Crystal and surface structural studies on Sol-gel derived Ga-doped ZnO thin films

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ABSTRACT

Highly transparent gallium-doped zinc oxide (GZO) thin films were prepared on glass substrate by optimized sol-gel spin coating technique. Zinc acetate and gallium nitrate were used as precursors for Zn and Ga ions respectively. Combined effects of doping concentration and thermal annealing temperatures in air on crystal and surface structural properties of the GZO films were investigated by X-ray diffraction (XRD) and atomic force microscopy (AFM) respectively. The X-ray diffraction studies revealed the polycrystalline nature of the films with hexagonal wurtzite phase and showed compressive stress along c-axis. The compressive stress was found to increase with increase in gallium concentration. The grain size of the films was calculated using the Scherrer formula. It was found that the grain size, lattice constant, and surface roughness were significantly affected by the doping concentration and annealing temperature. The GZO films deposited with doping concentration of 1 at% Ga, annealed at 500ºC exhibit optimum characteristics and could be used for the display applications and in optoelectronic devices.

Keywords: **Ga doped ZnO, Doping Concentration, spin-coating, annealing temperature**

1. INTRODUCTION

In the last decade, among various II-VI semiconductors, zinc oxide (ZnO) has received considerable attention due to its novel properties and used as a promising alternate transparent conducting oxide (TCO) material to replace indium tin oxide (ITO). ZnO is an inexpensive n-type semiconductor having hexagonal wurtzite structure with a direct energy wide band gap of 3.37eV and large exciton binding energy of 60 m eV at room temperature which are widely used as transparent electrodes for optoelectronic devices like light emitting diodes, flat panel displays, solar cells etc., [1]-[4]. Recently, ZnO-based TCO thin films have engrossed much attention due to their interesting opto-electrical properties. Group III metal elements such as In, Al and Ga have considered as the most suitable doping elements. Among these impurities, gallium is of great interest because the ionic and covalent radii of Ga^{3+} (0.62Å, 1.26Å) are much closer to the size of Zn^{2+} (0.74Å, 1.31Å) than to those of Al (0.5Å, 1.26Å) and In (0.81Å, 1.44Å). In addition to this, Ga^{3+} dopants are more resistant to oxidation and less reactive than Al^{3+} dopants. Therefore, the addition of Ga to the ZnO host lattice reduces the deformation and stress in the ZnO lattice [5]. GZO thin films have been synthesized by various techniques such as magnetron sputtering, chemical vapour deposition, pulsed laser deposition (PLD), sol-gel and spray pyrolysis [6]-[9]. Among these techniques, the sol-gel method has discrete advantages of homogeneity, controllability of compositions, simplicity and low cost.

In sol-gel method, the concentration of the precursor solution and annealing temperatures have a major role in defining the properties of the film. Therefore, in the present work, we report the combined effects of doping concentration and thermal annealing temperatures in air on crystal and surface structural properties of the GZO films.

2. EXPERIMENTAL

Sol is prepared by taking zinc acetate dehydrate and gallium nitrate as starting materials in appropriate quantity. 2-methoxyehanol and Monoethanolamine were used as a solvent and sol stabilizer respectively. Three different dopant concentrations (1at%, 2at%, 3at%) were selected. The total sol concentration was retained at 0.5 mol L^{-1} and the molar ratio of MEA to zinc acetate was maintained at 1.0. The resulting mixture was aged for 2 days at 30ºC. The Ga:ZnO films were deposited on a glass substrate (Corning1737) at 3000 rotations per minute (rpm) for 30s by the spin coating method at 30 ºC.

The resulted films were pre-heated at 150ºC for 15 min, to evaporate the solvent and to eliminate organic residuals. Multiple spin-bake process is followed to achieve the desired thickness of the films. The resulting films were annealed for an hour at various temperatures

The structural characteristics of GZO thin films were explored by Rigaku Miniflex 600 Table Top Powder X-ray diffractometer using Cu Kα radiation with wavelength 0.154059 nm. Debye-Scherrer formula is used to estimate the crystallite size of the GZO films using XRD data. The topography of the film surfaces was studied using the atomic force microscope (AFM-Nanosurf Easy Scan 2). Ellipsometer is used to measure the thickness of GZO films. SHIMADZU 1800, a UV-visible spectrophotometer, is used to study the optical properties of the films the in the wavelength range 300-800nm.

