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Influence of Doping and Annealing on Structural, Optical and Electrical properties Amorphous ZnO Thin Films Prepared by PLD

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Abstract

In this work, ZnO thin films pure and doped with GaO were deposited using pulsed laser deposition (PLD). Technique using a double frequency Q-switching Nd:YAG laser beam (λ = 532) nm, repetition rate 6 Hz and the pulse duration 10 ns. After the end of wet mixing and drying process, the ZnO:GaO mixtures were pressed to form pellets (1.3 cm) diameter by using 3 ton pressure and sintered at 1373 K for 5 h. The product was investigated using XRD. The data of X-ray diffraction shows polycrystalline structure, and exhibited hexagonal structure. The film thickness was equal to 300 nm with rate of deposition of 0.5 nm/s. ZnO thin films pure and GaO-doped from the pellets with 0.02, 0.06 and 0.1 wt% of were deposited on glass substrates at room temperature. These films were annealed at different temperatures (373, 473 and 673K). The structural characteristics of the pure and GaO-doped ZnO films show that all the films have amorphous structure at room temperature and 373K, but when the samples are annealed at 473 and 673K; the XRD detected a hexagonal phase of ZnO. The surface morphology of the deposit materials was studied using atomic force microscope (AFM). The grain size of the particles observed at the surface depended on the annealing temperature. UV-VIS transmittance measurements showed that the films are highly transparent in the visible wavelength region for samples annealed up to 473K, while at annealing temperature of 673 K the absorption edge of ZnO doped with GaO was shifted to near-infrared region. The optical gap of the films was calculated from the curve of absorption coefficient $(\alpha h\nu)^2$ vs. hν and was found to be 3.8 eV at room temperature, and this value decreases from 3.8 to 3.58 eV with increasing of annealing temperature up to 473-673 K, and increases with the Ga doping. λ_{cutoff} was calculated for ZnO and showed an increase with increasing annealing temperature and shifting to longer wavelength, while with doping the λ_{cutoff} shifted to shorter wavelength. The photoluminescence (PL) results indicate that the pure ZnO thin films grown at room temperature show strong peaks at 640 nm , but GaO doped ZnO films showed a band emission in the yellow-green spectral region (380 to 450nm).

Keywords: *thin films, GaO doped ZnO, PLD, PL, electrical conductivity and resistivity*

1. Introduction

Transparent conducting oxide (TCO) is very important in optoelectronic application, such as solar cell, sensor, and liquid crystal displays. In recent years, the appropriate materials of TCO are SnO_2, In_2O_3, $Sn:In_2O_3$ (ITO), Cd_2SnO_4 [1], and ZnO [2]. ITO is used usually to be a transparent conducting film [3-5], but the cost of ITO is too high to reduce the price of products which have a TCO film. ZnO is a semiconductor with a wide direct band gap (3.37 eV) and large exciton binding energy (60 meV). Exciton lasing mechanism from ZnO films at room temperature was reported recently [6]. Strong room temperature luminescence, high electron mobility, good transparency, etc. are some the advantages of ZnO [7, 8]. Wurtzite structured ZnO, a wide band gap semiconductor is a potential candidate for optoelectronics devices [9]. The conductivity of ZnO without intentionally doping is not high enough as TCO films. Thus, improving the conductivity of ZnO must rely upon doping elements into ZnO. The group-III elements, such as Al [10-14], Ga [15, 16], and In [17], are usually served as dopants for substituting zinc in order to increase more electronic carriers, then the conductivity can be improved. As doping concentration increased heavily, the amount of electronic carriers are also increased in general. Generally, ZnO films are fabricated by RF magnetron sputtering [18, 19], chemical vapor deposition [20], spray pyrolysis [21, 22] and sol–gel process [23, 24], etc. Among them, pulsed laser deposition [25] technique, metal-organic chemical vapour deposition (MOCVD) [26], arc plasma evaporation [27], dip-coating [28] and ion plating [29]. This outline provides a good context in which is pulsed laser deposition (PLD) can be viewed. PLD is a physical deposition technique: a physical process is used to deposit a vaporized form of the

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material onto a surface (substrate). No chemical reactions are involved. The advantages of pulsed laser ablation are flexibility, fast response, energetic evaporants and congruent evaporation

2. Experimentation

ZnO: GaO powders were mixed for 2h to obtained highly homogeneity samples. The powder then pressed to form a pellet of 1.3cm diameter at a pressure of 3 ton, using uniaxial hydraulic press. These pellets were then sintered at 1373K for 5hr.The concentrations of added oxide are given in Table 1.

