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The Influence of annealing temperature on Structural and Optical Properties for thin ZnO Films Prepared by pulse laser deposition

تاثيردرجة حرارة التلدين على الخصائص التركيبية والبصرية لغشاء أوكسيد الخارصين المحضر بطريقة الترسيب بالليزر النبضي

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Abstract:

In this work, structural and optical properties for thin ZnO films prepared by pulse laser deposition technique, on glass substrates, have been studied as a function of annealing temperature. This study shows that the films have energy gap decreases from 3.26 eV to 3.14 with increasing T_a from RT to 673 K.
Keywords: ZnO, pulse laser deposition, optical properties, Structural properties.

الخلاصة :

تم في هذا البحث دراسة الخصائص التركيبية والبصرية لأغشية أوكسيد الخارصين و المحضرة بطريق الترسيب بالليزر النبضي على أرضيات زجاجية كدالة لدرجة حرارة التلدين . بينت هذه الدراسة أن الاغشية تمتلك فجوة طاقة تتغير من 3.26 الى 3.14 الكترون فولت عند زيادة درجة حرارة التلدين من درجة حرارة الغرفة الى 673 كلفن

Introduction

Zinc oxide (ZnO) is an important electronic and photonic material because of its wide-bind semiconductor with a band gap of about to 3.37eV and large exciton binding energy of 60meV of excitons at room temperature [1-3].

ZnO can exist in three phases (a) hexagonal (wurtzite) [4] (b) zinc-blend [5] (c) rock salt [5]. The most stability ZnO structure is hexagonal (wurtzite) as shown in figure (1-2) with lattice parameters a=0.325nm and c=0.521nm.

Many different techniques such as chemical vapor deposition, organic chemical vapor deposition (MOCVD), plasma-assisted molecular beam epitaxy (PA-MBE), pulsed laser deposition (PLD), and spray pyrolysis technique have been used to growth the ZnO [6-8].

Among the various thin film deposition techniques, pulse laser deposition is one of the simplest growth techniques to deposit high quality films and nanostructures under optimized conditions of variety of materials ranging from superconductors to semiconductors to dielectrics to metals and many more [9].

The average crystalline size (D) was calculated using Debye-Scherrer's formula:[10]

$$D = \frac{K\lambda}{\beta_{hkl}\cos\theta} \qquad \text{.....1}$$

where K is shape factor =0.9, λ is the X- ray wavelength= 1.5406Å, β_{hkl} is the full width at half maximum in(rad) and θ is brag angle .

The strain induced in powders due to crystal imperfection and distortion (ε) was calculated using the formula:

$$\varepsilon = \frac{\beta_{hkl}}{4\tan\theta} \qquad \text{.....2}$$

From Equations 1 and 2, it was confirmed that the peak width from crystallite size varies as 1/cosθ strain varies as tanθ. Assuming that the particle size and strain contributions to line

broadening are independent to each other and both have a Cauchy-like profile, the observed line breadth is simply the sum of Equations 1 and 2.

$$\beta_{hkl} = \frac{K\lambda}{D\,\mathrm{Cos}\theta} + 4\varepsilon\,\tan\theta \qquad \ldots\ldots\ldots\ldots 3$$

By rearranging the above equation, we get

$$\beta_{hkl}\mathrm{Cos}\theta = \frac{K\lambda}{D} + 4\varepsilon\,\sin\theta \qquad \ldots\ldots\ldots\ldots 4$$

The above equations are Williamson and Hall equations. A plot is drawn with 4sinθ along the x-axis and β_{hkl} cosθ along the y-axis, the crystalline size was estimated from the y-intercept, and the strain ε, from the slope of the fit. In equation 4 the strain was assumed to be uniform in all crystallographic directions, thus considering the isotropic nature of the crystal, where the material properties are independent of the direction along which they are measured.[11]

Experimental Procedure

Pure zinc oxide powder with high purity (99.99%) were prepared by pressing under 5 Ton to formed a target with 2.5 cm diameter and 0.4 cm thickness. It should be as dense and homogenous as possible to ensure a good quality of the deposit.

Prior to deposit films, the glass substrates were cleaned in with commercial cleaner solution, distilled water and followed by alcohol using ultrasonic bath.

ZnO thin films were prepared using pulse laser deposition (PLD) technique which carried out inside a vacuum chamber generally at (10^{-3} Torr). The focused Nd:YAG (Huafei Tongda Technology—DIAMOND-288 pattern EPLS) SHG Q-switching beam (laser Power= 700 MJ, λ = 1064 nm and f=6Hz) coming through a window is incident on the target surface making an angle of 45° with it. The substrate is placed in front of the target with its surface parallel to that of the target. Sufficient gap is kept between the target and the substrate so that the substrate holder does not obstruct the incident laser beam.

