Effect of Carrier Gas and Vacuum Annealing on the Physical Properties of ZnO Thin Films Doped with Gallium by Chemical Spray Pyrolysis

T. Potlog, I. Lungu, V. Botnariuc, S. Raevschi, L.Gorceac
Department of Physics and Engineering
Chisinau, Republic of Moldova
tpotlog@gmail.com

S. Worasawat, H. Mimura
Research Institutue of Electronics
Shizuoka University
Hamamatsu, Japan
mimura.hidenori@shizuoka.ac.jp

***Abstract* - Structural, optical and electrical properties of zinc oxide thin films doped with 2% Ga, annealed in the vacuum at the same temperature and obtained onto glass substrates by the chemical spray pyrolysis method in the different gas atmospheres were investigated by X-ray Diffraction (XRD), UV-VIS spectrophotometry and Hall measurements, respectively. XRD studies revealed that all films were polycrystalline in nature, with a hexagonal wurtzite crystal structure and a predominant (002) c-axis orientation. All ZnO:Ga thin films had higher than 80 % transmittances in the visible region. Doping with 2% Ga led to a decrease in the optical band gap indifferent of the nature of the carrier gas. The synthesis of ZnO thin films with 2% Ga doping and annealing in the same conditions in Ar and O_2 atmospheres led to the lower conductivity with electron concentration of 10^{16} cm^{-3}.**

***Key words* - ZnO thin films, carrier gas, spray pyrolysis, optical properties, electrical parameters.**

I. INTRODUCTION

Wide band gap ZnO II-VI compound semiconductor can be used in the development of several optoelectronic device applications, such as ultraviolet (UV) light emitters [1], spin functional devices [2], gas sensors [3-5], transparent electronics [6], and surface acoustic wave devices [7,8]. ZnO crystallizes in a cubic zinc blende and/or hexagonal wurtzite structure with lattice parameters a = 3.2495 Å and c = 5.2069 Å, and the density 5.605 $g \cdot cm^{-3}$ [9]. ZnO films with cubic structure grow perpendicular to the (111) plane, while the hexagonal structure is textured in the [002] orientation. In addition to the intrinsic dopants, ZnO can be doped with Al, Ga and In to obtain an enhanced n-type conductivity and/or with N, Mn and Li to obtain the p-type conductivity. Al- and Ga-doped ZnO (AZO and GZO, respectively) form a class of transparent conductive oxides (TCO) with important potential applications in solar cells, window thermal coatings, and spintronic devices [10]. Ga-doped ZnO (GZO) is more stable with respect to oxidation due to Ga greater electronegativity in comparison with Al [11]. Among the various techniques to produce ZnO, the most popular method for ZnO thin films is considered spray pyrolysis, with the latter having significant advantages in simplicity and low cost. Other major advantages of spray pyrolysis for ZnO can be listed as follows: large area deposition, conformal coating, controllable thickness and compatibility with a variety of applicable substrates. On the basis of studies made on ZnO thin films and from an application point of view we can conclude that the Ga doping is very promising but there are some problems that limit mainly the transport properties, when the Ga is incorporated into the ZnO lattice. Therefore, the aims of the present paper are: 1) to prepare ZnO thin films doped with Ga by spray pyrolysis method in neutral and oxidizing atmosphere; 2) to anneal in vacuum; 3) to describe the physico-chemical processes responsible for the change of ZnO thin film properties as a result of the effect of carrier gas atmosphere and annealing.

II. EXPERIMENT DETAILS

The ZnO thin films doped with Ga were obtained using chemical spray pyrolysis technique. These layers were obtained by dissolving 0.2 M solution of zinc acetate (Zn $[CH_3COO]_2$) in a mixture of 12.5 ml H_2O (deionized water) + 32.5 ml CH_3COH (methanol) + 5 ml CH_3COOH (acetic acid) at room temperature. The gallium chloride (GaCl) was used for the doping. The concentration of Ga was maintained at 2 at%. The glass substrates were cleaned thoroughly with acetone, isopropanol and finally were kept in H_2 atmosphere for 10 min. The nozzle was at a distance of 30 cm from the substrate during deposition. The solution flow rate was held constant at 3 ml/min. Oxygen and argon gases were used as the carrier gas at the pressure of 2 atm. The ZnO:Ga thin films were deposited at substrate temperature of 673 K with different thicknesses. The as prepared samples were annealed for 1 hour in vacuum at 723 K temperature.

