Optik 126 (2015) 5407–5411

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Effect of annealing temperature on structural, optical and electrical properties of zinc oxide (ZnO) thin films deposited by spray pyrolysis technique

Yacine Aoun [a,b], Boubaker Benhaoua [c], Said Benramache [d,*], Brahim Gasmi [e]

[a] Mechanical Department, Faculty of Technology, University of El-Oued, El-Oued 39000, Algeria
[b] Mechanical Department, Faculty of Technology, University of Biskra, Biskra 07000, Algeria
[c] VTRS Laboratory, Institute of Technology, University of El-Oued, El-Oued 39000, Algeria
[d] Material Sciences Department, Faculty of Technology, University of Biskra, Biskra 07000, Algeria
[e] XRD Laboratory, University of Biskra, Biskra 07000, Algeria

ARTICLE INFO

Article history:
Received 20 September 2014
Accepted 31 August 2015

Keywords:
ZnO
Thin films
Annealing temperature
Spray pyrolysis technique

ABSTRACT

In the present paper, the structural, optical and electrical properties of zinc oxide thin films were studied before and after annealing temperature at 500 °C. The ZnO thin films were sprayed on glass substrates at 350 °C, which were heated using the solar cells method. Polycrystalline films with a hexagonal wurtzite structure with (0 0 2) preferential orientation corresponding to ZnO films were observed. It can be found that the good crystallinity are achieved in the films annealed at 500 °C. All films exhibit an average optical transmittance about 95% measured by UV–vis analyzer. The shift of optical transmittance towards high wavelength can be showed by the increases of band gap after annealing temperature which can be explain by the oxygen diffusion with annealing temperature. The electrical resistivity measured of our films in the order 0.4 (Ω. cm).

1. Introduction

During the past few years, Zinc oxide (ZnO) which is one of the most important binary II–VI semiconductor compounds have attracted the interest of many research groups due its application in light-emitting diodes (LEDs) and laser diodes. Among the II–VI semiconductors, ZnO is an important optoelectronic device material for use in the violet and blue regions because of its wide band gap (3.37 eV) and large exciton binding energy (60 meV) [1–5]. ZnO thin films are promising candidates for applications in short-wavelength light-emitting devices, lasers, field emission devices, solar cells gas sensors, surface acoustic wave and transparent contacts [6–10]. Furthermore, very interesting characteristics (fluorescence emission, laser action,. . .) have been shown by ZnO nanostructures.

Polycrystalline ZnO thin films can be produced by several techniques, such as molecular beam epitaxy (MBE) [11], chemical vapor deposition [12], electrochemical deposition [13], pulsed laser deposition (PLD) [14], sol–gel process [15], reactive evaporation [16], magnetron sputtering technique [17] and spray pyrolysis [18], have been reported to prepare thin films of ZnO. Compared with other techniques, the spray pyrolysis technique is one of these techniques to prepare large-scale production for technological applications. It is possible to alter the mechanical, electrical, optical and magnetic properties of ZnO nanostructures. It is known that ZnO films prepared by the spray pyrolysis technique can have a wide band gap between 3 and 3.37 eV.

B.W. Shivaraj et al. [19] studied the structural and optical properties of Dip and Spin coated ZnO Thin Films at two different temperatures of 400 and 500 °C, they found that the grain sizes annealed at 500 are higher than the annealed film at 400 °C for two methods. However, Huang and Liu [20] investigated the optical and electrical properties of gallium-doped ZnO thin film with post-annealing processes of various atmospheres, which were studied at different temperatures in the range of 300–500 °C; they found that the band gap of Ga doped ZnO increased with increasing the annealing temperature.

In present study, nanostructure ZnO based thin films can be deposited by spray pyrolysis technique on glass substrate at a substrate temperature of 350 °C. The thin films were prepared with 30 and 35 ml of deposition rate, the aim of this work to study the effect of annealing temperature at 500 °C of ZnO thin film on crystalline structure, optical gap energy and electrical resistivity.