Table 1. The concentration of added oxide

material ZnO	Doped with GaO
(9.998 gm)	0.002gm
(9.994 gm)	0.006gm
(9.990 gm)	0.010gm

3. Results and discussion

Figure 1 shows the X-ray diffraction pattern of ZnO thin films prepared by pulsed laser deposition (PLD) technique on glass substrate at room temperature with different annealing temperatures (373, 473K and 673K). There is not evidence of any phase present that means the formation of ZnO phase weak or amorphous. After annealing–at 673K for (2hr), X-ray diffraction detected a growth of ZnO on glass. We can be noticed from the X-ray pattern that the peaks at (2θ = 31.826 ^{o}, 34.481 ^{o}, 36.307 ^{o}, 56.598 ^{o}) referred to (100), (002), (101) and (110) crystalline planes, respectively. The X-ray diffraction data of thin films coincides with that of the known hexagonal structure**.** Table (2) shows the experiment and the standard peaks from International Centre for Diffraction Data **[Card No. (# 96-901-1663)]** of ZnO thin film annealed at 473K and 673K. The grain sizes of the prepared films after annealing 473K and 673K were calculated using the Scherrer's formula [30]:

$$D = \mathbf{k\,\lambda\,/\beta\,\cos\theta} \quad (1)$$

D:(G.S) is the grain size,
K: is a constant (0.94)
λ: is the wavelength of Cu Kα =1.54060 (^{0}A)
θ: is the Bragg's angle
β : Full Width at Half Maximum (FWHM)of the preferential plane**.**

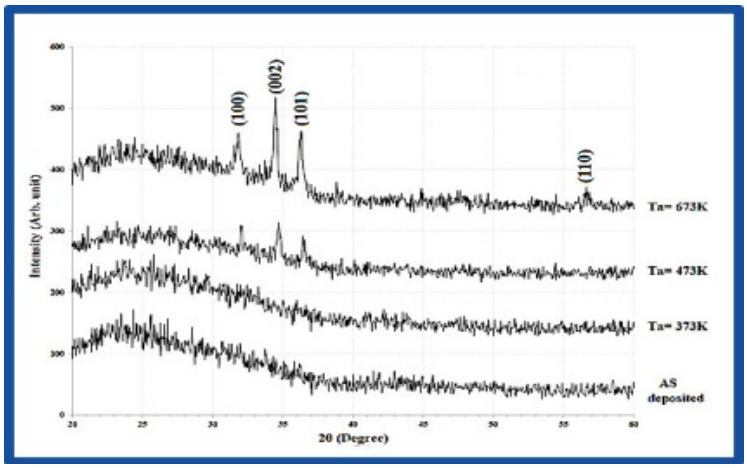

Figure 1. The X-ray diffraction patterns (XRD) of the un-doped ZnO thin film with different annealing temperature: (a) RT, (b) 373K, (c) 437 K, (d) 673K

Table 2. Represent the XRD parameters 2θ, hkl ,d exp, FWHM and Grain size for doped ZnO

\Ta (K)	2θ (deg)	hkl	FWHM (deg)	Int (arb. unit)	d_{hklExp}(Å)	d_{hklStd} (Å)	G.S (Å)	uniform strain*10^{-4}
303	-	-	-	-	-	-	-	-
373	-	-	-	-	-	-	-	-
473	32.033	(100)	0.332	52.917	2.7918	2.8137	235	-77.83
	34.730	(002)	0.332	70.828	2.5809	2.6035	236	-86.81
	36.432	(101)	0.332	55.360	2.4642	2.4754	237	-45.25
673	31.826	(100)	0.539	76.526	2.8095	2.8137	144	-14.93
	34.481	(002)	0.290	154.681	2.5990	2.6035	270	-17.28
	36.307	(101)	0.332	110.719	2.4724	2.4754	237	-12.12
	56.598	(110)	0.456	35.821	1.6249	1.6245	186	2.46

