Effect of Cu doping on optical and structural properties of ZnO thin films elaborated via sprayed moving nozzle.

M. Touati Tliba [a, b] , B. Benhaoua [a, c] A. Benhaoua [a, c], A. Rahal [a, c] and A. H. Hamzaoui [d].

Corresponding Author email address: meriemtouati39@gmail.com

[a] *Lab. VTRS, Faculty of Science & Technology, Univ. El-Oued, El-Oued 39000, Algeria*

[b] *Faculty of Mathematics and Material Sciences, Univ. Ouargla, Ouargla 30000, Algeria.*

[c] *Unité de Developpement des Energies Renouvelabes dans les Zones Arides, El oued 39000, Algeria.*

[d] *Centre National de Recherche en Sciences des Materiaux Tunisie.*

Abstract

In this work, 0-5wt.% copper doped zinc oxide thin films were deposited by spray pyrolysis technique (homemade) on 375°C heated glass. Zinc acetate ($Zn(CH_3COO)_2$, $2H_2O$) and copper chloride ($CuCl_2$,$7H_2O$) were used as sources precursor of ZnO and Cu doping, respectively. Effect of copper 0-5wt.% doping concentration on optical and structural properties was studied. UV-visible transmission techniques, X-ray diffraction were used respectively to characterize optical and structural properties of elaborated thin films. The average transmittance of all samples was more than 81% in the visible region and become more transparent with Cu doping. Optical gap energy was found to be in 3.25-3.28eV range. X-ray diffraction studies show nanocrystalline thin films with a hexagonal wurtzite structure exhibiting a strong (*002*) preferred orientation. Particles size ranges in 23-29nm for 0-5wt.% Cu doped ZnO thin films.

Key words: Thin films; Cu doped ZnO; Spray pyrolysis; X-ray diffraction.

I. INTRODUCTION

ZnO is one of the most important semiconductor material due to its wide band gap (3.3 eV) and large exciton binding energy (60 meV) at room temperature [1, 2]. Transparent conducting oxides (TCOs) are widely used in microelectronic devices, light emitting diodes, solar cells, transparent conducting contacts, liquid crystal displays, field-effect transistors, photocatalyst [3-6]. ZnO thin films can be produced by several techniques such as pulsed laser deposition [7], sol-gel techniques [8], chemical vapour deposition (CVD) [9], RF reactive magnetron sputtering technique [10] and spray pyrolysis [11]. Among these methods, the spray pyrolysis techniques were proceeded due to its simplicity, safety and low cost of the equipments for metallic oxides thin films deposition. Also possibilities of large-scale deposition, low temperature processing and direct control of film thickness are feasible [12].

The aim of this work is to focus more, particularly on spray pyrolysis technique with moving nozzle and effect of Cu doping concentration average stepped 0 - 5wt.% Cu/Zn on optical and structural properties of ZnO thin films deposited on glass substrate at temperature up to 375°C were investigated. For this UV-visible transmission and X-ray diffraction (XRD) techniques are used respectively to characterize optical and structural properties of these elaborated Cu doped ZnO thin films.

II. EXPERIMENTAL METHODS

A. Synthesis of thin films ZnO

In this study, 0-5wt% Cu doped ZnO thin films were prepared via spray pyrolysis technique. For the preparation of thin films, zinc acetate dehydrate (Zn $(CH_3COO)_2$, $2H_2O$) and copper chloride ($CuCl_2$,$7H_2O$) were used as sources for ZnO and dopant, respectively. First of all, zinc acetate dehydrate (0.5 M) were dissolved in 20 ml double distiller water as well as methanol solution in a volume ratio (1/2:1/2). Some drops of acetic acid (CH_3COOH) were added into solutions as stabilizer and the mixture stirred on magnetic for 90 min at 50 C° under vigorous stirring till getting a clear and homogeneous colorless solutions. For Cu doped ZnO, the molar percentages doping of Cu/Zn (0.5-5 wt.%) were added to the initial above solutions with kept in magnetic stirrer for the same time and temperature (90 min at 50 C°) until become a clear and homogeneous bleu solutions too. All our thin films samples deposited on heated 375C°glass slides (ref: 217102) during 12 min with a spray rate of the solution about 5mL/min with keeping distance nozzle-substrate equal 5 cm.

B. Characterization Techniques

The optical transmittance spectra of all samples were measured using a UV-Visible spectrophotometer (Shimadzu, Model 1800) working in the range of 300-900 nm. Structural analysis of the samples was investigated using X-ray diffraction (XRD, Bruker AXS type 8D) with Cu Kα radiation (λ=1.5406Å) as an X-ray source at 30 KV and 20 mA and 2θ value was swapped between 25-70°.