3. RESULTS AND DISCUSSION

X-ray diffraction patterns (XRD) of GZO films at different Ga dopant concentrations are shown in Fig.1. The dominant peaks are due to ZnO (002) planes, indicating that all the GZO films have polycrystalline nature with a preferred orientation along the c-axis i.e. [001] direction (JCPDS file no.36-1451) **[10].** The intensity of the (002) plane of the films decreased with increasing Ga dopant concentration. This clearly specifies the degradation in the film quality, which may be due to the lattice deformation produced by the substitution of the Ga atoms for Zn sites in the ZnO host lattice (Fig.2) and the stress developed by the smaller radius of Ga^{3+} ions (0.62Å) compared with Zn^{2+} ions (0.74Å) **[11]**. Details that characterizes the growth is obtained from the XRD data. These include the average grain size, lattice strain, lattice stress and defect density. The grain sizes of the GZO were estimated using the Debye-Scherrer formula **[12]**

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where, D is the grain size, λ is wavelength of X-ray (0.154059nm), β is the full width at half maximum of the peaks in radians and θ is the diffraction angle. The strain along c-axis (ε) and the dislocation density (δ) of Ga:ZnO films were computed using the equations

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad (2)$$

$$\delta = \frac{1}{D^2} \quad (3)$$

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 **[13]**

$$\sigma = -233\frac{c - c_o}{c_o} \quad (4)$$

Where, c and c_0 are the lattice constants of the Ga:ZnO thin films and strain free ZnO thin films respectively. The lattice constant c can be computed by the following formula:

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

The grain size, strain, dislocation density, c-parameter and calculated stress of the GZO thin films are presented in Table 1. It can be seen that the film with doping concentration 1 at% shows the better quality. The negative sign of the stress indicates that the stress of GZO films is compressive. Moreover, there is a slight increase in the compressive stress with the Ga doping concentration and also the expansion of the c-lattice parameter indicating there is more interstitial Ga^{3+} in ZnO lattice.

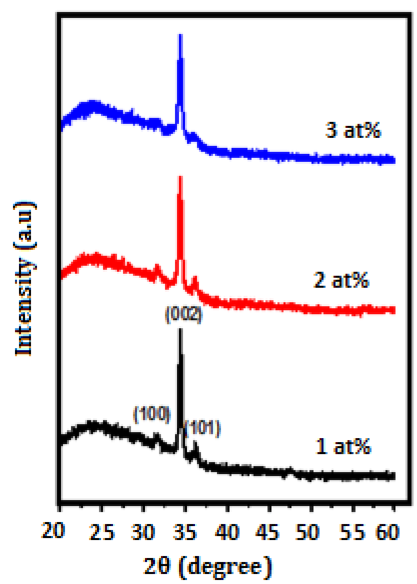

Fig.1: XRD patterns of GZO thin films with different gallium concentrations

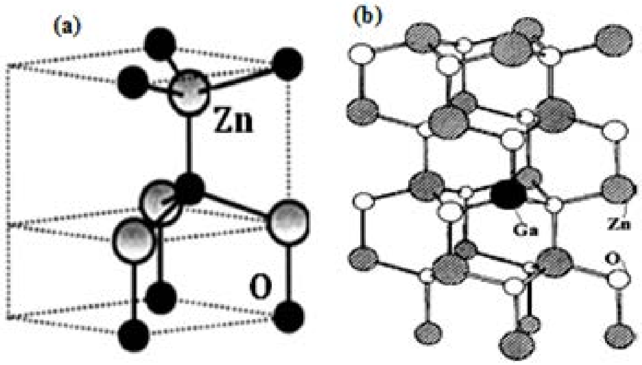

Fig.2: Schematic representation of hexagonal wurtzite a) ZnO structure b) ZnO:Ga structure

Fig.3 exhibits the XRD patterns of GZO films, post-annealed at different temperatures. All the films showed hexagonal wurtzite crystal structure with a preferential growth of (002) plane, oriented along c-axis. The intensity of the peaks increases with increase in post-annealing temperature. The (002) peak positions of GZO film shifts to a larger diffraction angle as the post heating temperature is increased. The lattice constant '*c*' and strain along *c* -axis were calculated and tabulated in Table 2. The negative sign of the strain indicates that strain in the films are compressive and decreases with annealing temperatures. The FWHM of the (002) plane decreases with increasing annealing temperature, indicating that the increase in crystallite size. The grain size of the films can be estimated using the XRD patterns and Debye-Scherrer's formula and are shown in Table 2.