The thickness of prepared films was about 150 nm which measured by Michelson interferometer. An optical transmittance and absorbance spectra were recorded, at room temperature, in the wavelength range 300-1100 nm using OPTIMA SP-3000 UV-VIS spectrophotometer.

Results and Discussion

Fig. (1) shows the X-ray diffraction for as deposited ZnO films and annealed 473 and 673 K, this figure shows that when the films annealed they were convert from amorphous to polycrystalline structure. Table (1) shows the experiment and the standard peaks from International Centre for Diffraction Data (JCPDS) for Wurtzite (Hex.) ZnO crystal [12] , this table shows a good identical between them. The preferred peak for ZnO film located at 2θ about 34.4◦ for (002) plane. The peaks intensities increase with increase T_a. The grain size increased with increasing T_a.

In addition we can also see from table (1) an increasing in d_{hkl} with increasing T_a i.e., slightly shift in 2θ to lower values because increasing the grain size, i.e increase in lattice constant as shown in table (2).

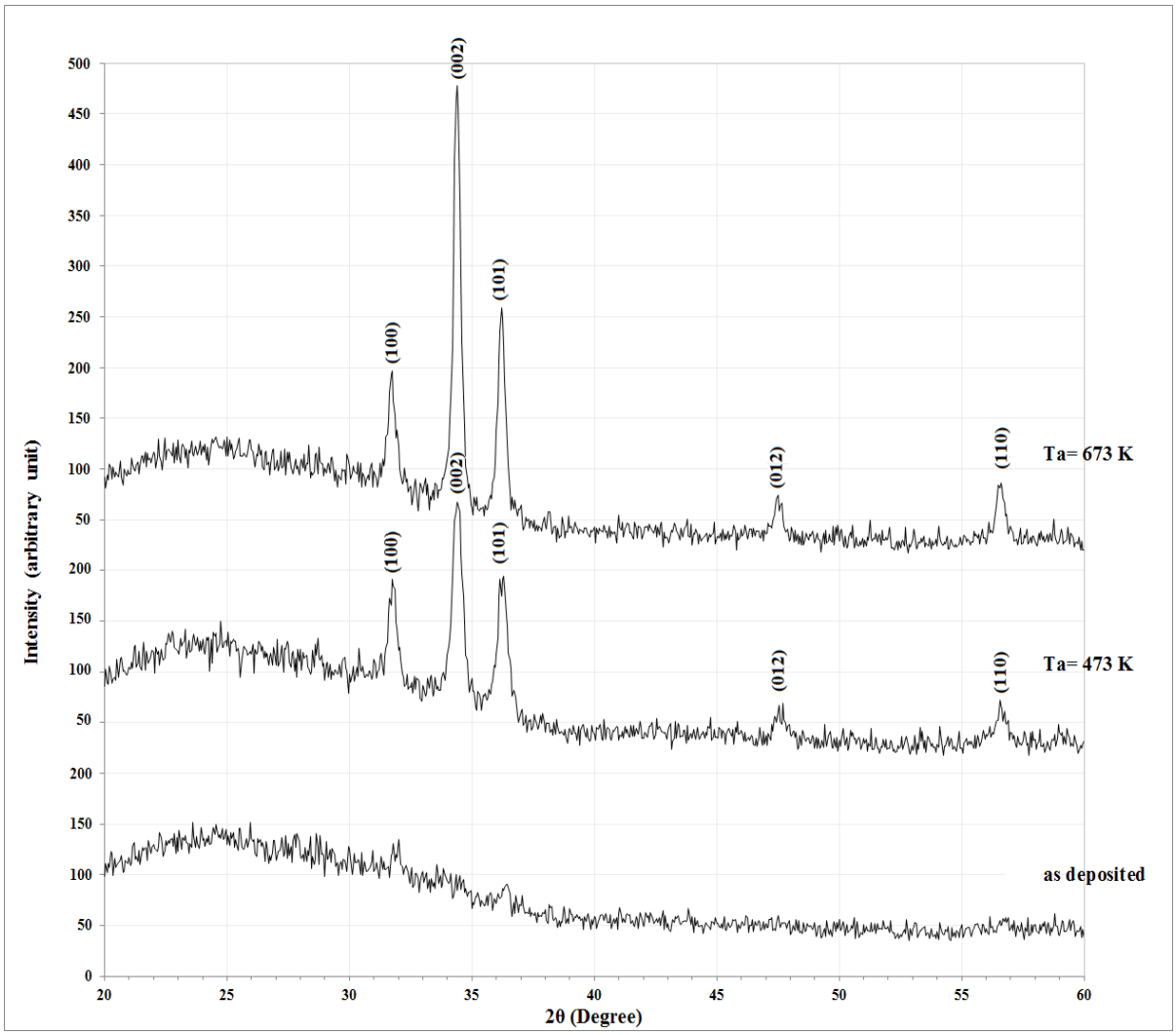

Fig. (1) X-ray diffraction patterns for as deposited and annealed ZnO films.