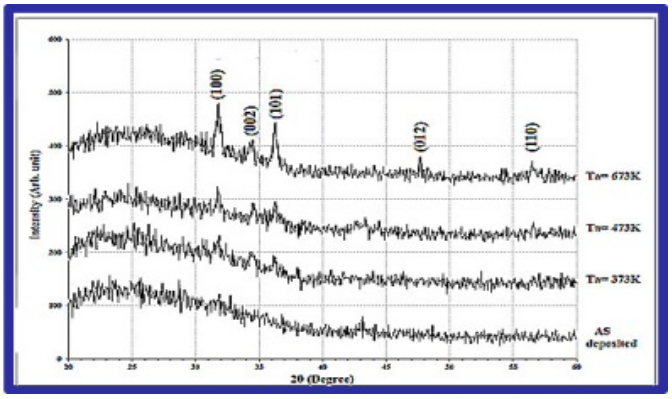

Figure 2. The X-ray diffraction patterns (XRD) of doped ZnO: Ga thin film with different annealing temperature: (a) RT, (b) 373K, (c) 437 K, (d) 673K

Table 3. Represent the XRD parameters 2θ, hkl ,d exp, FWHM and Grain size for Ga doped ZnO

Ta (K)	2θ (deg)	hkl	FWHM (deg)	Int (arb. unit)	d_{hklExp}(Å)	d_{hklStd} (Å)	G.S (Å)	uniform strain*10^{-4}
303	-	-	-	-	-	-	-	-
373	-	-	-	-	-	-	-	-
473	31.743	(100)	0.581	61.058	2.8167	2.8137	134	10.66
	34.564	(002)	0.373	38.263	2.5929	2.6035	210	-40.71
	36.224	(101)	0.415	52.103	2.4778	2.4754	190	9.70
	56.598	(110)	0.332	32.564	1.6249	1.6245	256	2.46
673	31.784	(100)	0.705	112.347	2.8131	2.8137	110	-2.13
	34.440	(002)	0.498	51.289	2.6020	2.6035	157	-5.76
	36.266	(101)	0.456	90.366	2.4751	2.4754	173	-1.21
	47.676	(012)	0.290	47.218	1.9060	1.9110	282	-26.16
	56.473	(110)	0.539	38.263	1.6282	1.6245	157	22.78

Figure 2 shows the XRD pattern for ZnO thin films doped with GaO in θ range from (20-60^{o}), prepared by Pulsed laser deposition (PLD) technique on glass at room temperatures and with different annealing temperatures (373K, 473K and 673K). No evidence of any phases present on glass substrate as deposited that means the formation of ZnO phase is weak or

amorphous. On the other hand, the XRD patterns of doped ZnO films with annealing temperature (673K) the structure of these films showed be a polycrystalline. We can be noticed from the X-ray pattern that the peaks at (2θ=31.784^{o}, 34.440 ^{o}, 36.266 ^{o}, 47.676 ^{o} and 56.473^{o}) referred to (100), (002), (101), (012) and (110) direction, respectively. Table 3 shows experimental (2θ) shifting for (GaO) and (hkl) for film deposed on glass substrate.

3.2. Optical Microscopic Examination

Figure 3 shows the results of microscopic examination (Nikon- Japan) of the ZnO thin films before and after doping with GaO. Observed before doping the presence of two phases one crystalline of ZnO, and the other for amorphous phase as proved by XRD. In case of doping samples the surface appear clear that mean has less voids and looks smooth and homogenous.

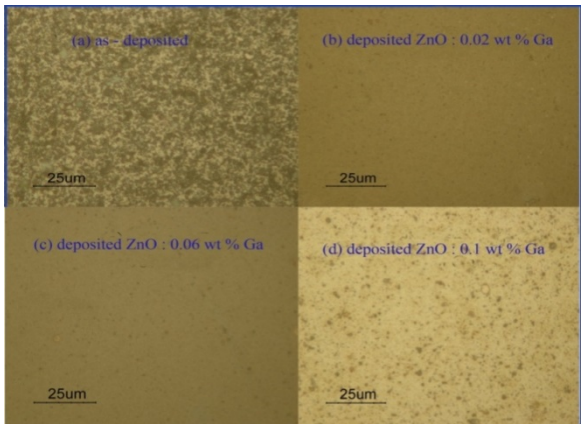

Figure 3. The image of Optical Microscopic of ZnO thin film. (a) ZnO without doped, (b) Doped with 2% Ga, (c) Doped with 0.06 wt% Ga, (d) Doped with0.1 wt % Ga

After annealing as show in Figure 4 and 5 observe the effect of annealing on the structural properties, when annealing at 473K note smoothing and clearly on the surface membranes, some disappearance of the voids and granular border as well as starts to crystallize and impurities are almost virtually non-existent, while annealing at 673K observe the disappearance of the most defects crystal line's improved the crystal structure and the surface becomes more homogeneity and fine.

