The effect of laser pulses on the structural and optical properties of pure ZnO and ZnO doped with Fe thin films

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Abstract: In this work, pure ZnO and doped ZnO with Fe (3%wt) were deposited on glass substrate using pulsed laser deposition (PLD) technique. pulsed Nd.YAG laser at 1064 nm, repetition rate 6HZ and the pulse duration 10ns has been used to deposit thin films under vacuum of 10-2mbar.

The effect of laser pulses (100,300,600 and 800), on the structure and optical properties of these films has been studied.The structure analysis of the samples was performed using X-Ray Diffraction (XRD). XRD results showed that pure ZnO had amorphous structure changed to polycrystalline structure at 800 laser pulses and ZnO:Fe(3%) thin films had a polycrystalline structure. The intensity and the grain size increase as the laser pulses is increased . The Morphology is measured by AFM. The AFM results showed that the Root Mean Square (RMS) roughness is increased with increasing no.of laser pulses from 5.96 nm to7.16 nm and from 3.23nm to 10.2nm for pure ZnO and ZnO:3%Fe respectively.

The optical properties were investigated using UV-Vis spectrometry . Samples is found high transparent in the visible region. Band gap for pure ZnO and ZnO:3%Fe is decreased from 3.13 eV to 2.9eV and from 2.8eV to 2.55eV respectively.

Keywords: Pulse laser deposition, Zinc oxide, Thin film, Fe, number of laser pulses.

1-Introduction

Zinc Oxide is attracting much attention for its application to UV light-emitters, varistors, transparent high power electronics, surface acoustic wave devise, piezoelectric transducers, solar cell and as window material. A common application gas sensors recent improvements in the quality and control of conductivity in bulk and epitaxial ZnO have increased interest in the use of this material for short wavelength light emitters and transparent electronics[1,2]

Zinc oxide(ZnO) is a compound semiconductor of the II-VI family, which has a direct band gap of (3.37 eV) , large exiton binding energy (60 meV) at room temperature in the ultraviolet (UV) range [3,4]. A variety of methods have been used to synthesize doped and undoped ZnO semiconductors including sol-gel [5], Spin-Coating Technique[6], pulsed laser deposition (PLD)[7], and vapor phase transport (VPD) [8]. Among these methods, pulsed laser deposition different materials, e.g.high-temperature superconductors and oxides with high deposition rates. In this paper we prepared Fe- doped and un doped ZnO thin films via PLD method on glass substrates and study the effect of laser pulses on the structure and optical of thin films.

2-Experimental work:-

Pure ZnO and ZnO:(3%wt)Fe films were fabricated by pulsed laser deposition system using a Nd:YAG laser for deposition of ZnO thin

film at different number of laser pulses (100,300,600 and 800). Thin films were grown in a vacuum chamber with background pressure of $1*10^{-2}$mbar. The Nd:YAG laser was operated at the wavelength of 1064nm, laser fluencies=800j/cm^2, repetition frequency=6Hz and pulse duration of 10ns. The distance between target and substrate was (1.5cm).The glass substrates were cleaned in methanol solutions in an ultrasonic bath for 30 minutes, then compress the mixture under 5 ton (hydraulic compressor) to get the final pellet2.5 cm diameter of ZnO powder and ZnO doped (3%wt)Fe.The target should be as dense and homogenous as possible to ensure a good quality of the deposit, the target before and after ablation is shown in Figure(1) .The structural properties of the films were analyzed by X-ray diffraction (XRD, Cu Kα1, λ = 0.154 nm), Atomic Force Microscope (AFM, model AA3000 scanning probe microscope) using tapping modeand The optical properties of the films were studied at room temperature with a UV-VIS spectrometer in the wavelength range of 200-1100 nm was analyzed to determine the refractive index and energy gap value for each sample.

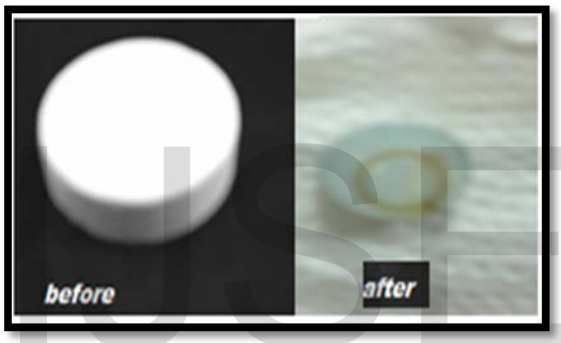


Figure. (1): The Target Before and After Being Ablated by The Laser.

3-Results and discussion:

3-1 X-Ray Diffraction Analysis.