* Corresponding author. Tel.: +213 67697692; fax: +213 335138477.
E-mail address: benramache.said@gmail.com (S. Benramache).

http://dx.doi.org/10.1016/j.ijleo.2015.08.267
0030-4026/

Fig. 1. The photograph of experimental setup.

2. Experimental

ZnO solution were prepared by dissolving 0.1 M ($Zn(CH_3COO)_2$, $2H_2O$) in the solvent containing equal volume absolute methanol solution (99.995%) purity, then we have added a few drops of concentrated HCl solution as a stabilizer, the mixture solution was stirred at 60 °C for 120 min to yield a clear and transparent solution.

The resulting solutions were sprayed on the heated glass substrates by spray pyrolysis technique, the substrates were heated by using the solar cells method, and this letter was prepared in our laboratory. The structure of the spray deposition system and fabricated organic solar cells are shown in Fig. 1. The substrate was heated by absorber plate and maintained temperature of 350 °C, when the active solution sprayed on substrate in the size of 30 mm × 7.5 mm × 1 mm, The prepared ZnO films were subjected to annealing treatment in air for 2 h at temperature of 500 °C [21,22].

The structures of the thin films were determined by X-ray diffraction (XRD, Bruker AXS-8D) with CuKα radiation ($\lambda = 0.15406$ nm) in the scanning range of (2θ) was between 20° and 60°. The optical transmittance of the films was measured in the range of 300–900 nm by using an ultraviolet–visible spectrophotometer (SHUMATZU 1800) and the electrical resistivity was measured in a coplanar structure obtained with evaporation of four golden stripes on the deposited film surface using the keithley Model 2400 Low Voltage Source Meter instrument.

3. Results and discussion

3.1. Thickness calculation

ZnO thin films with various thicknesses were deposited by varying the deposition rate on glass substrates with and without annealing temperature of. Thicknesses of the ZnO thin films are computed from transmission data and by using following formula [23]:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (1)$$

where,

$$n_{12} = \left[N_{12} + \left(N_{12}^2 - {n_s}^2 \right)^{1/2} \right]^{1/2} \quad (2)$$

$$N_{12} = 2n_s (T_{\max} - T_{\min})/T_{\max} T_{\min} + ({n_s}^2 + 1)/2 \quad (3)$$

with $n_s = 1$ is the refractive index of the substrate, n_1 and n_2 are the refractive index of thin film at the two adjacent maxima (or minima) at λ_1 and λ_2, $T_{\max}$ and $T_{\min}$ are maximum and minimum transmittances at the same wavelength in the fitted envelope curves on the transmittance spectrum. The variations of film thickness of our films are shown in Table 1, as can be seen, those film thicknesses of these films were found between 100 and 130 nm.

Table 1
The variation of film thicknesses of ZnO thin films calculated before and after annealing temperature at 500 °C.

	Deposition rate (ml)	Film thicknesses (nm)
Befor	30	122.1
	35	129.4
After	30	107.2
	35	103.8

3.2. The crystalline structure of ZnO thin films

The effect annealing temperature on crystal structure was demonstrated in Fig. 2; show the X-ray diffraction (XRD) spectrum of ZnO thin films with and without annealing temperature at 500 °C of sprayed films at 30 and 35 ml of deposition rate. A matching of the observed of the (100); (002) (101) and (102) diffraction peaks confirms that the films exhibit polycrystalline structure that belongs to the hexagonal wurtzite type of ZnO [24,25]. From analysis data, all deposited films have having preferential growth along *c*-axis or (002) plane but with the different peak intensity. The films annealed at 500 °C has higher and sharper diffraction peak indicating an improvement in (0 0 2) peak intensity compared to without annealed films. The crystalline quality of thin films enhanced with annealing temperature. Similar observations have been found by other researchers [22,26,27].