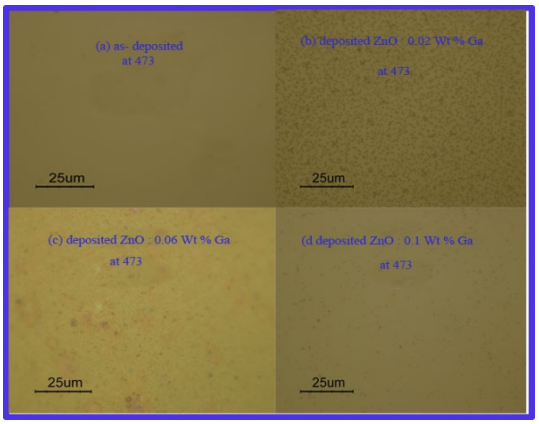

Figure 4. The image of Optical Microscopic of ZnO thin film annealing at 473K. (a) ZnO without doped, (b) Doped with 0.02 wt % Ga, (c) Doped with 0.06 wt% Ga, (d) Doped with 0.1 wt % Ga

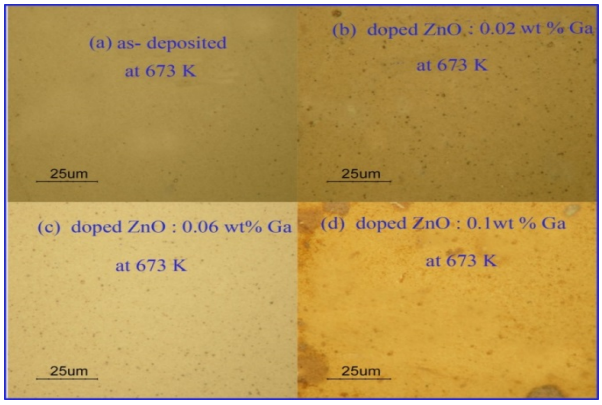

Figure 5. The image of Optical Microscopic of ZnO thin film annealing at 673K. (a) ZnO without doped, (b) Doped with 0.02 wt % Ga, (c) Doped with 0.06 wt% Ga, (d) Doped with 0.1 wt % Ga

3.3. Atomic Force Microscopy (AFM)

Figure 6 shows the influence of impurities on the grain size, where the doped leads to the decrease grain which that means with 0.06wt% Ga doping the crystalline nature of the film are decreased and also makes the surface more smoother and uniformed. In addition to taking into consideration the influence annealing at 673K on the grain size, the annealing cause increased the grain size and crystallized the membranes. Figure 7 shows the crystallization in the film was improved by a sufficient thermal crystallization at 673K.

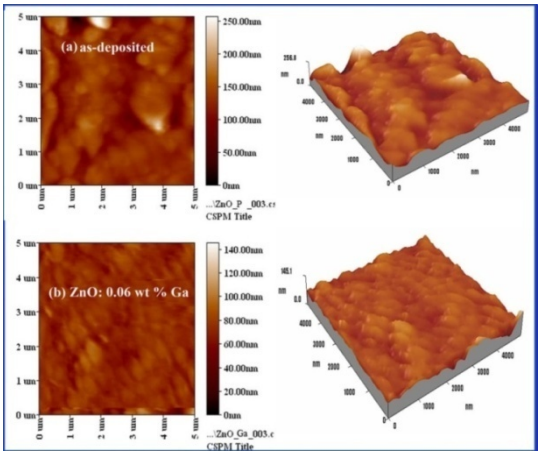

Figure 6. The AFM image of ZnO thin films at RT. (a) as- deposited, (b) Doped with 0.06 wt % Ga