Table (1) Structural parameters :inter-planar spacing, crystalline size (by Sherrer's formula) for ZnO films.

Ta (K)	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.(Å)	hkl
as deposited	-	-	-	-	-	-
473	31.7612	0.4800	2.8151	17.2	2.8137	(100)
	34.4154	0.4900	2.6038	17.0	2.6035	(002)
	36.2492	0.5000	2.4762	16.7	2.4754	(101)
	47.5327	0.5428	1.9114	16.0	1.9110	(112)
	56.6026	0.5850	1.6247	15.4	1.6245	(110)
673	31.7542	0.3400	2.8157	24.3	2.8137	(100)
	34.4011	0.3450	2.6049	24.1	2.6035	(002)
	36.2477	0.3483	2.4763	24.0	2.4754	(101)
	47.5298	0.3686	1.9115	23.6	1.9110	(112)
	56.6011	0.3900	1.6248	23.1	1.6245	(110)

The lattice constants 'a' calculated from (100) peaks while 'c' from (002) peaks for Hex. ZnO films with different Ta using the following equation [13]

$$\frac{1}{d^2} = \frac{4}{3}\frac{h^2+hk+k^2}{a^2} + \frac{l^2}{c^2} \quad \text{.....5}$$

Table (2) Comparison between standard and experimental lattice constants for hexagonal ZnO films.

Ta (K)	a (Å) Exp.	a (Å) Std.	c (Å) Exp.	c (Å) Std.
473	3.2506	3.2490	5.2076	5.2070
673	3.2513	3.2490	5.2097	5.2070

The calculated lattice constants decrease with annealing temperature and have a good agreement with standard card.[12]

The relation between β cos(θ) versus 4sin(θ) was shown in fig (2). The slope for these lines represent the non-uniform strain and the y intersections represent (0.9λ/Domain size) . The calculated values indicate that Domain size increase with increase T_a from 473 to 673K, while the non-uniform strain decrease due to increasing the grain size.

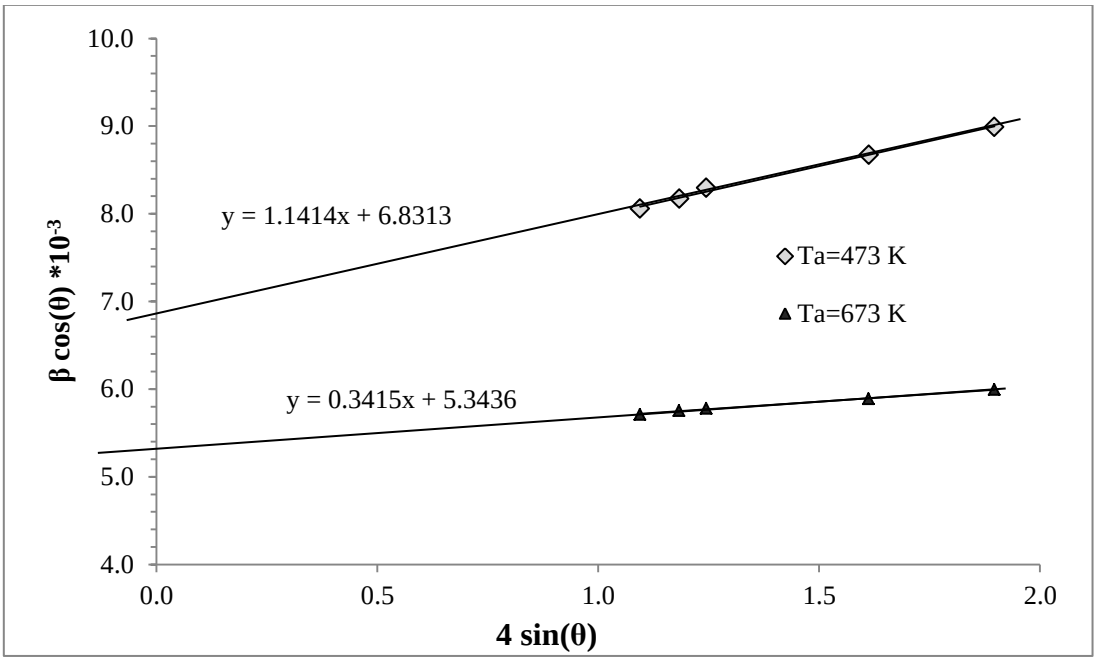

Fig. (2) Williamson and Hall relation for annealed ZnO films (Ta=473 and 673)K.

