JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 18, No. 7-8, July - August 2016, p. 672 - 678

Influence of Ga dopants on the structural, optical and electrical properties of solution processed ZnO thin films

FELCY JYOTHI SERRAO[a,b*], S.M. DHARMAPRAKASH[a]
[a]*Department of studies in Physics, Mangalore University, Mangalagangothri 574199, India*
[b]*Department of Physics, Karnataka Government Research Centre SCEM, Mangalore, 575007, India*

Gallium (1at% to 5at%) doped zinc oxide films (GZO) with thickness of 348 nm were grown on a glass substrate by sol-gel spin coating method. X-ray diffraction studies reveal that the excessive Ga doping deteriorates the crystallinity of the films. The optical properties were studied using an UV-Vis spectroscopy. All the films showed more than 90% optimal transparency in the entire visible region. The optical transmittance of the films increases with an increase in the Ga doping concentration. A sharp fundamental absorption edge with a slight blue shifting was observed with an increase in Ga doping concentration. In addition, the effect of Ga doping concentration on the band gap and optical constants of the films was investigated. The doping concentration significantly affects the optical constants and Urbach energy values of the films. The largest grain size, the lowest resistivity (2.62×10^{-3} Ωcm) and the highest figure of merit was achieved for a GZO film at doping concentration 1at%. The new results, obtained from this study indicate that spin coated GZO films have satisfactory optical and electrical properties for the display applications and optoelectronic devices.

(Received September 8, 2014; accepted August 3, 2016)

Keywords: Spin coating, GZO thin films, Structural, Optical and electrical

1. Introduction

In recent years, the transparent conducting oxides (TCOs) have attracted extensive attention due to their wide range of applications in optoelectronic devices such as solar cells, flat panel displays, liquid crystal displays(LCDs), organic light emitting diodes (OLEDs) [1-4]. TCO films based on ZnO are a promising alternative to high cost ITO and SnO_2 films, owing to a number of advantages, namely low cost, non-toxicity, resource availability and high thermal and chemical stability [5]. To increase the conductivity, transparency and stability, various dopants have been used to prepare high quality n-or p-type ZnO films. Doping of ZnO with Group III elements such as Indium (In), Aluminum (Al) and Gallium (Ga) gives rise to the n-type semiconductors by substituting dopants in a ZnO host lattice. Among these elements Ga is the best choice to enhance conductivity and transparency of ZnO. Since the ionic radius of Ga^{3+} is 0.62Å much close to the size of Zn^{2+} (0.74Å), and Ga^{3+} possesses one more valence than Zn^{2+}. In addition, the covalent bond length of Ga-O (1.92Å) is similar to that of Zn-O (1.97Å). Therefore, the addition of Ga to the ZnO matrix reduces the deformation and stress in the ZnO lattice [6-8]. A variety of techniques have been used to fabricate GZO thin films such as pulsed laser deposition (PLD), magnetron sputtering, chemical vapour deposition, sol-gel, spray pyrolysis and so on [9-12]. Among these methods sol-gel technique has distinct advantages such as cost effectiveness, simplicity, homogeneity, excellent compositional control at the molecular level and lower crystallization temperature. Moreover, in this technique incorporation of dopants is easier and large area substrates can be developed readily. Even though several researchers have prepared and characterized GZO thin films by different techniques and methods, report on the influence of Ga concentration on the optimization of structural, optical and electrical properties of GZO films using the spin-coating method is scarcely found in literature.

In the present work, as an effort to develop the most promising aspirant and an alternative to expensive ITO thin films, transparent conducting gallium doped ZnO thin films were prepared by a low cost sol-gel spin coating method. The influence of Ga concentration on the structural, optical and electrical properties of GZO films has been investigated.