The lattice constant *c* and diffraction peak angles of ZnO thin films (see Table 2) are calculated using the following equation [28]:

$$d_{hkl} = \left(\frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right)^{-1/2} \quad (4)$$

where a, c are the lattice parameters, (h, k, l) is the Miller indices of the planes and d_{hkl} is the interplanar spacing.

The strain ε values in our films were estimated from the observed shift, in the (0 0 2) diffraction peak between their positions in the XRD spectra via the formula [29]:

$$\varepsilon = \frac{c - c_0}{c_0} \times 100\% \quad (5)$$

where ε is the mean strain in ZnO thin films (Table 2), c the lattice constant of ZnO thin films and c_0 the lattice constant of bulk (standard $c_0 = 0.5206$ nm).

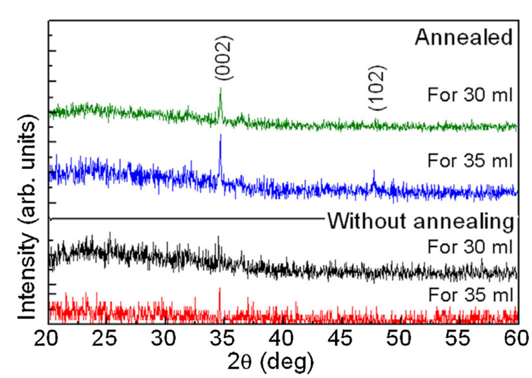

Fig. 2. X-ray diffraction spectra of ZnO thin films with and without annealing temperature at 500 °C of sprayed films at 30 and 35 ml of deposition rate.

Table 2
The unit cell parameters of ZnO thin films calculated from XRD patterns (a) before and (b) after annealing temperature at 500 °C.

Deposition rate (ml)	*hkl* (deg)	2θ (Å)	*d* (deg)	FWHM (nm)	*G* (Å)	*c* (Å)	*a* (Å)	ε (%)
(a)								
30 ml	002	34.54	2.59469	0.38	21.91	5.189391	3.243369	−0.319
35 ml	002	34.27	2.61452	0.52	16.01	5.229035	3.268147	0.443
(b)								
30 ml	002	34.48	2.61452	0.41	20.29	5.198146	3.248841	−0.151
35 ml	002	34.63	2.54125	0.41	20.29	5.082501	3.176563	−0.570

The crystallite size of ZnO thin films which are estimated using the well-known Debye–Scherrer formula [30]:

$$G = \frac{0.9\lambda}{\beta \cos\theta} \tag{6}$$

where G is the crystallite size, λ is the wavelength of X-ray ($\lambda = 1.5406$ Å), β is the full width at half-maximum (FWHM), and θ is the half diffraction angle of the centroid of the peak. Table 2 presents the some information's on the structure properties of ZnO thin films of (0 0 2) diffraction peak were measured as a function of deposition rates with and without annealing temperature at 500 °C. It can be seen from Table 2 that the good crystallinity are achieved in the films annealed at 500 °C, where also obtained by [22].

3.3. The optical properties of ZnO thin films

Fig. 3 shows the optical transmission spectra of ZnO thin films annealed at 500 °C, the inset of Fig. 3 present the without annealing films, al films were sprayed at 30 and 35 ml of deposition rate. For the longer wavelengths ($\lambda > 400$ nm) all the films become transparent, it is found that all the films show a high optical transmission, around 95%, in the visible region. The optical absorption at the absorption edge corresponds to the transition from valence band to the conduction band ($\lambda < 400$ nm), while the absorption in the visible region was related to some local energy levels caused by intrinsic defects. The films annealed at 500 °C and deposited with 35 ml show high transmission at lower wavelength indicated the enhancement of the crystallinity [22,31].