Figure (2) showed that the pure ZnO thin films are amorphous structure at laser pulses(100,300,600) then changed to polycrystalline at 800 pulses. From the same figure, it can be noticed that the dominant intensity peaks oriented at diffraction angle2θ= 31.6129,2θ= 34.3493, 2θ=36.2848 and2θ=49.3660 corresponding to the diffraction planes (100)(002)(101)(210) respectively. The average grain size is calculated e from Scherre's relationship[9]:

$D_{av}=K\lambda/\beta\cos\theta$ ……(1)

Where, λ is the wavelength of X-ray , β is the full width at half the maximum intensity (FWHM) of the peak, θ_β is the Bragg angle and K is the shape factor of the crystallite which equal to 0.9.

Figure(3)shows XRD patterns of the ZnO doped with Fe at (3%wt) concentration, thin film exposed to (100,300,600and 800)pulses.It was noticed that the intensity increases with growing no.of laser pulses and

thestructure of thin films transformed from amorphous to polycrystalline at 800 pulses. The XRD pattern indicates that the film exhibits polycrystalline hexagonal wurtzite structure is agreement with[10]. From table (2)the grain size of thin films increased as the No. of pulses increased[11,12]. The grain sizes were found to be increased with the increase of No. of laser pulses as shown in figure(4).

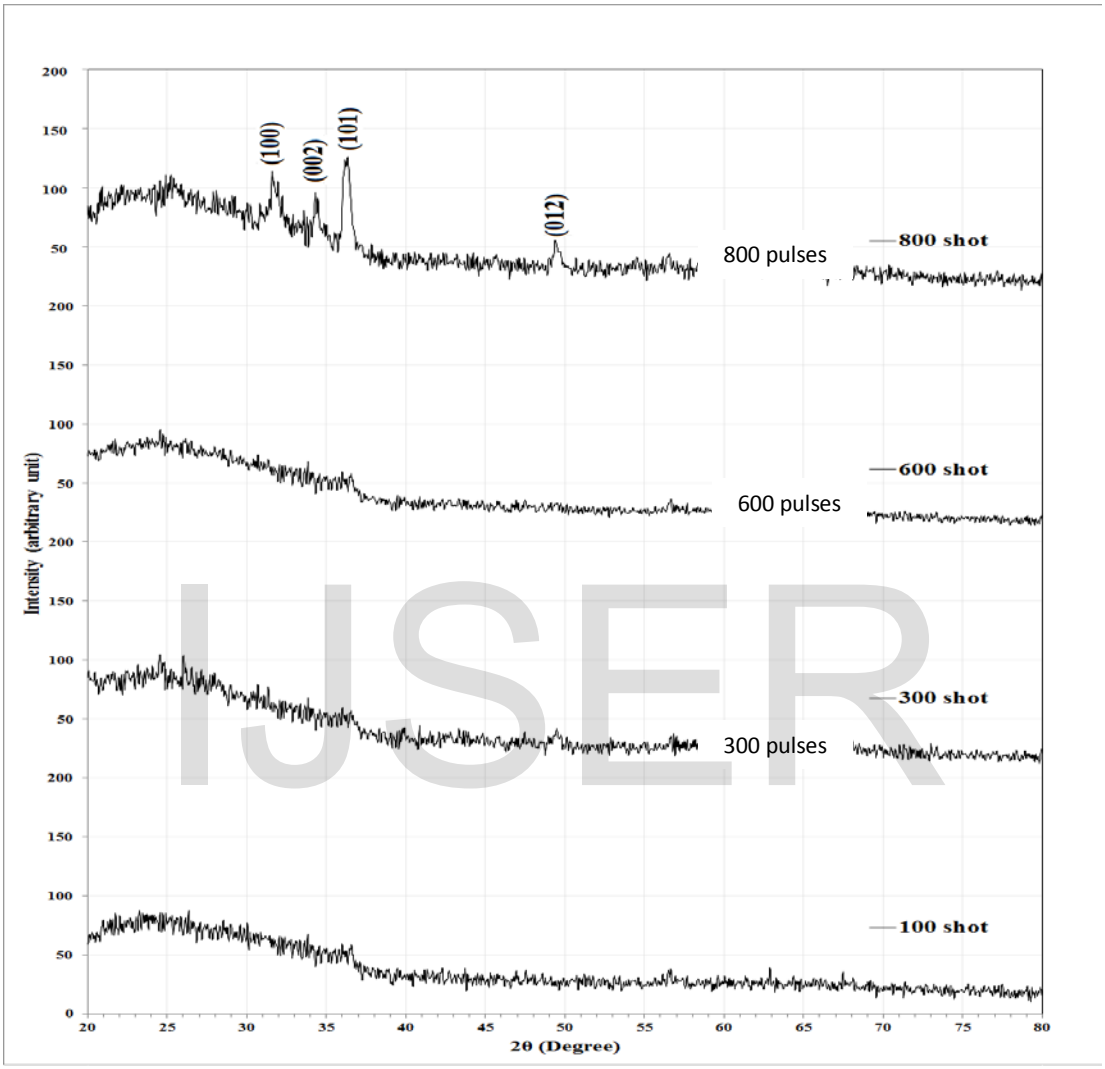


Figure (2):-XRD analysis of pure ZnO thin film at differentNd:YAG laser pulses

Table(1)The structural parameters of pure ZnO thin film at different No.of laser pulses