2. Experimental details

GZO thin films were grown on glass substrate at room temperature by sol-gel spin coating method. Fig.1 shows the flow chart of the preparation of GZO thin films. In this process, the GZO film synthesis includes three principal steps: (i) solution preparation, (ii) coating and (iii) heat treatment. The precursor solution for spin coating was prepared by dissolving an appropriate amount of Zinc acetate dihydrate and gallium nitrate in 2-methoxyehanol at room temperature. Monoethanolamine (MEA) was then added to the mixture as a sol stabilizer. The five different concentrations (1at%, 2at%, 3at%, 4at% and 5at% measured as an atomic weight percentage) were selected. The total concentration of the sol was maintained at 0.5 mol L^{-1} and the molar ratio of MEA to zinc acetate was maintained at 1.0. The resulting mixture was then stirred at 60^{o}C for 1 hr using a magnetic stirrer to form a clear

and transparent homogeneous mixture. The glass substrate was cleaned with standard cleaning procedure and then GZO films were deposited on a glass substrate by the spin coating method at room temperature with a rate of 3000rpm for 30s. After being deposited by sol-gel spin coating method, the films were preheated at 350°C for 15 min, to evaporate the solvent and to remove organic residuals. The process of coating is repeated to get the films of desired thickness and then the films were annealed in air at 500°C for an hour.

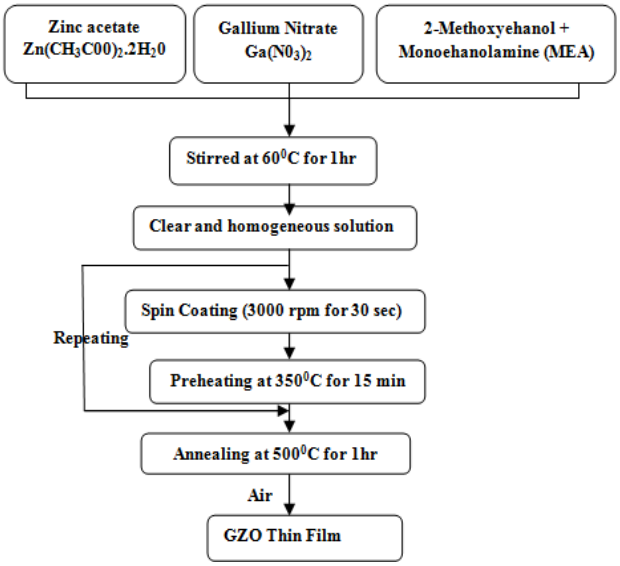

Fig. 1. The flow chart showing the procedure for preparing GZO thin films.

3. Characterization methods

Thermogravimetric (TGA) and differential thermal analysis (DTA) of GZO with Ga 1at% was carried out using SDT Q600 simultaneous DTA-TGA, in the temperature range 30-800°C at a heating rate of 10°C/ min under an air flux. The crystalline structures and orientations were investigated by Rigaku Miniflex 600 Table Top Powder X-ray diffractometer using Cu Kα radiation having wavelength 0.154059 nm. The surface topography of the GZO films was studied using the atomic force microscope (AFM-Nanosurf Easy Scan 2). The thickness of GZO films was measured by an ellipsometer. Optical properties of the films were measured by a UV-visible spectrophotometer (SHIMADZU 1800) in the wavelength range 300-800 nm. Electrical characterization of the films was also carried out by means of electrical resistivity measurements using the van der Pauw method.

4. Results and discussion

4.1. Thermal analysis of ZnO: Ga 1at%

The DTA and TGA curves of ZnO doped with Ga 1at% are shown in Fig.2. A large exothermic peak is observed in the DTA curve at about 468°C due to the decomposition of the organic residuals and crystallization of GZO, suggesting that crystallization of the GZO thin film occurs in the heat treatment above 468°C in order to avoid the presence of organic residues. The TGA curve indicates a strong weight loss up to 500°C, which must be due to the removal of the organic residues. Beyond 500°C, the TG curve remains constant, suggesting that a thermal treatment at this temperature could be used to obtain GZO. The total weight loss observed was about 54% of the initial weight.