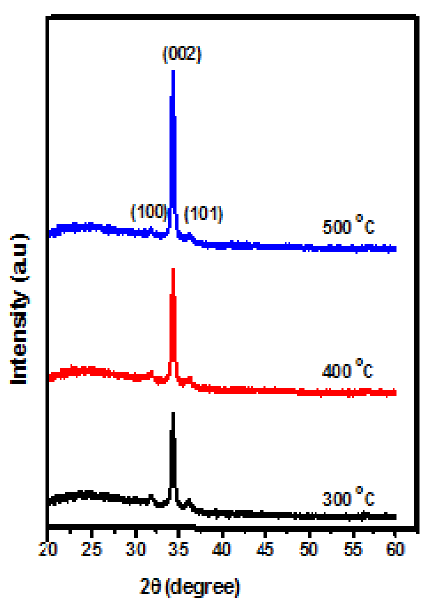

Fig.3: XRD patterns of the Ga:ZnO films annealed at various temperatures

Fig.4a shows the AFM images of gallium doped ZnO thin films at different doping concentrations. It can be realized that the surface morphology of the film changed with the dopant concentration. The surface roughness of the GZO films decreased from 18.268 nm to 5.318nm when the doping concentration was increased from 1at% to 3 at%. At 1 at% Ga, the largest grains were observed. This result is in agreement with the result of XRD. The AFM surface morphology (Fig.4b) indicates that the post-annealing treatment enhanced the grain size and morphology of the GZO film surface, significantly.

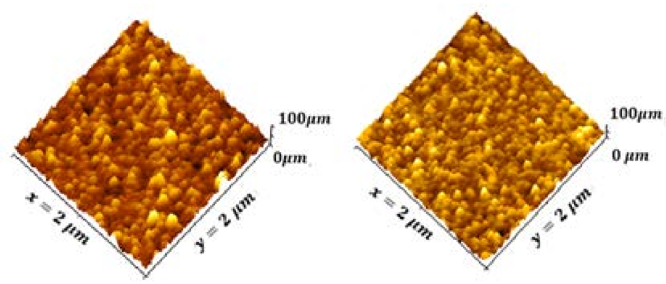

Fig.4a: AFM images of Ga:ZnO thin films (a) ZnO: Ga 1at% (b) ZnO: Ga 3at%

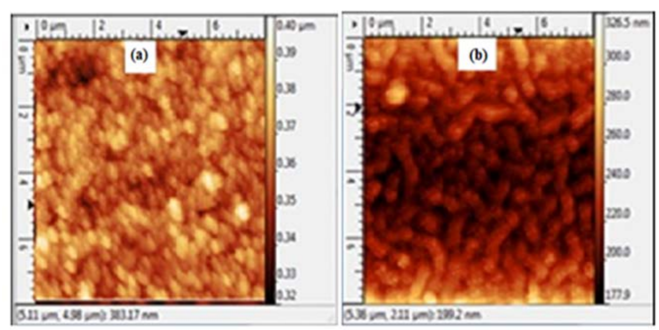

Fig.4b: AFM images of Ga:ZnO thin films annealed at (a) 300ºC (b) 500ºC

Optical transmittance spectra between 300 to 800 nm wavelengths of the Ga:ZnO thin films at different Ga dopant concentrations, annealed at 500ºC are shown in Fig.5. It is crystal clear that all the GZO films show the average transmittance above 90% in the visible wavelength range with a sharp absorption edge in the UV region. It shows that the GZO film would be a good material for the display applications. A slight blue shift was observed with increasing Ga concentration indicates the broadening of the optical band gap. This deviancy can be described by the Burstein-Moss effect and is associated with carrier concentration **[14]**. The optical band gap (E_g) was analyzed using the relation **[15]**

$$(\alpha h\nu)^2 = c\,(h\nu - E_g) \qquad (6)$$

Where, *h* is Planck's constant, *ν* is the frequency of the incident photon and *c* is the constant for direct transition.

Table 1: Structural and optical properties of GZO films with different Ga concentrations

Ga	(2θ) (002)	FWHM (°)	*D (nm)*	d_{hkl} (Å)	c (Å)	ε (10^{-3})	δ (10^{15})	σ (GPa)	T(%)	E_g (eV)
1at%	34.405	0.335	24.825	2.6046	5.2092	1.396	1.623	-0.1163	89.97	3.271
2at%	34.403	0.379	21.941	2.6047	5.2094	1.579	2.076	-0.1252	93.39	3.276
3at%	34.388	0.393	21.160	2.6058	5.2116	1.637	2.233	-0.2236	94.10	3.280