The optical band gap energy E_g was measured from the transmission spectra using the following relations [32,33]:

$$(Ah\upsilon)^2 = C(h\upsilon - E_g) \tag{7}$$

where A is the absorbance, d is the film thickness; T is the transmission spectra of thin films; α is the absorption coefficient values; C is a constant, hv is the photon energy ($h\nu = (1240/\lambda(\text{nm}))(\text{eV})$) and E_g is the band gap energy of the semiconductor. As it was shown in Fig. 4 a typical variation of $(Ah\nu)^2$ as a function of photon energy (hv) of ZnO thin films before annealing temperature. However, in the inset present the annealed ZnO films at 500 °C. They used for deducing optical band gap E_g, it is determined by extrapolation of the straight line portion to zero absorption ($A = 0$) [18] the values of E_g are listed in Table 3. Besides, we have used the Urbach tail energy (E_u), which is related to the disorder in the film network, as it is expressed follow [34]:

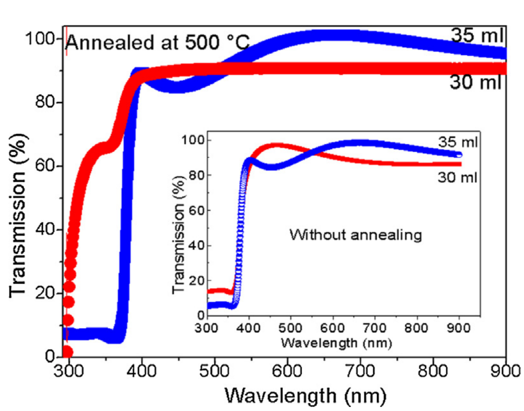

Fig. 3. Transmission spectra $T(\lambda)$ of ZnO thin films with and without annealing temperature at 500 °C of sprayed films at 30 and 35 ml of deposition rate.

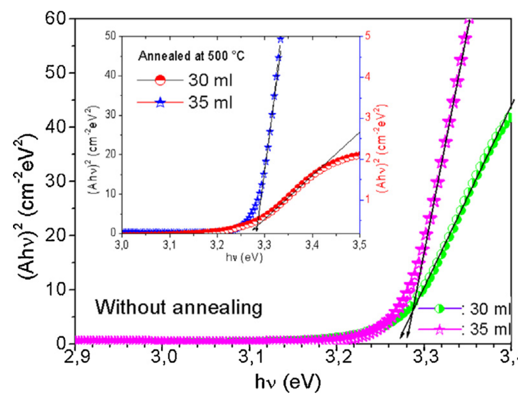

Fig. 4. The typical variation of $(Ah\nu)^2$ vs. photon energy of deposited ZnO thin films with and without annealing temperature at 500 °C of sprayed films at 30 and 35 ml of deposition rate.

$$A = A_0 \exp\left(\frac{h\upsilon}{E_u}\right) \tag{8}$$

where A_0 is a constant hv is the photon energy and E_u is the Urbach energy. The Urbach tail energy E_u is calculated from the slope of hv vs. photon energy (hv) plot and the obtained values are shown in Table 3.

As clearly seen in the Fig. 4, the optical gap energy of ZnO thin films are increased after annealed at 500 °C (see Table 3), the change can found for 30 ml 3.265 to 3.269 eV of sprayed film to annealing temperature at 500 °C, respectively, for 35 ml the optical gap energy of ZnO thin film increased from 3.279 to 3.288 eV, respectively. Can be explain the increase in optical gap energy from before to annealed by the oxygen diffusion with annealing temperature [22,35,36] (Fig. 5). We have obtained an increase in Urbach energy of sprayed ZnO thin film with 35 ml of 056.1 to 048.7 meV, respectively. For 30 ml obtained inversely which the Urbach energy is decreased after annealing temperature from 083.4 to 178.6 meV,

Table 3
Recapitulating measured values of band gap energy (E_g), Urbach energy (E_u), and electrical resistivity (ρ) of deposited ZnO thin films (a) before and (b) after annealing temperature at 500 °C.