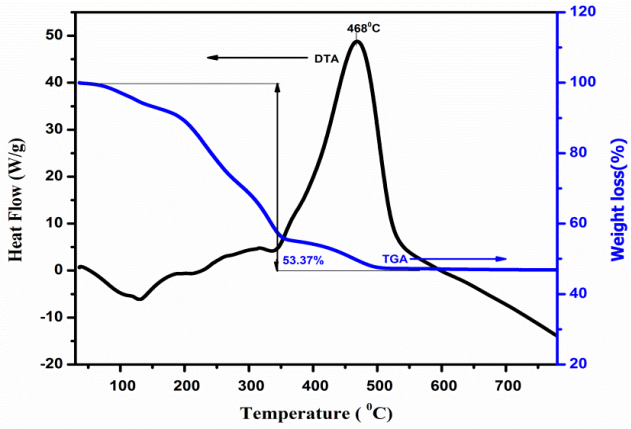

Fig. 2. TG-DTA analysis of GZO-dried gel.

4.2. Structural properties of Ga-doped ZnO films

Fig. 3 shows the X-ray diffraction patterns of GZO films at different Ga concentrations. The undoped ZnO films show the dominant peak at (002) plane and weak peaks at (100) and (101) planes, indicating the polycrystalline nature of the film. However, on Ga doing only the dominant peak corresponding to (002) plane is observed, indicating the preferred orientation along the c-axis, i.e. [001] direction perpendicular to the substrate (JCPDS file no.36-1451) [13-14]. It can be observed that, the intensity of the (002) plane of the Ga-doped ZnO films decreased with increasing Ga doping concentration. This clearly indicates that the excessive Ga doping deteriorates the crystallinity of the films, which may be because of the formation of stress by the smaller radius of Ga^{3+} ions (0.62Å) compared with Zn^{2+} ions (0.74Å) [15]. In order to verify the relation between crystallinity and Ga doping concentration, the stress in the direction of the c-axis is calculated based on biaxial strain model and using the following formula, which is valid for a hexagonal lattice [16]

$$\sigma = \frac{2c_{13}^2 - c_{33}(c_{11}+c_{12})}{2c_{13}} \frac{c-c_0}{c_0} \quad (1)$$

where c_{ij} represent elastic stiffness constants for single crystalline ZnO :c_{11} = 208.8 GPa, c_{33} = 213.8 GPa, c_{12} = 119.7 GPa, and c_{13} = 104.2 GPa . c and c_0 are the lattice constants of the GZO thin films and strain free ZnO thin

films (5.2066A^{o}), respectively. The lattice constant *c* can be calculated by the following formula:

$$\frac{1}{d^2} = \frac{4}{3}\frac{(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2} \quad (2)$$

The c-parameter, its error percentage and calculated stress of the GZO thin films are presented in Table 1. The negative sign of the stress indicates that the stress of GZO films is compressive. It can be observed that there is a slight increase in the compressive stress in the Ga doping concentration and also the expansion of the c-lattice parameter indicating there is more interstitial Ga^{3+} in ZnO lattice.

From the ZnO (002) peaks in Fig.3, the grain sizes of the GZO were calculated using the Debye-Scherrer formula [17]

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (3)$$

Where D is the grain size, λ is the X-ray wavelength (0.154059nm), β is the full width at half maximum of the peaks in radians (corrected for instrumental line broadening) and θ is the angle of diffraction. The variations of FWHM and the grain size are shown in the Table1. It can be seen that the FWHM of the (002) reflection of Ga-doped ZnO films increases with increasing Ga concentration (up to 5at%) and the grain size decreases from 26 nm to 17nm as the concentration is increased from 0at% to 5at%. The possible reason could be the disturbance of grain growth by stress due to the difference in ion radius between gallium and zinc.

Fig. 4 shows the AFM images of gallium doped ZnO thin films at different doping concentrations. It can be seen that the surface morphology of the film changed with the dopant concentration. The root mean square (RMS) roughness of the GZO films decreased from 22.378 nm to 5.318 nm when the doping concentration was increased from 1at% to 5 at%. In 1 at% Ga, the largest grains were observed. This result is in agreement with the result of XRD.

Table 1. Diffraction peak positions, FWHM, Grain Size, interplanar spacing, c-lattice parameter calculated for (002) plane and values of compressive stress of GZO films with different Ga concentrations.