Table (3) non-uniform strain and domain size for annealed ZnO films (Ta=473 and 673)K.

Ta (K)	non-uniform strain*10^{-3}	Domain size (nm)
473	1.14	20.3
673	0.34	26.0

Optical measurements for ZnO films on glass substrate by pulse laser deposition with different annealing temperature (T_a) was carried out in the wavelength range 300–1100 nm at room temperature (RT). Figure (3) shows the room temperature transmittance spectra for samples with different T_a.

All spectra show good transparency, the transmittance pattern of all deposited thin films increases with increasing of wavelength (λ). On the other hand the transmittance increases with the increase of T_a. It is obvious from the figure that the transmittance for as deposited ZnO film at wavelength equal to 500nm was found to be 80.63%, and decrease to 72.07% when T_a increase to 673 K.

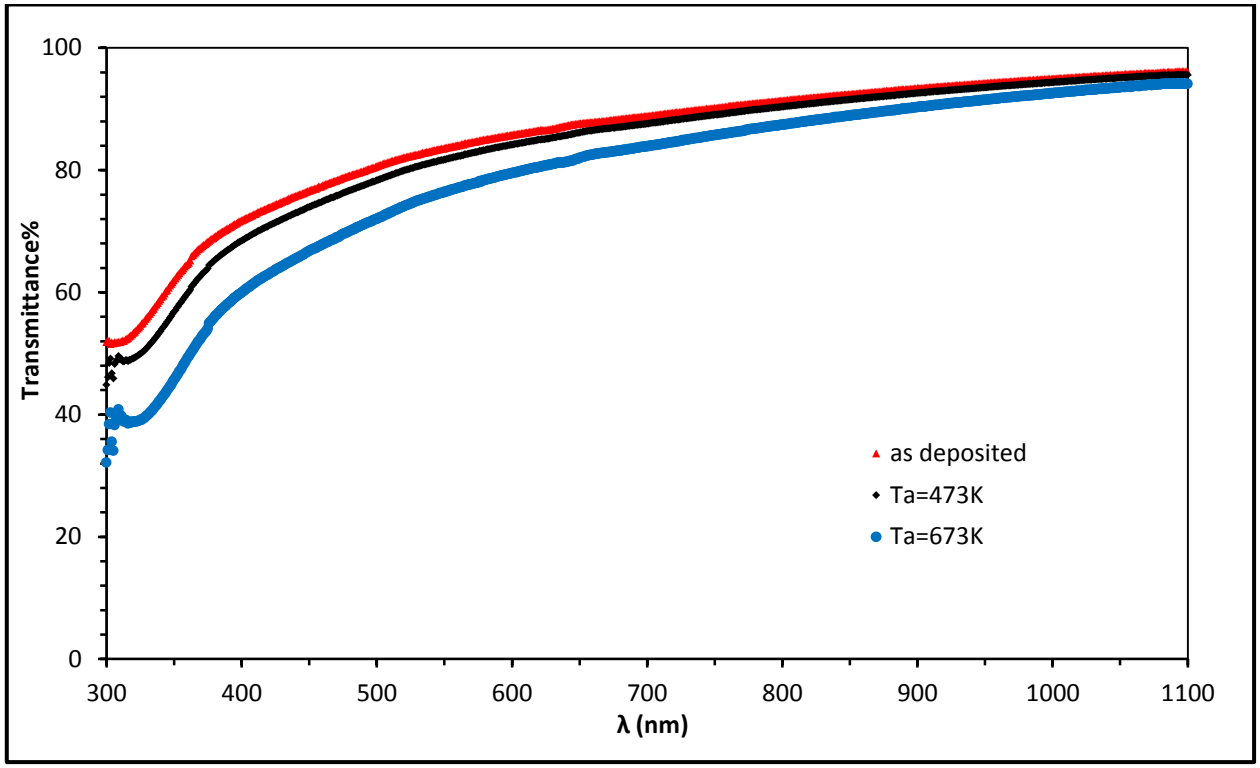

Fig.(3) Transmittance variation with the wavelength for as deposited and annealed ZnO films.

The absorption coefficient (α) of ZnO thin films was calculated from the optical transmittance spectrum measurements using the formula [14]:

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \qquad \text{.....5}$$

where t is the thickness of thin films, and T is the transmittance intensity. The energy gap and optical constants were calculated for two samples.