Deposition rate (ml)	E_g[a] (eV)	E_u (meV)	ρ (Ω.cm)
(a)			
30 ml	3.265	083.4	0.373
35 ml	3.279	056.1	0.509
(b)			
30 ml	3.269	178.6	0.331
35 ml	3.288	048.7	0.421

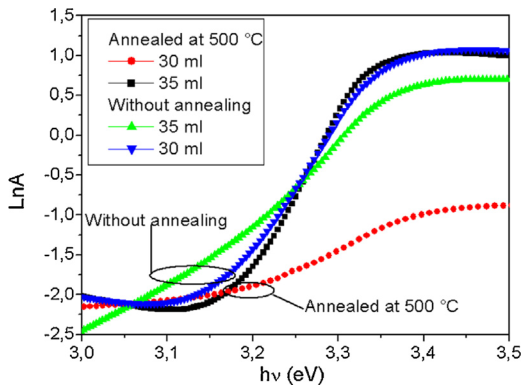

Fig. 5. The typical variation of *LA* vs. photon energy of deposited ZnO thin films with and without annealing temperature at 500 °C of sprayed films at 30 and 35 ml of deposition rate.

respectively. This means the adequate temperature for less disorder.

3.4. The electrical resistivity of ZnO thin films

Table 3 shows that the electrical resistivities of our films are in qualitative agreements with the band gap energy (see Table 3), the decrease in the electrical resistivity can be explained by increasing of the potential barriers, because the introduced atoms are segregated into the grain boundaries, this interpretation is consistent with the authors [22,29,37–39]. This can be explained by decreasing of the means strain (see Table 2). One can note that the annealing temperature effect is clearly observed in the layer quality.

4. Conclusions

In conclusion, highly transparent conductive ZnO thin films were deposited on glass substrate by spray pyrolysis technique. The ZnO thin films were deposited on substrate using the solar cells method at a temperature of 350 °C with 30 and 35 ml of deposition rate. The influence of annealing temperature at a 500 °C on structural, optical and electrical properties was investigated. The films exhibit a hexagonal wurtzite structure with a strong (0 0 2) preferred orientation. The average transmittance of obtain films is over of 95% measured by UV–vis analyzer. The band gap energy of ZnO thin films are increased after annealing temperature which can be explain by the oxygen diffusion with annealing temperature. The electrical resistivity measured of our films in the order 0.4 (Ω cm).

References

[1] L. Bahadur, M. Hamdani, J.F. Koenig, P. Chartier, Studies on semiconducting thin films prepared by the spray pyrolysis technique for photoelectrochemical solar cell applications: preparation and properties of ZnO, Sol. Energy Mater. 14 (1986) 107–120.

[2] L.M. Wong, S.Y. Chiam, J.Q. Huang, S.J. Wang, W.K. Chim, J.S. Pan, Examining the transparency of gallium-doped zinc oxide for photovoltaic applications, Sol. Energy Mater. Sol. Cell. 95 (2011) 2400–2406.

[3] D.R. Sahu, J.L. Huang, Development of ZnO-based transparent conductive coatings, Sol. Energy Mater. Sol. Cell. 93 (2009) 1923–1927.

[4] R.E. Marotti, D.N. Guerra, C. Bello, G. Machado, E.A. Dalchiele, Band gap energy tuning of electrochemically grown ZnO thin films by thickness and electrodeposition potential, Sol. Energy Mater. Sol. Cell. 82 (2004) 85–103.

[5] F. Benharrats, K. Zitouni, A. Kadri, B. Gil, Determination of piezoelectric and spontaneous polarization fields in $Cd_xZn_{1-x}O$/ZnO quantum wells grown along the polar (0 0 0 1) direction, Superlattices Microstruct. 47 (2010) 592–596.

[6] A. Maldonado, M. de la, L. Olvera, S. Tirado-Guerra, R. Asomoza, Sol. Energy Mater. Sol. Cell. 82 (2004) 75–84.

[7] M.A. Lucio-López, A. Maldonado, R. Castanedo-Pérez, G. Torres-Delgado, M. de la, L. Olvera, Thickness dependence of ZnO:In thin films doped with different indium compounds and deposited by chemical spray, Sol. Energy Mater. Sol. Cell. 90 (2006) 2362–2376.