Ga concentrations	**Peak positions(2θ)**	**FWHM (^{o})**	**Grain Size (nm)**	**d_{hkl} (A^{o})**	**c (A^{o})**	**Error (%)**	**σ (GPa)**
1at%	34.405	0.321	25.907	2.6046	5.2092	0.0499	-0.11625
2at%	34.403	0.366	22.722	2.6047	5.2094	0.0537	-0.12519
3at%	34.388	0.381	21.826	2.6058	5.2116	0.0960	-0.22356
4at%	34.395	0.391	21.269	2.6053	5.2106	0.0768	-0.17884
5at%	34.385	0.474	17.544	2.6060	5.2120	0.1037	-0.24144

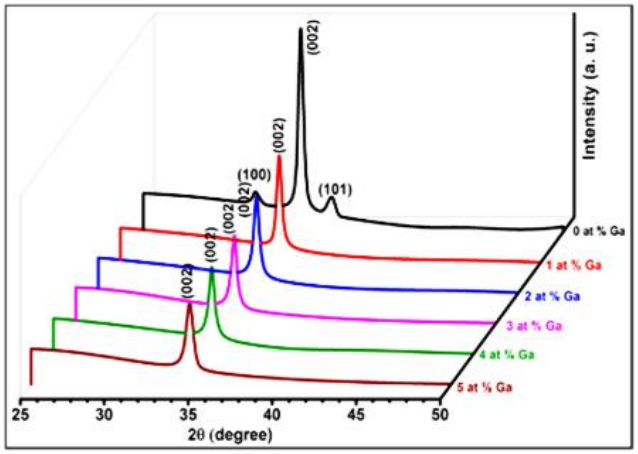

Fig. 3. XRD patterns of GZO thin films with different gallium concentrations

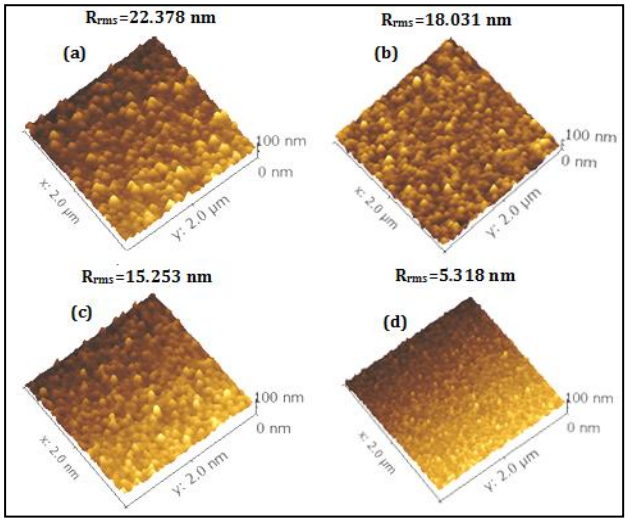

Fig. 4. AFM surface morphology of GZO films with different Ga concentrations. (a) 1at% (b) 2at% (c) 3at% (d) 5at%.

4.3. Optical properties of Ga–doped ZnO films

Optical transmittance spectra of the GZO thin films at different Ga concentrations are shown in Fig.5 in the wavelength range of 300 to 800nm. The average transmittance of all the GZO films is above 90% in the visible wavelength range (400-800nm) with a sharp absorption edge (transparency is very high compared to undoped ZnO 78%) in the UV region. It shows that the GZO film would be a good material for the display applications. It can also be seen that there is an increase in the average transmittance with an increase in the Ga-doping concentration, in other words the absorption edge is slightly blue shifted with increasing Ga concentration indicates the broadening of the optical band gap. This variation can be explained by the Burstein-Moss effect and is related to carrier concentration [18].

From the transmittance spectrum, the refractive index (n) and the extinction coefficient (k) of GZO thin films were calculated using the following relations [19]

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \tag{4}$$

$$k = \frac{\alpha\lambda}{4\pi} \tag{5}$$

where R is the reflectance and α is the absorption coefficient. Fig.6 shows (a) refractive index '*n'* and (b) extinction coefficient '*k'* of GZO thin films with different Ga concentrations. It can be seen that, the extinction coefficient '*k'* of GZO films is very small over the entire spectral region, indicating that the films are highly transparent. The refractive index and extinction coefficient of the GZO thin films decreased with the increasing Ga concentration. The decrease in the refractive index with Ga doping concentration was mainly attributed to an increase in the carrier concentration in the GZO thin films.