The structural properties of the fabricated films are studied by X-ray diffraction (XRD). From XRD patterns the crystallite size (d) was obtained by Scherer formula [12]

$$D = K\lambda/\beta cos\theta$$

where β is the peak width, K is the Scherer constant, λ is the wavelength of X-ray radiation, and θ is the diffraction angle. To determine the interplanar distance (d) Bragg's law was applied

$$2dsin\theta = n\lambda,$$

where n is a positive integer and λ is the wavelength of incident wave. The optical transmittance and E_g were studied by means of UV-VIS measurements. Based on Tauc relation [13]

$$h\nu = A(h\nu - Eg)^n$$

the values of E_g have been estimated from $(\alpha h\nu)^2$ versus $h\nu$ dependence, by taking the intercept of the extrapolation to zero absorption with hν axis. α is the absorption coefficient given by $\alpha = 2.303 \log(T/d)$ (d is film thickness and T is transmittance), $h\nu$ is the photon energy whereas exponent n denotes the nature of the transition (n = ½ for indirect allowed and n = 2 for direct transitions).

III. Results And Discussion

A. Structural properties

XRD patterns for obtained ZnO thin films in argon (Ar) and oxidizing atmosphere (O_2) before and after vacuum annealing at 450°C illustrated in Fig.1 show no evidence of secondary phases, except a crystalline ZnO phase. The revealed main high intensity (002) peak in all films, with exception of as-deposited and undoped ZnO thin films located at approximately 34.45° has been assigned in the literature as corresponding to hexagonal modifications textured in the [002] direction [14]. From this it follows that these films are polycrystalline with hexagonal structure and the predominant orientation of the c axis perpendicular to the plane of the substrate. This result is in good agreement with the literature data [14,15]. A shifting of the (002) peak is observed for the ZnO thin films doped with 2% Ga and annealed at 450°C in vacuum from $2\theta = 34.45°$ to 34.50° for all doped samples. For the obtained film in the oxidizing atmosphere and non-annealed, the more intensive peak is located close to 36.25° with ZnO phase textured in the [101] orientation. The structural parameters are estimated and presented in Table 1.

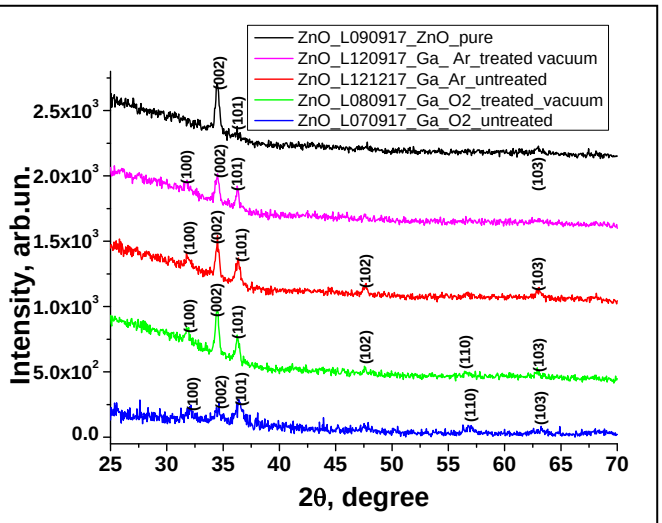

Figure 1 XRD patterns of pure ZnO thin films and prepared in argon (Ar) and oxidizing atmosphere (O_2) before and after vacuum annealing at 450°C