[8] G. Torres Delgado, C.I. Zúnîga Romero, S.A. Mayén Hernández, R. Castanedo Pérez, O. Zelaya Angel, Optical and structural properties of the sol–gel-prepared ZnO thin films and their effect on the photocatalytic activity, Sol. Energy Mater. Sol. Cell. 93 (2009) 55–59.

[9] K. Zitouni, A. Kadri, P. Lefebvre, B. Gil, k.P energy-band structure of $ZnO/Zn_{1-x}Mg_xO$ quantum well heterostructures, Superlattices Microstruct. 39 (2006) 91–96.

[10] T. Bretagnon, P. Lefebvre, P. Valvin, B. Gil, C. Morhain, Xiaodong Tang, Time resolved photoluminescence study of ZnO/(Zn,Mg)O quantum wells, J. Cryst. Growth 287 (2006) 12–15.

[11] A. Gahtar, S. Benramache, B. Benhaoua, et al., Preparation of transparent conducting ZnO:Al films on glass substrates by ultrasonic spray technique, J. Semicond. 34 (2013) 033001.

[12] E. Amoupour, A.A. Ziabari, H. Andarva, F.E. Ghodsi, Influence of air/N_2 treatment on the structural, morphological and optoelectronic traits of nanostructured ZnO:Mn thin films, Superlattices Microstruct. 65 (2014) 332–343.

[13] N. Karak, P.K. Samanta, T.K. Kundu, Green photoluminescence from highly oriented ZnO thin film for photovoltaic application, Optik 124 (2013) 6227–6230.

[14] E.F. Keskenler, G. Turgut, S. Dogan, Investigation of structural and optical properties of ZnO films co-doped with fluorine and indium, Superlattices Microstruct. 52 (2012) 107–115.

[15] J. Ramesh, G. Pasupathi, R. Mariappan, V. Senthil Kumar, V. Ponnuswamyc, Structural and optical properties of Ni doped ZnO thin films using sol–gel dip coating technique, Optik 124 (2013) 2023–2027.

[16] A.D. Acharya, B. Sarwan, R. Panda, S.B. Shrivastava, V. Ganesan, Tuning of TCO properties of ZnO by silver addition, Superlattices Microstruct. 67 (2014) 97–109.

[17] H. Zhang, S. Yang, H. Liu, et al., Preparation and characterization of transparent conducting ZnO:W films by DC magnetron sputtering, J. Semicond. 32 (2011) 043002.

[18] S. Benramache, A. Rahal, B. Benhaoua, The effects of solvent nature on spray-deposited ZnO thin film prepared from Zn $(CH_3COO)_2$, $2H_2O$, Optik 124 (2013) 663–666.

[19] B.W. Shivaraj, H.N. Narasimha Murthy, M. Krishna, B.S. Satyanarayana, Effect of annealing temperature on structural and optical properties of dip and spin coated ZnO thin films, Proc. Mater. Sci. 10 (2015) 292–300.

[20] C.S. Huang, C.C. Liu, The optical and electrical properties of gallium-doped ZnO thin film with post-annealing processes of various atmospheres, Microelectron. Eng. 148 (2015) 59–63.

[21] C.Y. Zhang, The influence of post-growth annealing on optical and electrical properties of p-type ZnO films, Mater. Sci. Semicond. Process. 10 (2007) 215–221.

[22] S. Benramache, B. Benhaoua, Influence of annealing temperature on structural and optical properties of ZnO:In thin films prepared by ultrasonic spray technique, Superlattices Microstruct. 52 (2012) 1062–1070.

[23] C. Gümü, O.M. Ozkendir, H. Kavak, Y. Ufuktepe, Structural and optical properties of zinc oxide thin films prepared by spray pyrolysis method, J. Optoelectron. Adv. Mater. 8 (2006) 299–303.