The fundamental electron excitation spectrum of the film is described by the frequency dependence of the complex dielectric constant. The real (ε_r) and imaginary (ε_i) parts of the dielectric constant (ε) can be calculated using the following equations [20]

$$\varepsilon_r = n^2 - k^2 \tag{6}$$

$$\varepsilon_i = 2nk \tag{7}$$

The dependence of ε_r and ε_i values of the undoped and Ga doped ZnO thin films on photon energy is shown in Fig.7 (a) and (b) respectively. It is seen that both ε_r and ε_i increase with increasing photon energy. The values of ε_r for all the doped ZnO films are higher than the ε_i values. Moreover the value of ε_i of GZO thin films is lower than that of the undoped ZnO film, indicating the low dielectric loss in the GZO thin films.

The optical absorption coefficient (α) can be determined using the following formula [21]

$$\alpha = \frac{2.303A}{d} \tag{8}$$

Where '*d*' is the film thickness and *A* is the optical absorbance of the film.

The optical band gap (E_g) was analyzed by the following relationship [22]

$$(\alpha h\nu)^2 = A(h\nu - E_g) \tag{9}$$

Where *h* is Planck's constant, *v* is the frequency of the incident photon and *c* is the constant for direct transition. Fig.8 shows the plots of $(\alpha h\nu)^2$ against h*v* for the GZO films at various Ga concentrations. Since GZO thin films have a direct band gap, the optical energy gap (E_g) can be determined by the extrapolation of the straight line portion at $(\alpha h\nu)^2$ is zero. The variation of the band gap energy (E_g) and average transmittance (T %) of GZO films with different Ga concentrations are shown in Table 2. It is seen that the direct optical band gap (E_g) has increased from 3.2602 eV to 3.297 eV as the concentration of Ga is increased from 1at% to 5at%.

The absorption coefficient near the fundamental absorption edge is exponentially dependent on the incident photon energy and obeys the empirical Urbach relationship, in which $ln\alpha$ varies as a function of $h\nu$. The Urbach energy which reflects the disorder in the film network is expressed as [23]

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_U}\right) \tag{10}$$

where E_U is the Urbach energy, which characterizes the slope of the exponential edge and α_0 is a constant. The E_U values were calculated from the inverse of the slope of $ln\alpha$ versus $h\nu$. The variation of the bandgap energy and the Urbach energy of the doped ZnO thin films as a function of different dopant concentrations are shown in Fig.9. It is observed that the Urbach energy varies inversely with the optical band gap energy.

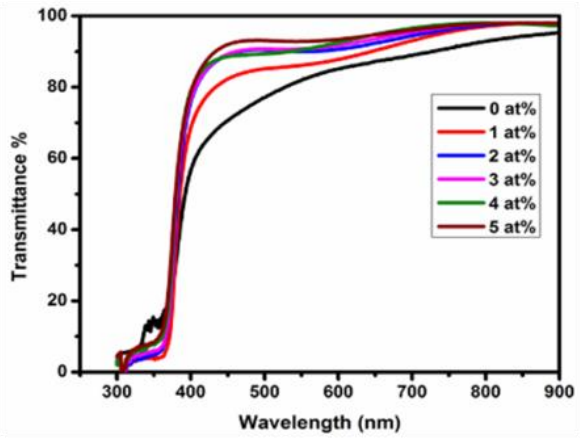

Fig. 5. The optical transmission spectra of GZO thin film deposited with different Ga doping concentrations