The optical energy gap values (E_g^{opt}) for thin ZnO films on glass have been determined by using Tauc equation [15].

$$\alpha h\upsilon = A\left(h\upsilon - E_g\right)^r \qquad \text{.....6}$$

where hυ is the photon energy, E_g is the optical band gap energy, A is inversely proportional to amorphousity and r is used to find the type of the optical transition by plotting the relations $(\alpha h\upsilon)^{1/2}$,$(\alpha h\upsilon)^{1/3}$,$(\alpha h\upsilon)^{2/3}$,and $(\alpha h\upsilon)^2$ versus photon energy (hυ). The energy gap (E_g) is then determined by the extrapolation of the linear portion at $(\alpha h\upsilon)^2 = 0$. It is found that the relation for r=1/2 yields linear dependence part at which the absorption coefficient $\alpha \geq 10^4 cm^{-1}$, which describes that ZnO film has the allowed direct transition.

The variation of $(\alpha h\upsilon)^2$ as a function of photon energy for as deposited and annealed ZnO films. has been plotted in Fig. (4).This figure reveals that the annealing leads to decrease the energy gap from approximately 3.26 eV to 3.14 eV. This can be attributed to increase the grain size and which leads to decrease the strain causing increase in lattice constants.

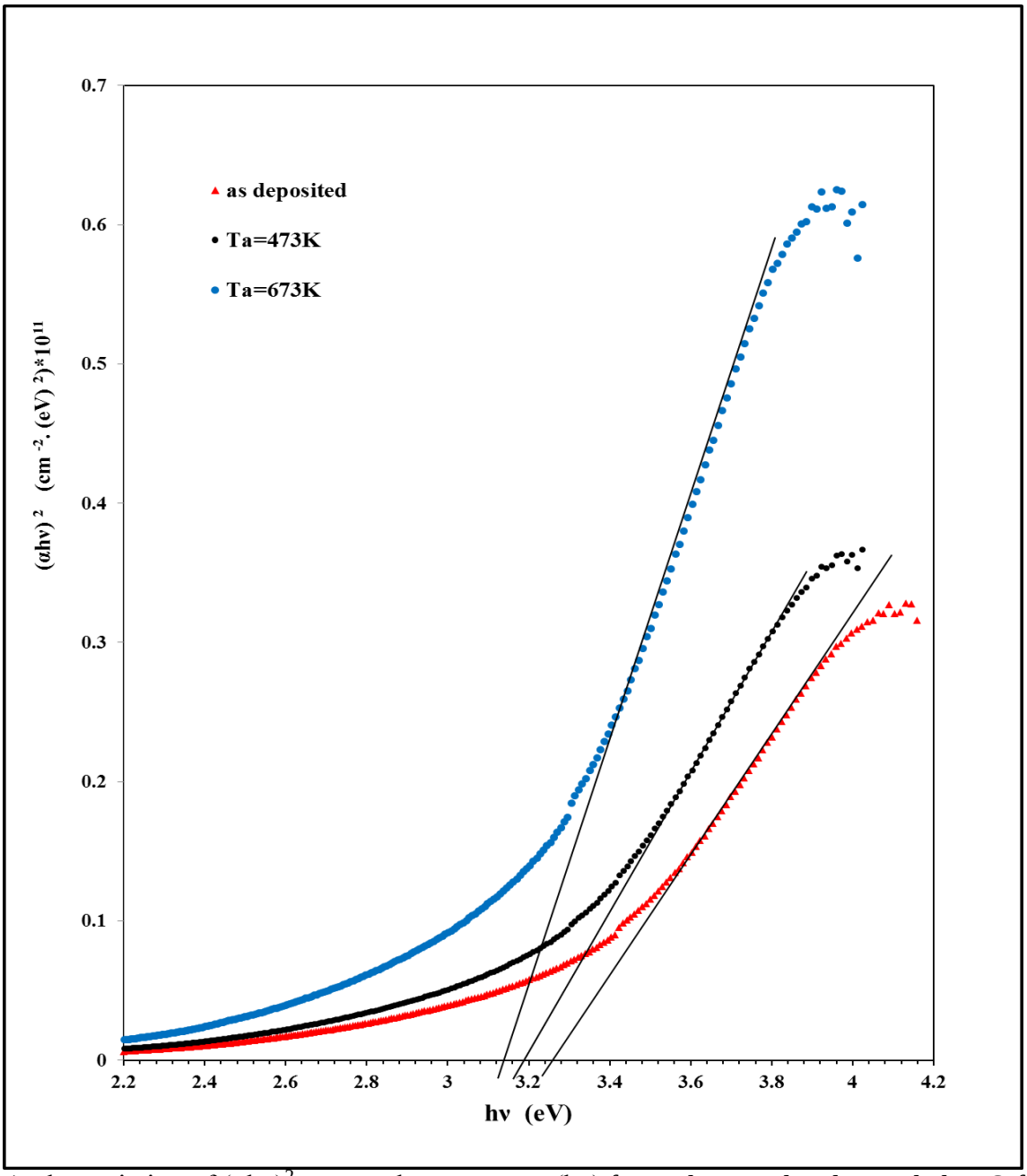

Fig.(4) The variation of $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) for as deposited and annealed ZnO films.