[24] A. Souissi, A. Boukhachem, Y. Ben Taher, A. Ayadi, A. Mefteh, M. Ouesleti, S. Guermazi, M. Amlouk, Structural and vibrational studies of Mo and In-doped ZnO sprayed thin films, Optik 125 (2014) 3344–3349.

[25] N. Renaut, M. Jimenez, J. Dutroncy, M. Traisnel, High speed atmospheric plasma deposition of transparent ZnO thin films without post-deposition annealing, Thin Solid Films 589 (2015) 161–164.

[26] D. Fang, P. Yao, H. Li, Influence of annealing temperature on the structural and optical properties, Ceram. Int. 40 (2014) 5873–5880.

[27] A. Purohit, S. Chander, A. Sharma, S.P. Nehra, M.S. Dhaka, Impact of low temperature annealing on structural, optical, electrical and morphological properties of ZnO thin films grown by RF sputtering for photovoltaic applications, Opt. Mater. 49 (2015) 51–58.

[28] S. Benramache, F. Chabane, B. Benhaoua, et al., Influence of growth time on crystalline structure, conductivity and optical properties of ZnO thin films, J. Semicond. 34 (2013) 023001.

[29] S. Benramache, B. Benhaoua, Influence of substrate temperature and Cobalt concentration on structural and optical properties of ZnO thin films prepared by ultrasonic spray technique, Superlattices Microstruct. 52 (2012) 807–815.

[30] A.J. Hashim, M.S. Jaafar, A.J. Ghazai, N.M. Ahmed, Fabrication and characterization of ZnO thin film using sol–gel method, Optik 124 (2013) 491–492.

[31] Y. Aoun, B. Benhaoua, S. Benramache, B. Gasmi, Effect of deposition rate on the structural, optical and electrical properties of Zinc oxide (ZnO) thin films prepared by spray pyrolysis technique, Optik 126 (2015) 2481–2484.

[32] S. Duman, G. Turgut, F.Ş. Özçelik, B. Gurbulak, The synthesis and characterization of sol–gel spin coated CdO thin films: as a function of solution molarity, Mater. Lett. 126 (2014) 232–235.

[33] M. Thirumoorthi, J.T.J. Prakash, Structural, morphological characteristics and optical properties of Y doped ZnO thin films by sol–gel spin coating method, Superlattices Microstruct. 85 (2015) 237–247.

[34] H. Mahdhi, Z. Ben Ayadi, J.L. Gauffier, K. Djessas, S. Alaya, Effect of sputtering power on the electrical and optical properties of Ca-doped ZnO thin films sputtered from nanopowders compacted target, Opt. Mater. 45 (2015) 97–103.

[35] C. Guillén, J. Herrero, Les caractéristiques optiques, électriques et structurales de Al: films minces de ZnO avec différentes épaisseurs déposées par pulvérisation cathodique à courant continu à la température ambiante et recuit à l'air ou sous vide, Vacuum 84 (2010) 924–929.

[36] N. Bouhssira, S. Abed, E. Tomasella, J. Cellier, A. Mosbah, M.S. Aida, M. Jacquet, Influence of annealing temperature on the properties of ZnO thin films deposited by thermal evaporation Influence de la température de recuit sur les propriétés des films minces de ZnO déposées par évaporation thermique, Appl. Surf. Sci. 252 (2006) 5594–5597.
[37] A. Hafdallah, F. Yanineb, M.S. Aida, N. Attaf, In doped ZnO thin films, J. Alloys Compd. 509 (2011) 7267–7270.
[38] Z. Zhang, C. Bao, W. Yao, S. Ma, L. Zhang, S. Hou, Influence of deposition temperature on the crystallinity of Al-doped ZnO thin films at glass substrates prepared by RF magnetron sputtering method, Superlattices Microstruct. 49 (2011) 644–653.
[39] A. Benhaoua, A. Rahal, B. Benhaoua, M. Jlassi, Effect of fluorine doping on the structural, optical and electrical properties of SnO_2 thin films prepared by spray ultrasonic, Superlattices Microstruct. 70 (2014) 61–69.