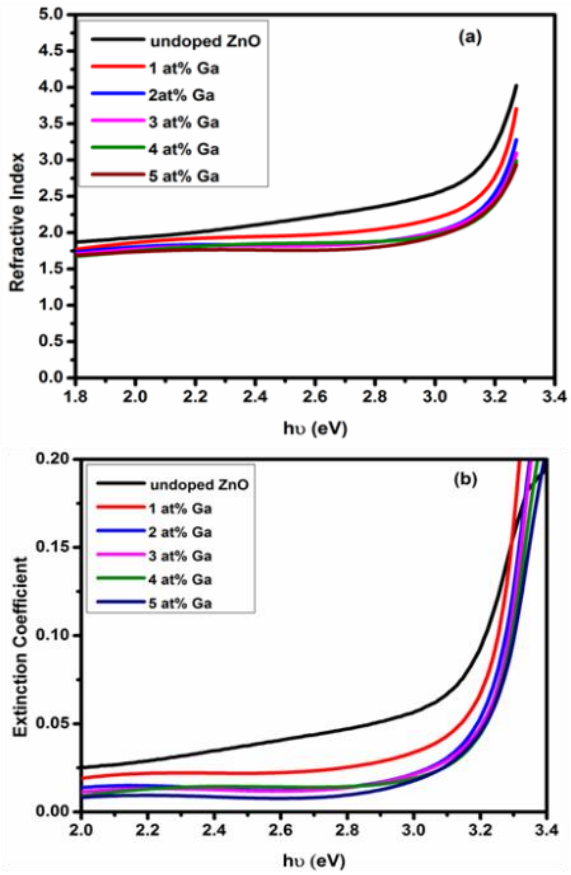

Fig. 6. (a) Refractive index and (b) Extinction coefficient of the undoped and Ga doped ZnO thin films with different Ga concentrations.

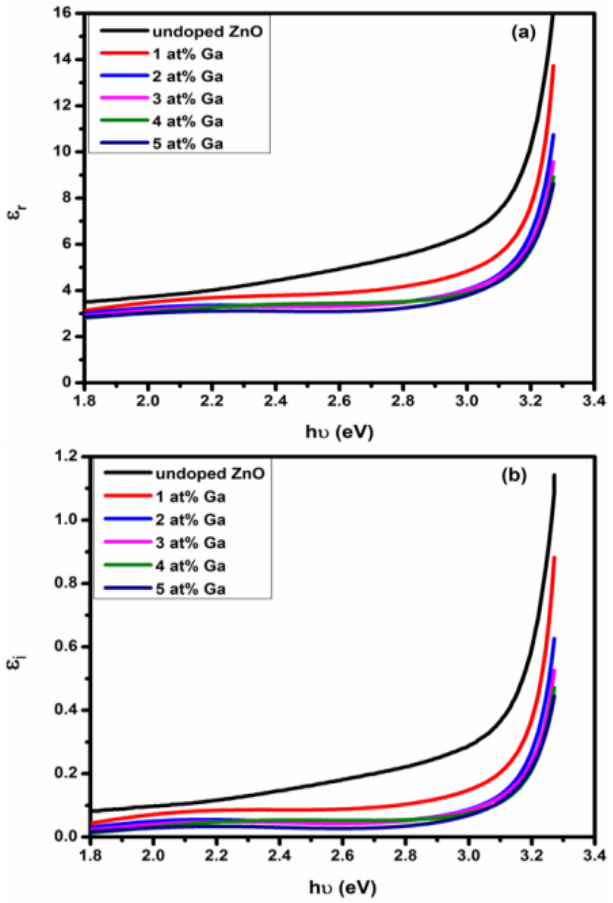

Fig. 7. The real (a) and imaginary (b) parts of the dielectric constant of the GZO films.

Table 2. *Band gap (E_g), Urbach energy (E_U) and average transmittance of GZO films with different Ga concentrations.*

Ga concentration	Band gap E_g (eV)	Urbach energy (meV)	Average Transmittance (%)
1at%	3.260	103.73	89.97
2at%	3.273	96.98	93.39
3at%	3.281	89.60	94.10
4at%	3.289	88.97	94.45
5at%	3.297	63.29	95.63

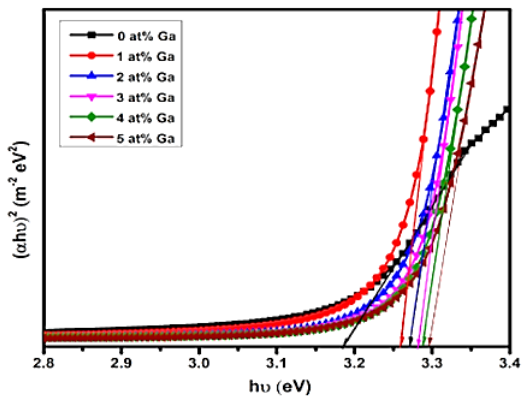

Fig. 8. Plot of $(\alpha h\upsilon)^2$ vs. $(h\upsilon)$ for different Ga doping concentrations of GZO thin films.