III.RESULTS AND DISCUSSION

A. Optical analysis

Fig.1 illustrates the optical transmittance spectra of thin films for different concentrations doping (0, 0.5, 1.5, 2 and 5 wt%) measured in range 300-900 nm. All the samples have transmittance about (81-91%) in the wavelength range higher than 400nm, values transmittance after doping is superior than undoped, this increase is may be assigned to high-quality of the thin films with feeble absorption losses or scattering [13] as reveled by the feeble Urbach energy see table 1. Transmittance values are mentioned in Table 1. While at region wavelength lower 400 nm, an abrupt fall of the transmittance, for all the thin films, can be seen, exhibiting the onset fundamental absorption due to the transition between the valence band and conduction one. The energy band gap was calculated using well know Tauc equation;

$$(\alpha h\upsilon)^2 = B(h\upsilon - E_g) \quad (1)$$

where E_g and h are the band gap energy and the photon energy respectively; α is the absorption coefficient and B is a constant.

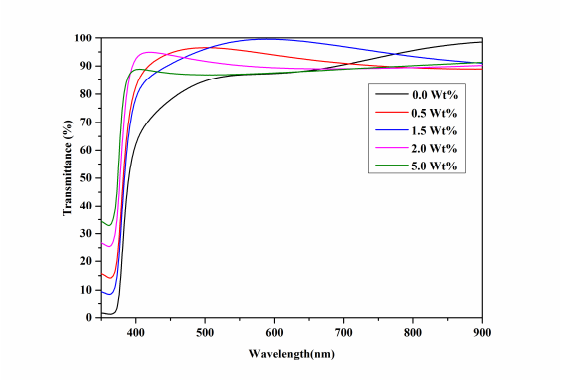

Fig.1. Transmittance spectra of ZnO thin films with different Cu doping concentration.

The variation of $(\alpha h)^2$ plot as a function of (h) is shown in Fig.2. The optical band

gap E_g of all the samples are obtained by extrapolating the linear part of the $(\alpha h\ )^2$ vs $(h\ )$ to the energy axis at $(\alpha h\ )^2 = 0$. Fig.2 displays the deduction of E_g values which are found to be about (3.25-3.28 eV) as listed in Table I. A decreasing in the optical band gap for the Cu doped samples compared to the undoped one (3.275eV) in the cases of (0.5, 1.5 and 2 Cu%) then increase. This reduce may be caused by the increase p-d spin-exchange interactions between the band electrons of ZnO as well as the localized d-electrons of Cu^{+2} ions substituting Zn^{+2} ions [14,15-17].On the other hand, the decrease of band gap by Cu doping is moreover attributed to the strong p-d mixing of O and Cu . Whereas the increase from 3.268 to 3.284 eV in the case for 5Cu%. This increase in the value of E_g may perhaps explained by Burstein-Moss effect [18].

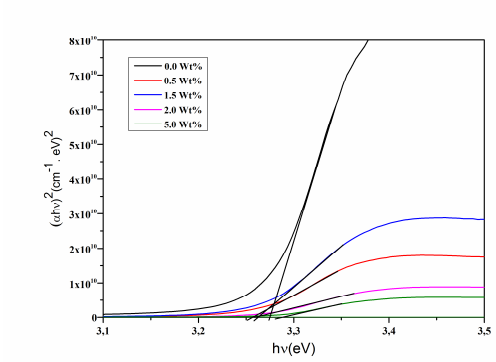

Fig.2. Plot of $(\alpha h\ )^2$ versus $(h\ )$ for the band gap determination for different Cu doping concentration.

We have used the band tail energy E_u, which characterizes the disorder defects in thin films, the band tail energy was calculated using well know following relation:

$$\alpha = \alpha_0 \exp(h\upsilon / E_u) \qquad (2)$$

where α is the absorption coefficient, α_0 is constant; h and E_u are photon energy and Urbach energy respectively. The Urbach energy was determined from the inverse of slop of *ln(a)* versus (*hν*), as depicted in Fig.3. The found Urbach energy values varied between (88-104 meV), which are feeble values indicating the feeble disorder defects in thin films product.

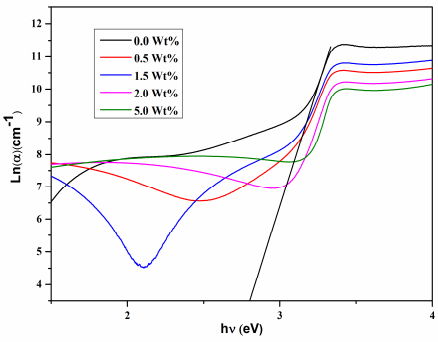

Fig.3. Plot of (lnα) versus (h) for the Urbach energy determination for different Cu doping concentration.