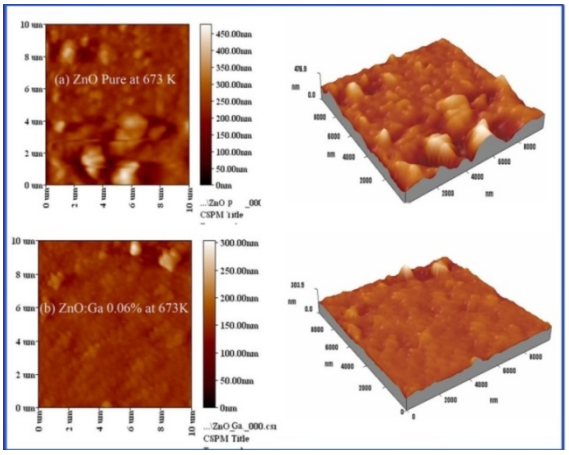

Figure 7. The AFM image of ZnO thin films annealing at 673K. (a) as- deposited, (b) Doped with 0.06 wt % Ga

5, Optical Properties of ZnO films

The optical properties of the deposited amorphous ZnO films on glass at room substrate temperature have thickness of (300) nm, at different annealing temperatures ranging from (373-673)K doping with different concentration of oxides, have been determined using UV-VIS in the region (200–1200) nm .The properties include the UV-VIS absorption, transmission spectrum have been measured. The optical energy gap is given by Tauc relationship [31].

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \quad (2)$$

Where, α is the absorption coefficient, A is the constant, h is the Planck's constant, υ is the photon frequency, Eg is the optical energy gap and n is the 1/2 for direct energy gap semiconductors. The optical energy gap decrease with increasing annealing temperature [32, 33], as show in Table 4. The direct energy gap values for amorphous ZnO pure and doped with different elements of mixed oxides (GaO) for doped is (0.02, 0.06 and 0.1)wt ٪ are in the range of (3.8 –4.1) eV, as shown in the Figure 8. It is also observed that the direct energy gap energy inecreases with doping elements. This is presumably because of the effect exerted by the perturbation in the carrier concentration in the conduction band. The λ cut off calculate when wavelength = 0. The λ cut off increase shift to short of wavelength with increasing impurities ration [34] as show in Figure 7. The Table 5 explain effect doping on λ cut off.

Table 4. Gives the evolution of the band gap with deferent annealing temperature

Samples	Optical energy gab (eV) (direct)
ZnO at RT	3.8
ZnO at 373K	3.78
ZnO at473K	3.7
ZnO at 673K	3.58