Table 2: Properties of GZO films annealed at different temperatures

T_{an} (°C)	2θ (°)	FWHM (°)	D (nm)	d (A°)	C (A°)	ε (%)	T (%)	E_g (eV)
300	34.398	0.353	23.570	2.605	5.210	0.065	89.338	3.253
400	34.453	0.331	25.140	2.601	5.202	-0.088	91.020	3.279
500	34.519	0.323	25.768	2.596	5.192	-0.280	93.705	3.289

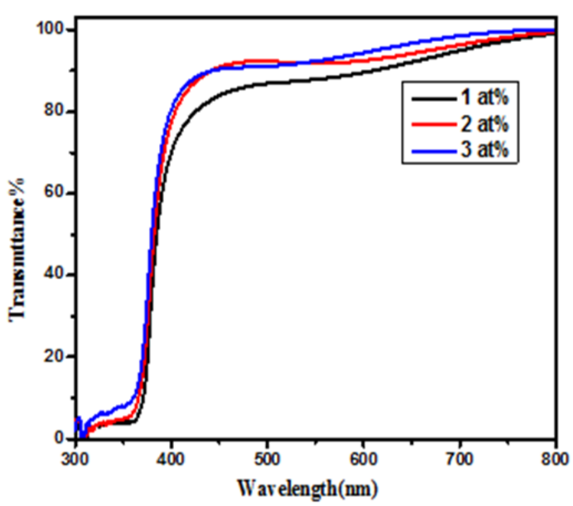

Fig.5: Optical Transmittance spectra of GZO films with different Ga doping concentrations

Fig.6 shows the plots of $(\alpha h\nu)^2$ against hν for the Ga:ZnO films at various Ga concentrations. The variation of the band gap energy (E_g) and average transmittance (T%) of GZO films with different Ga concentrations are shown in Table 1. It is clear that the direct optical band gap value (E_g) raised from 3.271 eV to 3.280 eV, when the concentration of Ga is increased from 1 at% to 3 at%. This widening of the optical band gap is associated with Burstein-Moss effect.

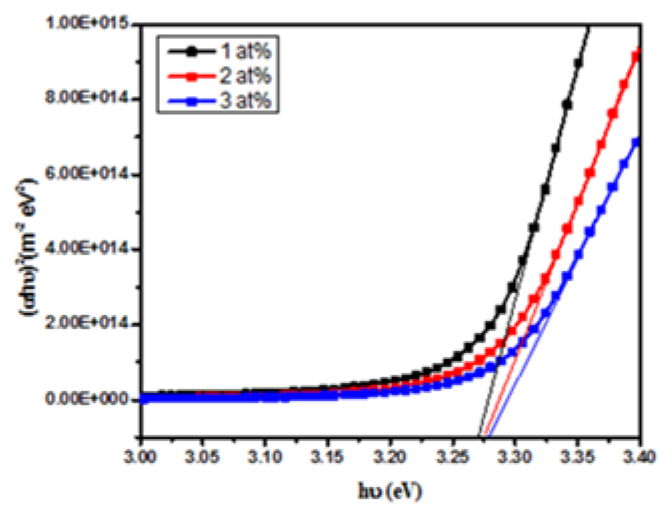

Fig.6: Plot of $(\alpha h\nu)^2$ **Vs** $h\nu$ **for ZnO: Ga (1, 2 and 3 at %) thin films**

From the optical transmission spectra of GZO films annealed at different temperatures (Fig.7), it can be seen that all the GZO thin films exhibited a good transmittance in the 400 to 800 nm region (>89%). The optical band gap values (*E*g) of GZO films can be estimated by the absorption coefficient *(α)* and photon energies *(hν)* and are presented in Table 2. It can be observed that the energy gap rises as the annealing temperature is elevated from 300°C to 500°C.

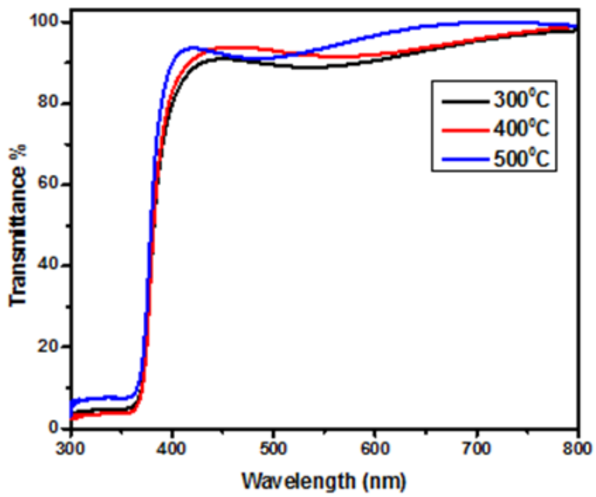

Fig.7: Optical Transmittance spectra of GZO films Annealed at different temperatures

4. CONCLUSION

The Ga- doped ZnO thin films were prepared by simple sol-gel spin coating method. The Influences of doping concentration and post-annealing temperatures on the structural and optical properties of the films were investigated. We observed that the properties of GZO thin films significantly affected by the doping concentration and annealing temperature.