It is important to determine the optical constants of thin films such as refractive index (n), extinction coefficient (k), and the real (ε_r) and imaginary (ε_i) parts of dielectric constant.

Fig.(5) shows the variation of extinction coefficient ($k = \alpha\lambda / 4\pi$) with wavelength) for as deposited and annealed ZnO films. The extinction coefficient depends mainly on absorption coefficient; for this reason, the behavior of it is similar for absorption coefficient i.e., the increasing of extinction coefficient with increasing photon energy because the absorption is increased and the peak shift to higher wavelength (red shift) with annealing.

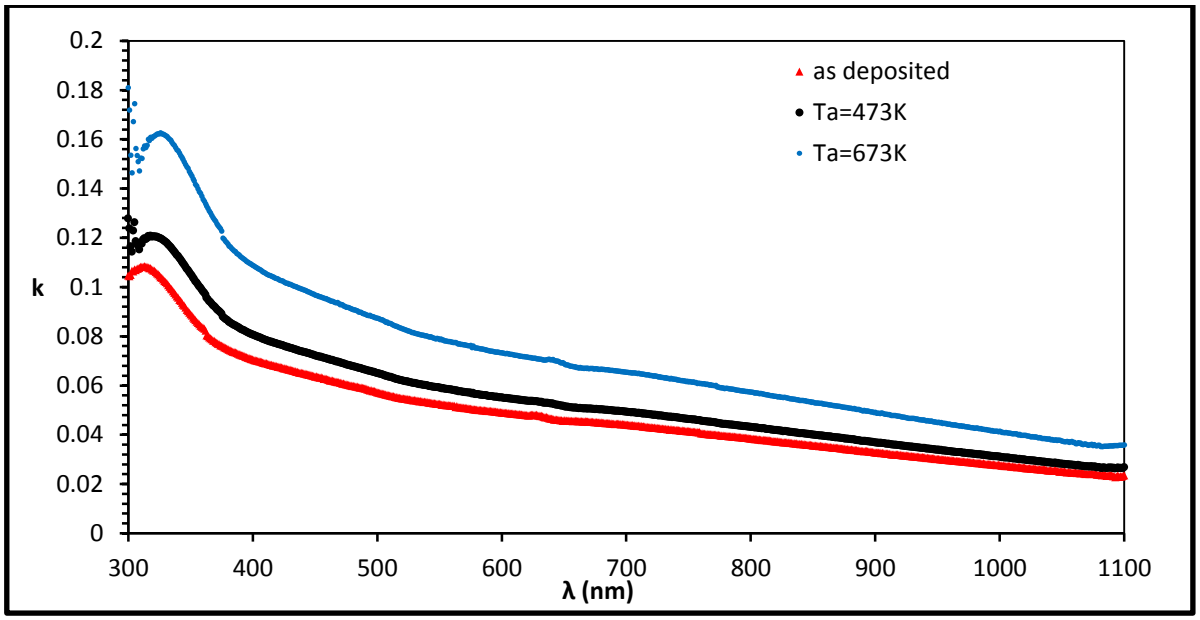

Fig. (5) Extinction coefficient versus wavelength for as deposited and annealed ZnO films.

The index of refraction for as deposited and annealed ZnO films was estimated from the reflectance (R) data using the relation [16].

$$n = \sqrt{\frac{4R}{(1-R)^2} - k^2} - \frac{R+1}{R-1} \qquad \text{.....7}$$

The variation of the refractive index versus wavelength in the range 300–1100 nm, for as deposited and annealed ZnO films on glass. has been shown in Fig. (5). It is clear from this figure that the refractive index in general increases with increasing of annealing temperature. This behavior is due to the decrement in energy gap.