Table 1 shows that thermal annealing of the samples leads to a decrease in the size of the crystallites (see more intensive (002) plane) in the case of the O_2 gas atmosphere, while in the case of the Ar gas leads to an increase in the grain size. It can, also, be argued that annealing and nature of the gas atmosphere did not change the nature of the texture but resulted in the appearance of additional low intensity reflections of the hexagonal lattice in some samples. The (110) plane has a very small intensity. The undoped ZnO and ZnO:Ga thin films had compressive strains because of different values of thermal coefficient of glass and material or may be due to a slight increase in relative strain originating from the substitution of Zn^{2+} ions with relatively smaller Ga^{3+} ions. Doping was observed to have insignificant effects on the strain as evidenced by almost similar (002) peak positions and about equal interplanar distances for all films at this peak position. The intensity of the diffraction peaks decreases after doping and annealing at 723 K and their width at half-height slightly changes. The shifting of the position of the peaks in comparison with tabular data [16] indicates the presence in them of various kinds of defects. On the other hand, the annealing of ZnO thin films in vacuum at 723 K decrease the interplanar distance for both types of gas atmospheres in comparison with ZnO pure. This shows that Ga managed to substitute Zn and can reasonably reside on zinc site in the hexagonal lattice [17]. This may be due to the fact that Ga^{3+} ions replace the Zn^{2+} ions in the ZnO lattice in the case of doping with 2 at% Ga.

B. Optical properties

Band gap engineering is a crucial step in the optoelectronic device applications. Fig. 2 shows the optical transmittance spectra of pure ZnO thin films and of their prepared from solution with a gallium concentration of 2 at% in different gas atmospheres.

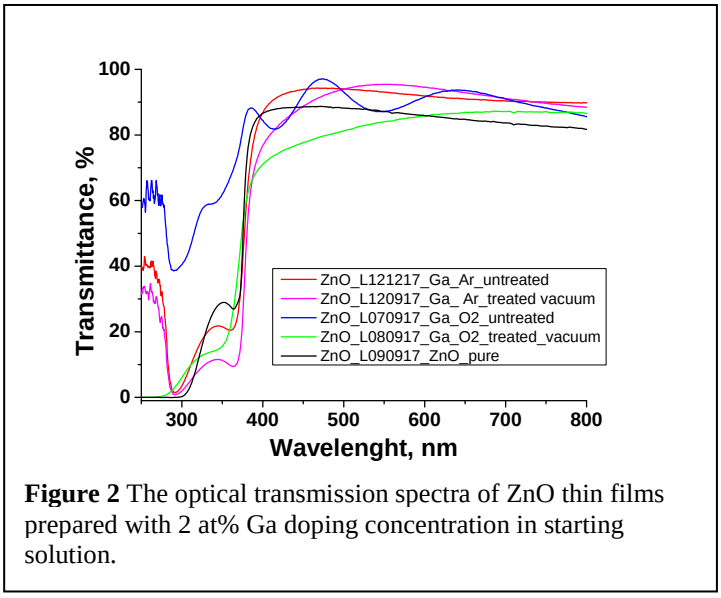

Figure 2 The optical transmission spectra of ZnO thin films prepared with 2 at% Ga doping concentration in starting solution.

Table 1 Structural parameters of ZnO thin films doped with 2% Ga, before and after vacuum annealing prepared in argon (Ar) and oxidizing atmosphere (O_2)

Samples	N	2θ	d,Å	Intensity (arb.un)	(hkl)	cosθ	FWHM (b)	D,Å	ε (strain)
ZnO									
	1	34.45	2.6279	691	(002)	0.96	0.008	203.2	0.00640
	2	36.25	2.4761	368	(101)	0.95	0.004	355.9	0.00337
ZnO_L080917_Ga_O2_ vacuum anneal									
	1	31.94	2.7998	546	(100)	0.96	0.010	160.3	0.00874
	2	34.49	2.5984	671	(002)	0.96	0.008	201.6	0.00644
	3	36.25	2.4761	490	(101)	0.95	0.007	233.4	0.00535
	4	47.55	1.9108	251	(102)	0.92	0.007	240.7	0.00397
	5	57.09	1.6120	171	(110)	0.87	0.012	146.4	0.00552
	6	62.90	1.4764	238	(103)	0.85	0.006	302.1	0.00245
ZnO_L120917_Ga_Ar_ vacuum anneal									
	1	31.80	2.8118	491	(100)	0.96	0.015	106.9	0.01317
	2	34.49	2.5984	539	(002)	0.96	0.007	230.6	0.00564
	3	36.25	2.4761	446	(101)	0.95	0.007	238.5	0.00519
ZnO_L070917_Ga_O2_non-anneal									
	1	31.74	2.8170	22	(100)	0.96	0.008	192.6	0.00732
	2	34.50	2.5984	23	(002)	0.96	0.009	171.4	0.00758
	3	36.35	2.4695	26	(101)	0.95	0.013	120.4	0.01017
	4	57.09	1.6120	4	(110)	0.91	0.007	228.2	0.00353
	5	63.05	1.4732	10	(103)	0.85	0.008	225.9	0.00326
ZnO_L121217_Ga_Ar_non-anneal									
	1	31.90	2.8032	511	(100)	0.96	0.011	145.7	0.00962
	2	34.50	2.5976	534	(002)	0.96	0.009	179.2	0.00725
	3	36.24	2.4768	389	(101)	0.95	0.014	115.8	0.01070
	4	47.84	1.8998	240	(102)	0.91	0.012	140.6	0.00676
	5	62.94	1.4755	200	(103)	0.85	0.009	200.7	0.00368