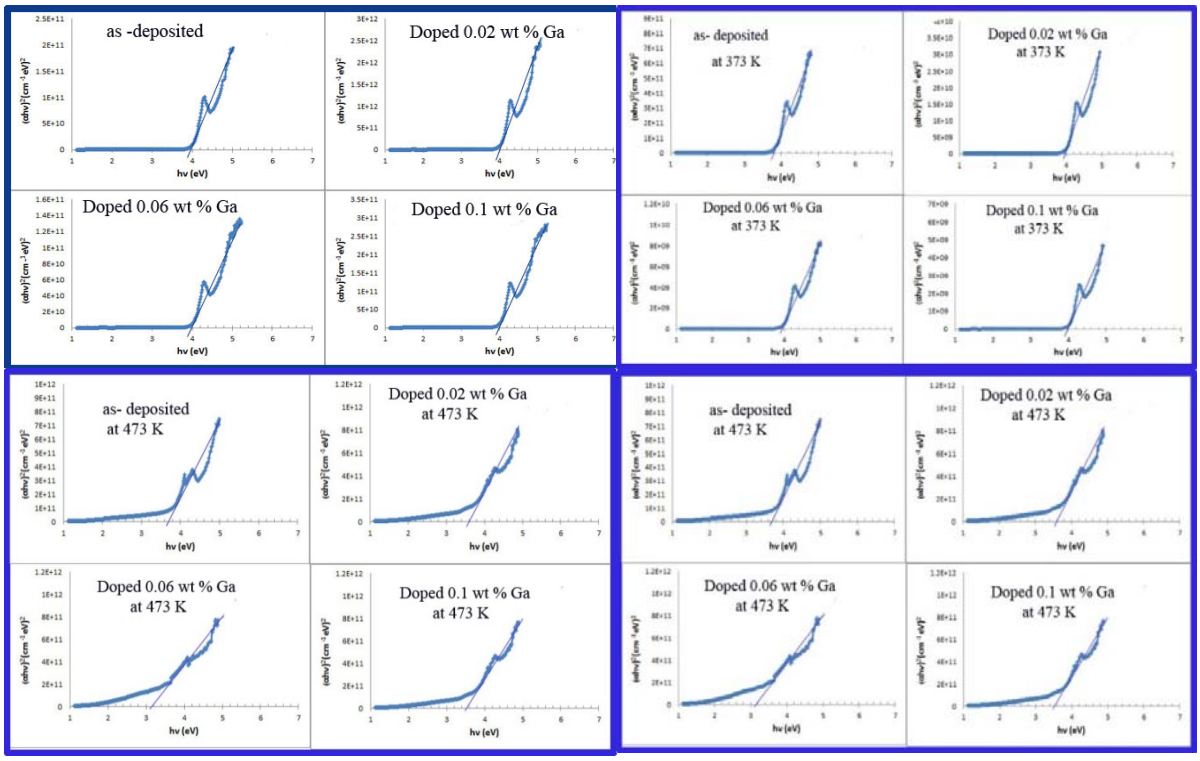

Figure 8. Measurement of energy band gap for ZnO pure and ZnO:Ga (0.02- 0.1%) thin films

Table 5. $\lambda_{cut\ off}$ values of ZnO undoped and doped thin film with deferent annealing temperature

Type of th film	$\lambda_{cut\ off}$ (nm) at RT	$\lambda_{cut\ off}$ (nm) at 373K	$\lambda_{cut\ off}$ (nm) at 473K	$\lambda_{cut\ off}$ (nm)at 673K
ZnO pure	340	350	350	358
ZnO:Ga0.02wt%	325	330	390	370
ZnO:Ga0.06wt%	320	325	395	380
ZnO:Ga0.1wt%	318	320	360	460

Figure 9 and 10 shows the spectral optical transmittance and absorbance as a function of wavelength in the range 200–1200 nm for amorphous ZnO thin films and doped with different elements of mixed oxides (GaO) of (0.02,0.06 and 0.1)wt% on glass substrate at room temperature by pulse laser deposition. An increment in the transmittance is observed as the doping oxides were changed from (GaO). The films were found to be highly transmittance in the visible wavelength region. The maximum transmission observed for amorphous ZnO was almost (70%)up to 400nm, while for the doped films, the maximum transmittance equal (90%) for ZnO:GaO of (0.1 wt%).

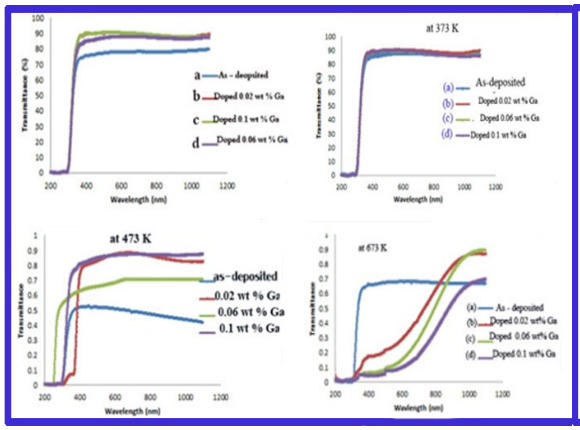

Figure 9. ZnO and ZnO: Ga (0.02-0.1) wt% thin films transmittance. a) ZnO pure, b) ZnO 0.02% Ga, c) ZnO 0.06 % Ga, d) ZnO 0.1% Ga with deferent tempareture

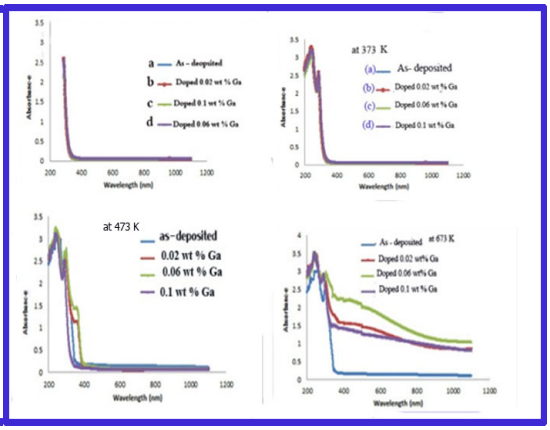

Figure10. ZnO and ZnO: Ga (0.02-0.1) wt% thin films absorbance. a) ZnO pure, b) ZnO 0.02% Ga, c) ZnO 0.06 % Ga, d) ZnO 0.1% Ga with deferent tempareture

The maximum transmittance observed for amorphous ZnO deposited at room temperature equal to (70%) in the UV region, while for the annealing films. the maximum transmittance equal (89%) at annealing temperature (373K). The behavior of the transmittance spectra is opposite completely to that of the absorption spectra. In general, we can observe from this figures that transmittance increases with increasing of annealing temperature and this may be due to improving the crystallite size which means a decrease in the absorption. The films were found to be highly transmittance in the visible wavelength region with an average transmittance in excess of 80%. This is probably ascribed to the increase of particle sizes and surface roughness.