TABLE.1. Optical parameters for ZnO:Cu thin films.

Cu/Zn (Wt%)	T%	E_g(eV)	E_u(meV)
0.0	81.25	3.275	88.58
0.5	86.12	3.259	104.70
1.5	85.04	3.262	104.15
2.0	91.71	3.268	89.68
5.0	89.86	3.284	95.69

B. Structural analysis

Fig.4 shows the XRD patterns of (0-5wt%) Cu doped ZnO. The obtained diffraction peaks obviously exhibits the crystalline nature of ZnO with peaks corresponding to (100), (002), (101), (110) and (103) are in good according with the standard Join Committee Powder Diffraction JCPDS (Card No. 36-1451, space group $p6_3mc$) corresponding to hexagonal wurtzite structure of ZnO [19], with growth preferred direction along *c*-

axis (002) plane in all the thin films except ones (for 0.0 and 1.5 wt%). Comparing with undoped sample, one can detect from the XRD spectra that a small shift of the peaks towards the greater values of 2θ angles with (2 and 5 wt%) Cu doped ZnO conforming the substation of Zn^{2+} by Cu^{2+} in the lattice. There are no additional or any peaks corresponding to copper. The averages size crystallite at (002) peaks were evaluated using Debye Sherrer's formula:

$$G = \frac{0.9\lambda}{\beta \cos \theta} \quad \text{.....(3)}$$

where λ, β and θ are the wavelength of X-ray, the full width at half maximum (*FWHM*) and the Bragg's angle of (*hkl*) reflections, respectively. The crystallite size of all thin films ZnO was averaged between (23-29 nm). After doping this average gradually increases with doping compared to the undoped ZnO. The maximum crystallite size was obtained with 2% wt Cu/Zn doping then decreases. For further information, the lattice parameter *c* is estimated using the following relations:

$$2 d_{hkl} \sin \theta = n \lambda \quad \text{.....(4)}$$

and

$$\frac{1}{d^2_{hkl}} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \quad \text{.....(5)}$$

where *n* is the order of diffraction, d_{hkl} is the plane spacing and *hkl* are the Miller indices of the planes. Compared to undoped sample, there is slight decreasing in the lattice parameter *c* of ZnO matrix for (2 and 5 wt% doping) which can be attributed to replacement of Zn^{+2} by Cu^{+2} having ionic radius (0.73Å) into ZnO crystal lattice. The later is a less than Zn^{+2} ionic radius (0.74 Å) leading to a decrease in the *d* inter spacing and unit cell. All those structural parameters of ZnO thin films are tabulated in Table II.

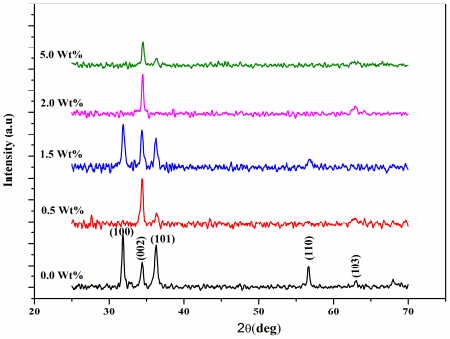

Fig.4. X-ray diffraction pattern of ZnO thin films with different Cu doping concentration.

TABLE.II. Structural parameters for (0-5wt%) Cu doped ZnO thin films.

Samples	2θ	Lattice parameters(Å)		Calculated d(Å)	Average grain size (nm)
		c	$\Delta c = c - c_0$		
0.0	34,424	5,2089	0,0029	2,6045	23.82
0.5	34,417	5,2099	0,0039	2,6049	26.98
1.5	34,406	5,2117	0,0057	2,6058	26.02
2.0	34,488	5,1996	-0,0064	2,5998	29.99
5.0	34,538	5,1923	-0,0137	2,5961	26.54

IV. CONCLUSION

In this work, ZnO and copper doped zinc oxide (ZnO:Cu) thin films were deposited by spray pyrolysis technique with moving nozzle on 375°C heated glasses. Effect of copper 0-5wt.% doping concentration on optical and structural properties was studied. The average transmittance of all samples was more than 81% in the visible region, and become more transparent with Cu doping. Optical gap energy found to be

in 3.25-3.28 eV. X-ray diffraction (XRD) studies show nanocrystalline films with a hexagonal wurtzite structure show a strong (002) preferred orientation, The maximum value of crystallite size *G* was about 29.99 nm attained in ZnO:Cu film with 2 wt% doping. Also it can be concluded that Cu is a good quality dopant for producing transparent ZnO thin films which may be widely applied in optoelectronic devices.