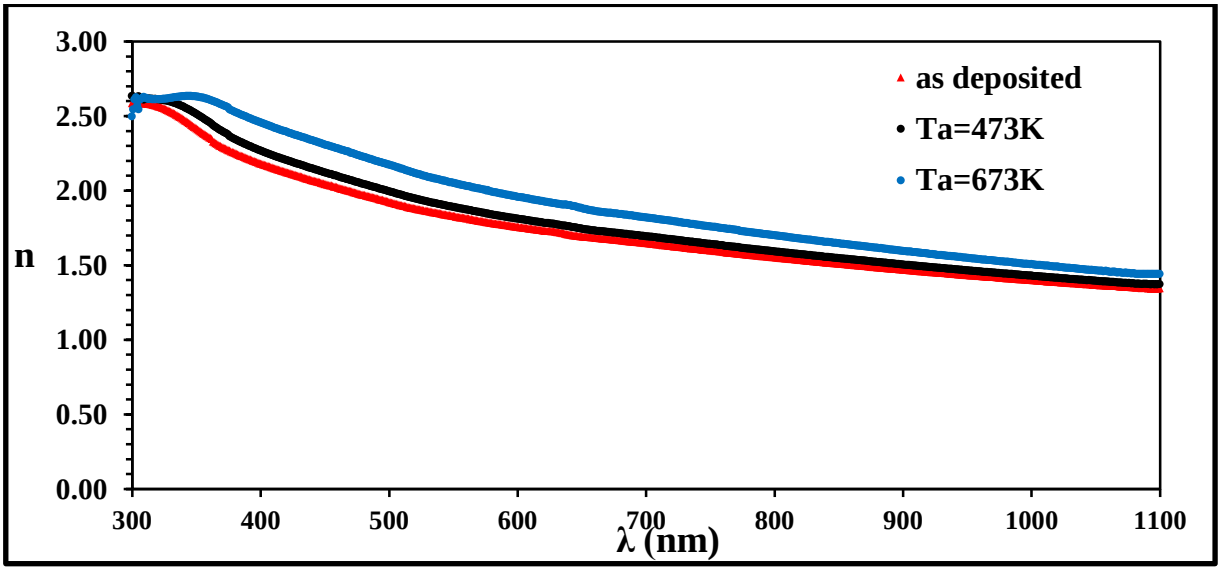

Fig. (6)The variation of refractive index with the wavelength for as deposited and annealed ZnO films.

The real and imaginary parts of dielectric constant were evaluated using the formulas [17]:

$\varepsilon_r = n^2 - k^2$ ……..……8

$\varepsilon_i = 2nk$ ……..……9

The variation of the real and imaginary parts of the dielectric constants values versus wavelength have been shown in figures (7 and 8) for as deposited and annealed ZnO films on glass. Their value are decreased with wavelength more than 500nm.The variation of the dielectric constant depends on the value of the refractive index. By contrast, the dielectric loss depends mainly on the extinction coefficient values which are related to the variation of absorption.

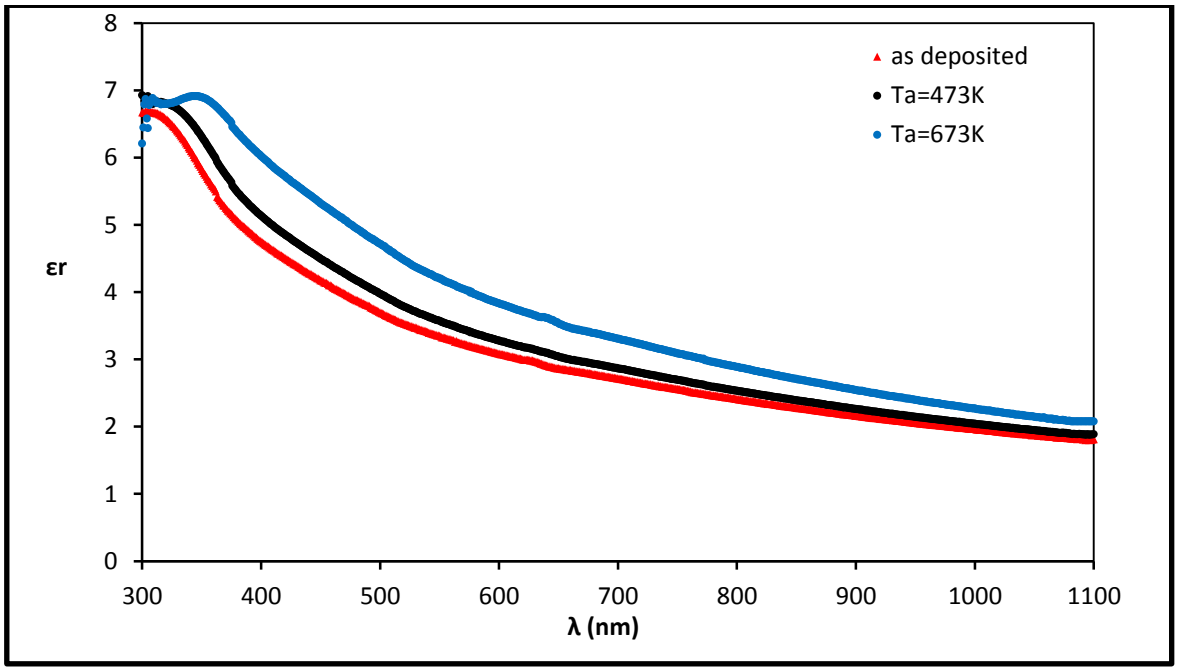

Fig.(7) The variation of ε_r with the wave length for as deposited and annealed ZnO films.