The variation of absorption coefficient with wavelength for amorphous ZnO films deposited on glass substrate at room temperature at different annealing temperatures (373, 473 and 673) K are shown Figure 11. It is observed that the absorption coefficient decreases with increasing wavelength. This means that direct electronic transition happens. Also, we can notice from this figure that (α) in general increases with the incrase of annealing temperatures

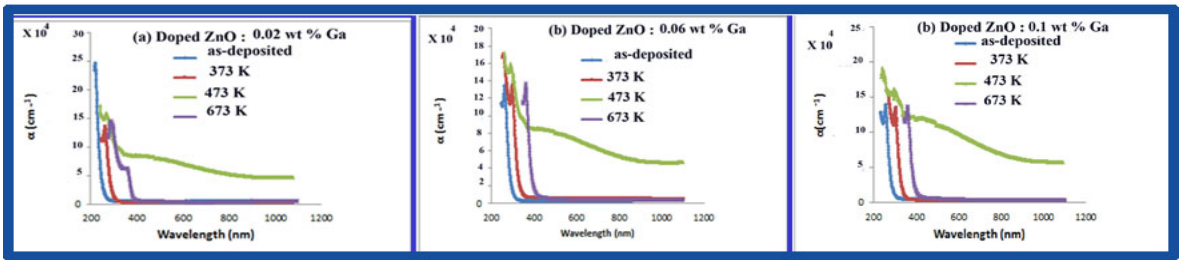

Figure 11. The absorption coefficient α (cm^{-1}) vs wavelength (nm) of ZnO undoped and doped thin films. a) ZnO 0.02% Ga, b) ZnO 0.06 % Ga, c) ZnO 0.1 % Ga calculate $\lambda_{cut\ off}$ values with different temperature

6. Conclusion

Undoped and doped ZnO with (Ga) oxide films were successfully deposition on glass and silicon substrates by pulsed laser technique and thermally annealed at (373, 473 and 673)K, states were investigated. All films are semiconducting in nature with n-type conductivity.

The XRD results for undoped, doped and heated samples at 373K of ZnO thin films were amorphous. Thin films exhibit hexagonal crystal structure of undoped ZnO thin film at 473K and 673K. The intensity of peaks increased with increasing growth temperature at 673K.

The optical microscopic examination of thin film samples show the disappearance of voids, with smooth and relatively high homogenity, AFM images also support the slow growth of crystallite sizes for the undoped and doped ZnO and also for the annealed films.

The transmission of undoped ZnO thin film was found to be above 70%, but higher for other doped one (85-90)%. After annealing an improvement were found in transmission for both undoped and doped film samples. In case of Samples annealed at 673K show low in transmission in UV region for ZnO thin film doped with Ga. The band gap for as prepaded was 3.8 eV ,then after annealed at 373K slightly decreased to be 3.78eV, then show a value of 3.70 eV at 473K and 3.59 eV at 673K. The $\lambda_{cut\ off}$ increase shift to shorter wavelength with doping, while the $\lambda_{cut\ off}$ increase with increasing annealing and shifted to longer wavelength.

PL emission spectrum from undoped ZnO thin film has a broad yellow-orange at wave length (610 nm). For doping ZnO with (0.02 and0.0 6)wt% Ga have a band emission in yellow-green regions (380-450)nm, In addition to the first emission(broad yellow-orange) and less intensity. ZnO doped with Ga 0.1wt%, give high intensity in the region of yellow-orange band, and then vanished at yellow-green band.