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REFERENCES

1. W. S. Han, Y. Y. Kim, B. H. Kong, H. K. Cho, “Ultraviolet light emitting diode with n-ZnO/Ga/i-ZnO/p-GaN:Mg heterojunction”, Thin Solid Films, Vol: 517, pp.5106, 2009.
2. P. K. Song, M. Watanabe, M. Kon, A. Mitsui A, Y. Shigesato Y, “Electrical and optical properties of gallium- doped zinc oxide films deposited by dc magnetron sputtering”, Thin solid Films, Vol:411, pp.82-86, 2002.
3. G. X. Liang, P. Fan, X. M. Cai, D. P. Zhang and Z. H. Zheng, “The Influence of Film Thickness on the Transparency and Conductivity of Al-Doped ZnO Thin Films Fabricated by Ion-Beam Sputtering”, Journal of Electronic Materia, Vol: 40, pp.267_273, 2011.
4. Q. Zhang, C. Dandeneau, X. Zhou, G. Cao, “ZnO Nanostructures for dye sensitized Solar cells”, Adv. Mater., Vol: 21, pp.4087_4108, 2009.
5. K. Yim, H. W. Kim, C. Lee, “Effects of annealing on structure, resistivity and transmittance of Ga doped ZnO films”, Materials Science and Technology, Vol.: 23, pp.108-112, 2007.
6. C. E. Kim, P. Moon, I. Yun, S. Kim, J. M. Myoung , H.W. Jang , “ Process estimation and optimized recipes of ZnO:Ga thin film characteristics for transparent electrode applications”, J. Bang. Expert Syst. Appl., Vol: 38, pp. 2823_2827, 2011.
7. J. S. Park, J. P. Kim, Y. R. Noh, K. C. Jo, S. Y. Lee, H. Y. Choi, J. U. Kim, “X-ray images obtained from cold cathodes using carbon nanotubes coated with gallium-doped zinc oxide thin films”, Thin Solid Films, Vol: 519, pp.1743_1748, 2010.
8. S. J. Henley, M. N. R. Ashfold, D. Cherns, “The growth of transparent conducting ZnO films by pulsed laser ablation”, Surf. Coat. Technol., Vol: 177, pp.271_276, 2004.
9. J. Hu, R. G. Gordon, “Textured aluminum-doped zinc oxide thin films from atmospheric pressure chemical-vapor deposition”, J. Appl. Phys., Vol:71, pp. 880, 1992.
10. H. H. Shin, Y. H. Jong, S. J. Kang, “Influence of the substrate temperature on the optical and electrical properties of Ga-doped ZnO thin films fabricated by pulsed laser deposition”, J. Mater. Sci: Mater. Electron, Vol: 20, pp. 704_708, 2009.
11. P. K. Nayak, J. Yang, J. Kim, S. Chung, J. Jeong, C. Lee and Y. Hong, “Spin-coated Ga-doped ZnO transparent conducting thin films for organic light-emitting diodes”, J. Phys. D: Appl..Phys., Vol: 42, pp.035102, 2009.
12. A. R. Babar, P. R. Deshamukh, R. J. Deokate, D. Haranath, C. H. Bhosale, K.Y. Rajpure, “Gallium doping in transparent conductive ZnO thin films prepared by chemical spray pyrolysis”, J. Phys. D: Appl. Phys., Vol: 41, pp.135404, 2008.
13. M. C. Jun, S. U. Park and J.H. Koh, “Comparative studies of Al-doped ZnO and Ga-doped ZnO transparent conducting oxide thin films”, Nanoscale Research letters, Vol: 7, pp.639, 2012.
14. J. Zhou and Z. Y. Zhong, “Structural and optoelectrical properties of Ga-doped ZnO semiconductor thin films grown by magnetron sputtering”, Cryst. Res. Technol., Vol: 47, pp.944, 2012.
15. D. Raoufi, T. Raoufi., “The effect of heat treatment on the physical properties of sol–gel derived ZnO thin films”, Appl. Sur. Sci., Vol: 255, pp. 5812_5817, 2009.