No significant differences in the optical transmittance in the visible region for as-deposited, doped and annealed films were found with exception of ZnO:Ga sample untreated and prepared in O_2 atmosphere where the interference peaks are observed. The differences in the shape of the transmittance envelope are related to differences in film thickness according to the data from the Table 2. The band gap was calculated from the optical absorption data based on the common procedures for direct energy band gap semiconductors. The optical absorption coefficient, α was estimated from the absorbance spectra and taking in consideration thicknesses from Table 2.

Plots of $(\alpha h\nu)^2$ vs. $h\nu$ shown in Figure 3 for all ZnO thin films indicating direct transition between the valence band and conduction band were used to calculate the optical band gap of the samples. For the ZnO:Ga films treated in vacuum and

obtained in the O_2 atmosphere rather allowed interband transition take place according to the inset in the Figure 3. The estimated E_g values are summarized in Table 2. In the as-deposited films we noticed a maximum band gap. A reduction of 0.14 eV in the case of ZnO:Ga vacuum treated and prepared in O_2 atmosphere film, compared with the ZnO pure is revealed. No significant differences are seen in the band gap values of the other samples.

Table 2 Band gap and thickness values of ZnO:Ga films

Samples	E_g, eV	d, nm
ZnO_L090917_ZnO_pure	3.290	1570.0
ZnO_L080917_Ga_O2_treated_vacuum	3.150	908.5
ZnO_L070917_Ga_O2_untreated	3.266	518.05
ZnO_L120917_Ga_ Ar_treated vacuum	3.273	950.0
ZnO_L121217_Ga_Ar_untreated	3.271	1066.0

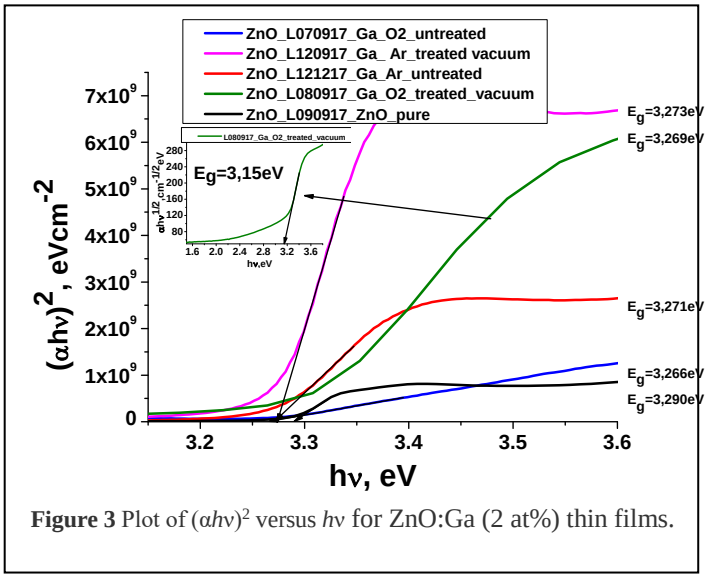

Figure 3 Plot of $(\alpha h\nu)^2$ versus $h\nu$ for ZnO:Ga (2 at%) thin films.