References

[1] R Mamazza Jr, DL Morel, CS Ferekides. *Thin Solid Films*. 2005; 484(26).
[2] DR Sahu, S Yuan, JL Huang. *Microelec*. 2007; 38(245).
[3] GH Takaoka, D Yamazaki, J Matsuo. *Mat. Chem. Phys*. 2002; 74(104).
[4] T Nakaoa, T Nakada, Y Nakayama, K Miyatania, Y Kimura, Y Saitob, C Kaitoa. *Thin Solid Films*. 2000; 307(155).
[5] H Yumoto, T Inoue, SJ Li, T Sako, K Nishiyama. *Thin Solid Films*. 1999; 345(38).
[6] ZK Tang, GKL Wong, P Yu, M Kawasaki, A Ohtomo, H Koinuma, Y Segawa. *Appl. Phys. Lett*. 1998; 72: 3270.
[7] DC Look, DC Reynolds, JW Hemsky, RL Jones, JR Sizelove. *Appl. Phys. Lett*. 1999; 75: 811.
[8] Y Caglar, S Ilican, M Caglar, F Yakuphanoglu. *Sol-Gel Sci Technol*. 2010; 53: 372.
[9] KJ Kim, YR Park. *Appl Phys*. 2003; 94: 867.
[10] D Song, J Xia, AG Aberie. *Appl. Sur. Sci*. 2002; 195: 291.
[11] DC Altamirano-Juarez, G Torres-Delgado, S Jimenez-Sandoval, O Jimenez-Sandoval. *Sol. Ener. Mat. Sol. Cell.* 2004; 82: 35.
[12] RF Silva, MED Zaniquelli. *Thin Solid Films*, 2004; 449: 86.
[13] K Tominaga, T Murayama, I Mori, T Ushiro, T Moriga, I Nakabayashi. *Thin Solid Films*. 2001; 386: 267.
[14] MA Martinez, J Herrero, MT Gutierrez. *Sol. Ener. Mat. Sol. Cell.* 1997; 45: 75.
[15] JD Ye, SL Gu, SM Liu, YD Zheng, R Zhang, Y Shi. *Appl. Phys. Lett*. 2005; 86: 192111.
[16] JD Ye, SL Gu, S Zhu, SM Liu, YD Zheng, R Zhang, Y Shi, HQ Yu, YD Ye. *Cryst. Grow*. 2005; 283: 279.
[17] MT Young, SD Keun. *Thin Solid Films.* 2002; 410: 8.
[18] Y Zhou, PJ Kelly, A Postill, O Abu-Zeid, AA Alnajjar. *Thin Solid Films.* 2004; 33: 447–448.
[19] EG Fu, DM Zhuang, G Zhang, M Zhao, WF Yang. *Microelectr.* 2004; 35: 383.
[20] TM Barnes, J Leaf, C Fry, CA Wolden. *Cryst. Growth*. 2005; 274: 412.
[21] H Kim, A Pique, JS Horwitz, H Murata, ZH Kafafi, CM Gilmore, DB Chrisey. *Thin Solid Films.* 2000; 798: 377–378.
[22] SH Mondragon, A Maldonado, A Reyes. *Appl. Surf. Sci.* 2002; 193: 52.
[23] JH Lee, B O Park, *Mater. Sci. Eng. B*. 2004; 106: 242.
[24] Y Natsume, H Sakata. *Thin Solid Films.* 2000; 372: 30.
[25] GG Valle, P Hammer, SH Pulcinelli, CV Santilli. *Eur. Ceram. Soc*. 2004; 24: 1009.
[26] Kaul AR, Gorbenko OY, Botev AN, Burova LI. *Superlatt. Microstruct*. 2005; 38: 272.
[27] Minami T, Ida S, Miyata T, Minamino Y. *Thin Solid Films.* 2003; 445: 268.
[28] Fathollahi V, Amini MM. *Mater. Lett.* 2001; 50: 235.
[29] Iwata K, Sakemi T, Yamada A, Fons P, Awai K, Yamamoto T, Matsubara M, Tampo H, Niki S. *Thin Solid Films.* 2003; 445: 274.
[30] Th H DE Keijser, et al. *Appl. Cryst*. 1982; 15: 308-314.

[31] JI Pankove. Optical Processes in Semiconductors. Prentice-Hall, New Jersey. 1971.
[32] N Tigau, et al. *Optoelectronics Adv. Mater.* 2004; 6: 449.
[33] M Popa, V Lisca, M Stancu, E Buda, T Pentia. *Botila, Optoelectro. Adv. Mater*. 2006; 46.
[34] Hayder Mohammad Ajeel. Study effect of annealing Temperature on the structural and optical Properties of CdO Thin Films Prepared by SILAR Deposition Technique.