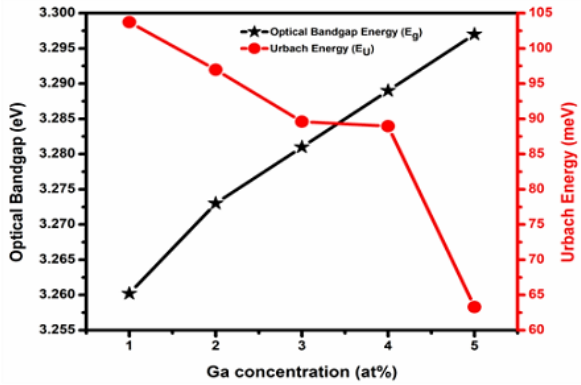

Fig. 9. The effect of Ga doping concentration on the optical bandgap energy and Urbach energy of the films.

4.4. Electrical properties of Ga–doped ZnO films

The variation of electrical resistivity and the figure of merit (FOM) of GZO films at different Ga doping concentrations are shown in Fig. 10. The resistivity of the undoped ZnO thin film was found to be $6.6\text{x}10^{-2}$ Ω cm. It can be observed that the resistivity decreases significantly with the incorporation of Ga dopants. The decrease in the resistivity of the GZO films can be attributed to the enhancement of the carrier concentration due to the substitutional incorporation of Ga^{3+}ions at Zn^{2+} sites or the incorporation of Ga ions in the interstitial positions. A lowest resistivity of $2.63\text{x}10^{-3}$Ω cm was obtained from the GZO film with doping concentration of 1at% of Ga. At higher doping concentrations (>1at% Ga), an increase in the resistivity was observed due to segregation of dopant which acts as carrier traps at the grain boundaries [24].

The quality of GZO films as TCO can be judged by the FOM and is defined by the following equation [25]

$$FOM = \frac{T^{10}}{R_S} \qquad (11)$$

Where T is the average visible transmittance and R_s is the sheet resistance of the film. The higher values of the FOM represent the better performance of the TCO film. As can be seen from Fig.10, the FOM of the GZO thin films decreases, as the dopant content in the film is increased. The highest FOM value of $1.195\text{x}10^{-2}$ Ω^{-1} was obtained for the ZnO film doped with 1at% of Ga. From these results, it is clear that the film resistivity strongly depends on the doping concentration.

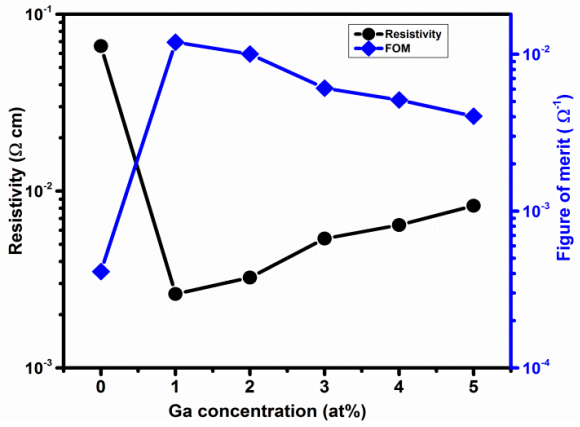

Fig. 10. Electrical resistivity and FOM of GZO films with different Ga doping concentrations.

5. Conclusion

Gallium doped zinc oxide thin films were prepared at 500°C substrate temperature using a low cost sol-gel spin coating method. The effect of Ga doping concentration on the structural, optical and electrical properties was investigated. All the GZO films are polycrystalline with a hexagonal wurtzite crystal structure having a preferred orientation along the (002) plane. The grain size was found to decrease with increase in Ga-doping concentration. All the GZO films showed more than 90% of transparency in the entire visible region. Gallium doping leads to a considerable increase in optical transmittance of the GZO films. The widening of the band gap is observed which can be explained by the Burstein-Moss effect. The optical constants and Urbach energy were found to be affected by the Ga incorporation. The minimum resistivity of 2.62×10^{-3} Ω cm was obtained from the GZO thin film doped with 1at% Ga. The obtained results indicate the possibility that spin coated GZO film would be a good material for the display applications and optoelectronic devices.