C. *Electrical properties*

Electrical conductivity and electron concentration were measured by four-probe method in the van der Pauw configuration. The measurements were performed under constant magnetic field induction (0.24 T) and stabilized direct current. Each sample was measured for three different values of current (100 μA–2 mA). The measured values of the specific electrical conductance and charge carrier concentration (at 295 K) for the ZnO thin films prepared in different atmospheres are summarized in Table 3. As one can see, the ZnO layer untreated and obtained in the Ar atmosphere are too resistive to be measured with a 4-point probe configuration. The large concentration of charge carriers is noticed for ZnO pure. For the doped with Ga and annealed samples at the same temperature in vacuum, indifferently of substitutional donor-like defects partially compensated by acceptor-like zinc vacancy (V_{Zn}) defects [18,19]. However, these ZnO thin films have lower conductivities (see Table 3).

Table 3 Electrical properties of ZnO:Ga thin films

Samples	ρ, Ω·cm	σ, 1/Ω·cm	n,10^{18} cm^{-3}
ZnO_L090917_ZnO_pure	1.21	0.82	15
ZnO_L080917_Ga_O2_treated_vacuum	92	0.01	0.015
ZnO_L070917_Ga_O2_untreated	217	0.004	0.0003
ZnO_L120917_Ga_ Ar treated vacuum	123	0.008	0.06
ZnO_L121217_Ga_Ar_untreated	~500 kΩ		

According to [20, 21] since Ga acts as a shallow donor in ZnO, the electron concentration equals the net doping density $c_{net} = c(Ga_{Zn}) – 2c(V_{Zn})$, where $c(Ga_{Zn})$ is the concentration of electron-producing Ga donors, and $c(V_{Zn})$ is the concentration of compensating doubly charged acceptor-like Zn vacancies) in the wurtzite ZnO phase.

IV. Conclusions

ZnO thin films doped with 2% Ga were prepared on glass substrates at about 673 K in Ar and O_2 atmospheres using spray pyrolysis. Then the ZnO thin films were annealed in vacuum at 723 K. The structural properties studies revealed that all the undoped ZnO and Ga doped thin films had a polycrystalline hexagonal wurtzite structure with a preferred (002) c-axis orientation with exception of ZnO non-annealed obtained in O_2 atmosphere with orientation in (101). Ga doping also resulted in a decrease in grain sizes in the preferred orientation. All ZnO thin films exhibited higher transparencies than 80% in the visible region. The optical band gap shifted towards longer wavelengths with Ga doping. The experimental data of the electron concentration of the nature of the carrier gas, the charge carrier's concentration is the same order (10^{-16} cm^{-3}) and is in agreement zinc oxide thin films doped with 2%Ga and prepared in O_2, and Ar atmospheres fully support the theoretical model of Ga_{Zn}.

Acknowledgments

This research was supported by the Japan bilateral collaboration project between Research Institute of Electronic, Shizuoka University and Physics Department and Engineering of Moldova State University, and the National Grant **15.817.02.39A.**

REFERENCES

[1] GaofengZheng, Ping Zhu, Lingling Sun, Jiaxin Jiang, Juan Liu,Xiang Wang, Wenwang Li. *Thin film zinc oxide gas sensor fabricated usingnear-field electrospray.*AIP ADVANCES 6. 2016.

[2] S.J. Pearton, D.P. Norton, Y.W. Heo, L.C. Tien, M.P. Ivill, Y. Li, B.S. Kang, F. Ren, J. Kelly, A.F. Hebard. *ZnO Spintronics and Nanowire Devices*. Journal of Electronic Materials, Vol. 35. 2006. P.862-868

[3] Athanasios Tamvakos, Kiprono Korir, DimitriosTamvakos, Davide Calestani, Giancarlo Cicero, Daniele Pullini. *NO_2 gas sensing mechanism of ZnO thin-film transducers: physical experiment and theoretical correlation study.* ACS Sensors. 2016.

[4] Xiaosheng Fang, Yoshio Bando, Ujjal K. Gautam, TianyouZhai, Haibo Zeng,Xijin Xu,Meiyong Liao,Dmitri Golberg. *ZnO and ZnS Nanostructures: Ultraviolet-Light Emitters, Lasers, and Sensors*. SolidStateandMaterialsScience. 2009. P. 190–223.

