane, *J. Optoelectron. Adv. Mater.* **22**, 518 (2020).
15. X. Zi-qiang, D. Hong, L. Yan, C. Hang, *Mater. Sci. Semicond. Proc.* **9** No 1-3, 132 (2006).
16. P. Scherrer, G. Gött, *Nachr.amp;ouml;tt. Nachr.* **2**, 98 (1918).
17. A. Ashour, M.A. Kaid, N.Z. El-Sayed, A.A. Ibrahim, *Appl. Surf. Sci.* **252**, 7844 (2006).
18. M. de la L. Olvera, A. Maldonado, J. Vega-Pérez, O. Solorza-Feria, *Mater. Sci. Eng. B* **174**, 42 (2010).
19. B. Rahal, B. Boudine, A.R. Khantoul, M. Sebais, O. Halimi, *J. Optik* **127**, 6943 (2016).

Властивості тонких плівок ZnO, легованих ZnO та Al, отриманих розпилювальним піролізом

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Високопрозорі та електропровідні тонкі плівки оксиду цинку, леговані алюмінієм, нанесені на скляну підкладку, що витримується при 450 °C методом розпилювального піролізу. Структурний аналіз за допомогою рентгенівської дифракції показав, що плівки мають структуру вюрциту з переважною орієнтацією відповідно до напрямку (002) для нелегованого оксиду цинку ZnO, з іншого боку, ZnO:Al має напрямок (101). Розмір кристалітів змінювався від 34 до 36 нм залежно від концентрації допанту. Результати скануючої електронної мікроскопії показали, що на мікроструктуру плівок ZnO:Al сильно впливає легування алюмінієм. Оптичні вимірювання показали, що шари ZnO:Al мають пропускання близько 85% і енергетичний зазор 3,2 еВ, 3,4 еВ для ZnO:Al і ZnO відповідно. Питомий опір плівок зменшувався зі збільшенням концентрації легуючої домішки і становить 3×10^{-2} Ом·см для 1 ат.% Al, за межами якого він зростав.

Ключові слова: ZnO, ZnO:Al, Спрей, Мікроструктурний аналіз, Електричні та оптичні властивості.