ACKNOWLEDGMENTS

This work was supported in part by El-Oued University for measuring UV-Visible data. X-ray diffraction data in this work were acquired with an instrument supported by Centre National de Recherche en Sciences des Materiaux Tunisie.

REFERENCES

[1] C. Klingshirn, R. Hauschild, H. Priller, M. Decker, J. Zeller, H. Kalt. Superlattice and Microstructures 38 (2005) 209-222.

[2] M. Mihailovic, A.-L. Henneghien, S. Faure, P. Disseix, J. Leymarie, A. Vasson, D.A. Buell, F. Semond, C. Morhain, J. Zuniga Perez. Optical and excitonic properties of ZnO films. Opt. Mater. 31 (2009) 532-536.

[3] H. Zhang, H. Liu, C. Lei, et al. Low-temperature deposition of transparent conducting Mn-W co-doped ZnO thin films. J. Semicond. 2010, 31(8): 083005.

[4] C. Zuo, J. Wen and C. Zhong. First-principles study of the electronic structures and optical properties of C-F-Be doped wurtzite ZnO. J. Semicond. 2012, 33(7): 072001.

[5] Z.-X. Xu, V.A.L. Roy, P. Stallinga, M. Muccini, S. Toffanin, H.-F. Xiang, C.-M. Che. Appl. Phys. Lett. 90, 223509 (2007).

[6] S. Anandan, A. Vinu, T. Mori, N. Gokulakrishnan, P. Srinivasu, V. Murugesan, K. Ariga. Cata. Commun. 8 (2007) 1377-1382.

[7] M. A. Gluba, N. H. Nickel, K. Hinrichs, and J. Rappich. Improved passivation of the ZnO/Si interface by pulsed laser deposition. J. Appl. Phys. 2013, 113 (4) 043502.

[8] F. Ran, L. Miao, S. Tanemura, M. Tanemura, Y. Cao, S. Tanaka, N. Shibata . Effect of annealing temperature on optical properties of Er-doped ZnO films prepared by sol-gel method. Mater. Sci. and Engineering B 148 (2008) 35-39.

[9] Y. Ito, O. Sakai, K. Tachibana. Study of plasma enhanced chemical vapor deposition of ZnO films by non-thermal plasma jet at atmospheric pressure. Thin Solid Films 518 (2010) 3513-3516.

[10] Z. B. Fang, Y.S. Tan, H.X. Gong, C.M. Zhen, Z.W. He, Y. Y. Wang. Transparent conductive Tb-doped ZnO films prepared by rf reactive magnetron sputtering. Mater. Lett. 59 (2005) 2611-2614.

[11] I. Soumahoro, G. Schmerber, A. Douayar, S. Colis, M. Abd-Lefdil, N. Hassanain, A. Berrada, D. Muller, A. Slaoui, H. Rinnert, and A. Dinia. Structural, optical, and electrical properties of Yb-doped ZnO thin films prepared by spray pyrolysis method. J. Appl. Phys. 109, 033708 (2011).

[12] Z. Sofiani, B. Derkowska, P. Dalasinski, M. Wojdyła, S. D.-Seignon, M. A. Lamrani, L. Dghoughi, W. Bała, M. Addou, B. Sahraoui. Optical properties of ZnO and ZnO:Ce layers grown by spray pyrolysis. Opt. Commun. 267 (2006) 433-439.

[13] R. Baghdad, B. Kharroubi, A. Abdiche, M. Bousmaha, M.A. Bezzerrouk, A. Zeinert, M. El Marssi, K. Zellama. Mn doped ZnO nanostructured thin films prepared by ultrasonic spray pyrolysis method. Superlattices and Microstructures 52 (2012) 711–721.

[14] K.J. Kim and Y. R. Park, Appl. Phys. Lett. **81**, 1420 (2002).

[15]. Y.Z. Peng, T. Liew, W.D. Song, C.W. An, K.L. Teo, T.C.J. Chong, Supercond. Incorp. Novel Magn. 18, 97 (2005).

[16]. J. Diouri, J.P. Lascaray, M. El Amrani, Phys. Rev. B 31, 7995(1985).

[17]. M. Bouloudenine, N. Viart, S. Colis, J. Kortus, A. Dinia, Appl. Phys. Lett. 87, 052501/1 (2005).

[18] E. Burstein, Physical Review 93 (1954), p.632-633.

[19] Jianwei Wang, Jiaqi Wan, Kezheng Chen, Mater. Lett. 64 (2010) 2373–2375.