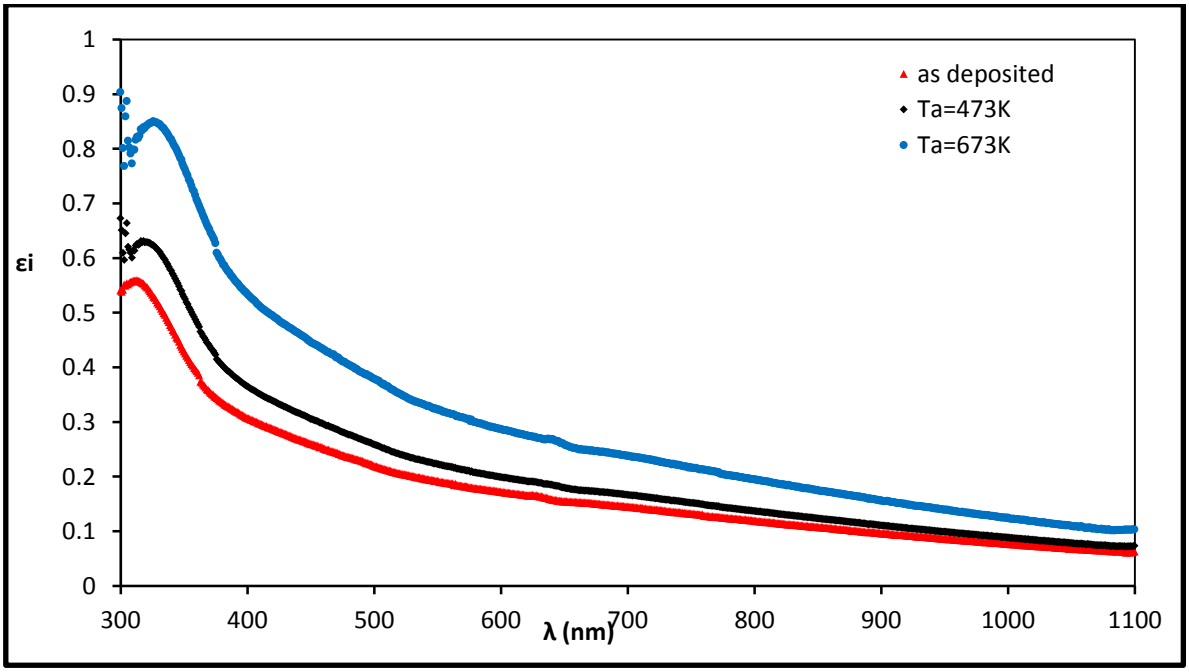

Fig. (8) The variation of ε_i with the wave length for as deposited and annealed ZnO films.

Table (1) shows the optical constants for as deposited and annealed ZnO films on glass at $\lambda = 500$ nm and the optical parameters values for these prepared samples. This Table illustrates that the values of α, k, n, ε_r and ε_i increase with annealing, whereas T and E_g are opposite i.e., they decrease with annealing.

Table (4) The optical parameters at $\lambda = 500$ nm and E_g for as deposited and annealed ZnO films.

T_a (K)	T%	α (cm^{-1})	K	n	ε_r	ε_i	E_g (eV)
as deposited	80.63	14355	0.057	1.924	3.698	0.220	3.26
473	78.30	16314	0.065	1.995	3.976	0.259	3.20
673	72.07	21839	0.087	2.171	4.707	0.378	3.14

Conclusions

Optical properties for as deposited and annealed ZnO films, prepared by pulse laser deposition technique have been studied. The outcome of this investigation can be summarized as follows:

- ZnO films were convert from amorphous to hexagonal polycrystalline structure when annealed at 473 K under 10^{-3} mbar vacuum for one hour and with increasing annealing temperature to 673 K leads to increase the crystallinety
- It is shown that the grain size increases as the annealing temperature increases, which lead to decrease the non-uniform strain.
- It can also see from table (1) an increasing in d_{hkl} with increasing T_a i.e., slightly shift in 2θ to lower values, i.e increase in lattice constant which effect on the energy gap.
- The transmittance increases with increasing wavelength while it decreases with annealing.
- The energy gap decreases from 3.26 eV to 3.14 eV with annealing.
- The optical constants values(α, k, n, ε_r and ε_i) increase with annealing**.**

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