[5] Mohamed A. Basyooni, Mohamed Shaban, Adel M. El Sayed. *Enhanced Gas Sensing Properties of Spin-coated Na-doped ZnO Nanostructured Films*. Scientific reports. 2017. P.1-12.

[6] Sylwia Gieraltowska,Lukasz Wachnicki, Bartlomiej S. Witkowski, ElzbietaGuziewicz, Marek Godlewski. *Thin Films of High-k Oxides and ZnO for Transparent ElectronicDevices.* Chemical vapor deposition. 2013. P. 213–220.

[7] Wen-Ching Shih, Tzyy-Long Wang, Yan-Kai Pen. *Enhancement of characteristics of ZnO thin film surface acoustic wave device on glass substrate by introducing an alumina film interlayer*. Applied Surface Science. 2012. P. 5424– 5428.

[8] Xingli He, HongweiGuo, Jinkai Chen, Wenbo Wang, Weipeng Xuan, Yang Xu, Jikui Luo. *Bendable ZnO thin film surface acoustic wave devices on polyethyleneterephthalate substrate*. Applied Physics Letters. 2014.

[9] D. R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 73rd Edition, CRC Press, New York, 1992

[10] T. Hanada, "Oxide and Nitride Semiconductors," in Advanced Materials Research, edited by T. Yao and S.-K. Hong (Springer, Berlin, 2009), p. 1

[11] Xingli He, HongweiGuo, Jinkai Chen, Wenbo Wang, Weipeng Xuan, Yang Xu, Jikui Luo. *Bendable ZnO thin film surface acoustic wave devices on polyethyleneterephthalate substrate*. Appl. Phys. Lett. 104, 213504 (2014); https://doi.org/10.1063/1.4879850

[12] P. Scherrer, "Bestimmung der Grösse und der Inneren Struktur von er Gröss Kolloidteilchen Mittels Nachrichten von der Gesellschaft der Wissenschaften, Göttingen," Mathematisch-Physikalische Klasse, Vol. 2, 1918, pp. 98-100.

[13] R.Bhatt, I.Bhaumik, S.Ganesamoorthy, A.K.Karnal, M.K.Swami, H.S.Patel, P.K.Gupta, Physics Status Solidi A, 209, 1, 176-180, 2012.

[14] L. Jung_Chul, K. Yang_Do, S. Pung_Keun et al. *Characteristic of Ga_doped ZnO films deposited by DC magnetron sputtering with a sintered ceramic ZnO:Ga targe*t.// Journal of the Korean Physical Society, 2008, Vol. 53,No 1. – P. 416–420.

[15] / L. Ma, S. Ma, H. Chen et al. *Microstructures and optical properties of Cu_doped ZnO films prepared by radio frequency reactive magnetron sputtering*. // Applied Surface Science. – 2011. – Vol. 257, No 23, P.10036–10041.

[16] American Standard for Testing Materials, X-ray Powder Diffraction Data, File Card 5-0664.

[17] A R Babar et al. *Gallium doping in transparent conductive ZnO thin films prepared by chemical spray pyrolysis* J. Phys. D: Appl. Phys. 41 (2008) 135404

[18] K. Biswas and S. Lany, *Non-equilibrium origin of high electricalconductivity in gallium zinc oxide thin films*. Phys. Rev. B 80, 115206 (2009). https://doi.org/10.1103/PhysRevB.80.115206 .

[19] S. Lany and A. Zunger, Phys. Rev. Lett. 98, 045501 (2007). https://doi.org/10.1103/PhysRevLett.98.045501.

[20] B. K. Meyer, J. Sann, D. M. Hofmann, C. Neumann, and A. Zeuner, *Improvements in quantum efficiency of excitonic emissions in ZnO epilayers by the elimination of point defects*. Semicond. Sci. Technol. 20, S62 (2005). https://doi.org/10.1088/0268-1242/20/4/008.

[21] L. J. Brillson, Y. Dong, F. Tuomisto, B. G. Svensson, A. Yu. Kuznetsov, D. Doutt, H. L. Mosbacker, G. Cantwell, J. Zhang, J. J. Song, Z.-Q. Fang, and D. C. Look, *Native point defects at ZnO surfaces, interfaces and bulk films.* Physica Status Solidi C **9**, 1566
(2012).