Acknowledgements

The authors gratefully acknowledge Coordinator, DST FIST and UGC SAP, Department of Physics, Mangalore University for providing facilities for the characterization of thin films and technical support to carry out the work.

References

[1] J. Loffler, R. Groenen, J. L. Linden, M. C. H. Van de Sanden, R. E. I. Schropp, Thin solid Films **392,** 315 (2001).
[2] G. X. Liang, P. Fan, X. M. Cai, D. P. Zhang, Z.H. Zheng, Journal of Electronic Material **40,** 267 (2011).
[3] J. Wienke, B. van der Zanden, X. Tijssen, M. Zeman, Sol. Energy Mater. Sol. Cells. **92,** 884 (2008).
[4] W. S. Han, Y. Y. Kim, B. H. Kong, H. K. Cho, Thin Solid Films **517**, 5106 (2009).
[5] K. Ellmer, J. Phys. D. Appl. Phys. **34**, 3097 (2001).
[6] L. Shuang, M. Z. Xia, D. X. Long, Chin. Phys. B **21,** 067306 (2012).
[7] K. Yim, H. W. Kim, C. Lee, Materials Science and Technology **23**, 108 (2007).
[8] T. P. Rao, M. C. S. Kumar, Crystallization Process and Technology **2,** 72 (2012).
[9] H. Kim, J. S. Horwitz, W. H. Kim, A. J. Makinen, Z. H. Kafafi, D. B. Chrisey, Thin Solid Films **420**, 539 (2002).
[10] Q. B. Ma, Z. Z. Ye, H. P. He, S. H. Hu, J. R. Wang, L. P. Zhu, Y. N. Zhang, B. H. Zhao, J. Cryst. Growth **304** 64 (2007)..
[11] K. Y. Cheong, N. Muti, S. R. Ramanan, Thin Solid Films **410**, 142 (2002)
[12] P. Nunes, E. Fortunato, R. Martins, Int. J. Inorg. Mater. **3**, 1125 (2001).
[13] A. R. Babar, P. R. Deshamukh, R. J. Deokate, D. Haranath, C. H. Bhosale, K. Y. Rajpure, J. Phys. D: Appl. Phys. **41**, 135404 (2008).
[14] H. H. Shin, Y. H. Jong, S. J. Kang, J. Mater Sci: Mater Electron **20**, 704 (2009).
[15] P. K. Nayak, J. Yang, J. Kim, S. Chung, J. Jeong, C. Lee, Y. Hong, J. Phys. D: Appl. Phys. **42**, 035102 (2009).
[16] T. P. Rao, M. C. Santhosh Kumar, N. Sooraj Hussain, Journal of alloys and compounds **541**, 495 (2012).

[17] D. Raoufi, T. Raoufi, Applied Surface Science **255**, 5812 (2009).
[18] J. Zhou, Z. Y. Zhong, Cryst. Res. Technol**. 47**, 944 (2012).
[19] S. Aydogu, O. Sendil, M. B. Coban, Chinese Journal of Physics **50,** 89 (2012).
[20] Z. Z You, G. J. Hua, Journal of Alloys and Compounds **530**, 11 (2012)
[21] S. Ilican, M. Caglar, Y. Caglar, Material Science-Poland **25**, 709 (2007).
[22] X. Q. Meng, W. Zhen, J. P. Guo, X. J. Fan, Appl. Phys. A **70**, 421 (2000).
[23] N. Shakti, P. S. Gupta, Applied Physics Research **2**, 19 (2010).
[24] M. C. Jun, S. U. Park, J. Hyukkoh, Nanoscale research Letters **7,** 639 (2012).
[25] V. Shelke, B. K. Sonawane, M. P. Bhole, J. Mater Sci: Mater Electron. **23**, 451 (2012).

*Corresponding author: jyothiserrao@gmail.com