No. of pulse	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.	hkl
100	-	-	-	-	-	-
300	-	-	-	-	-	-
600	-	-	-	-	-	-
800	31.6129	0.5139	2.8279	16.1	2.8137	(100)
	34.3493	0.4672	2.6087	17.8	2.6035	(002)
	36.2848	0.4789	2.4738	17.5	2.4754	(101)

	49.3660	0.5339	1.8446	16.4	2.4754	(101)

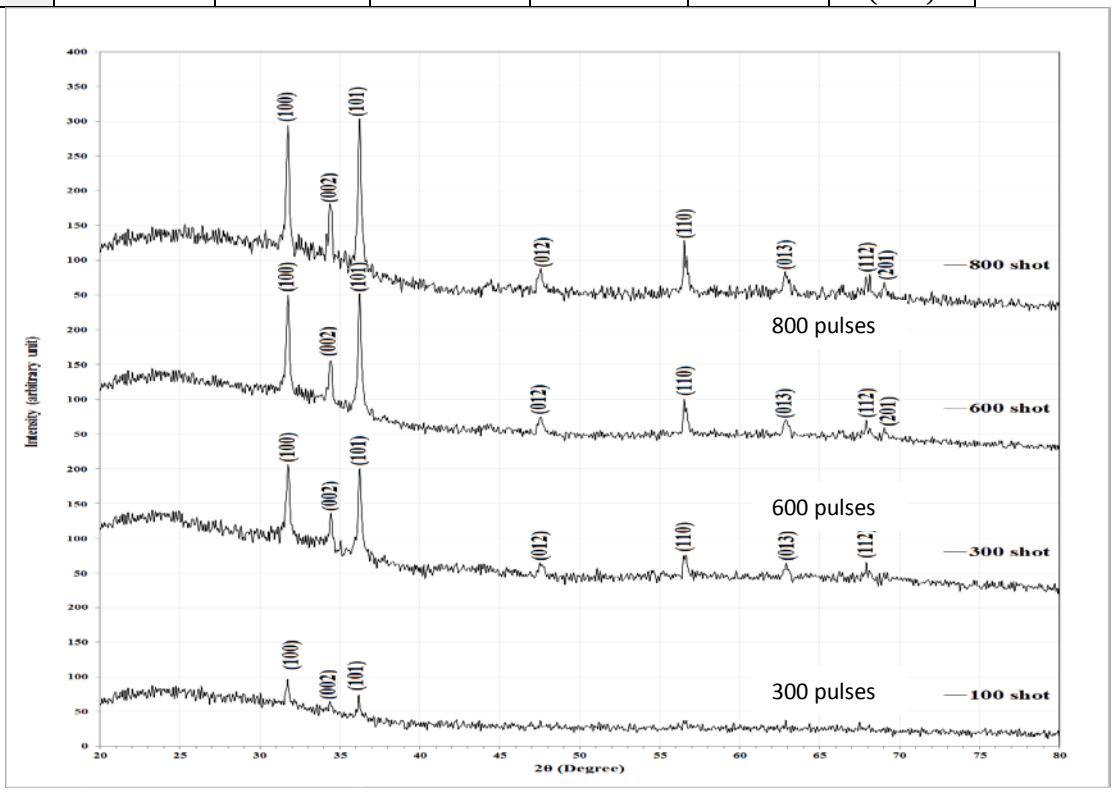


Figure (3):-XRD analysis of ZnO thin film doped with (3.%wt)Fe at different Nd:YAG laser pulses .

Table (2): Parameters of XRD pattern of ZnO with (3.wt%)Fe thin f films at (100,300,600,800) laser pulses

No. of pulses	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.	Phase	hkl
100	31.8259	0.5882	2.8095	14.0	2.8137	ZnO	(100)
	34.2353	0.4118	2.6171	20.2	2.6035	ZnO	(002)
	36.1765	0.3120	2.4810	26.8	2.4754	ZnO	(101)
300	31.7559	0.4118	2.8155	20.1	2.8137	ZnO	(100)
	34.4118	0.2941	2.6041	28.3	2.6035	ZnO	(002)
	36.2353	0.3010	2.4771	27.8	2.4754	ZnO	(101)
	47.4706	0.4706	1.9137	18.4	1.9110	ZnO	(012)
	56.5294	0.3529	1.6267	25.6	1.6245	ZnO	(110)
	62.8824	0.4706	1.4767	19.8	1.4772	ZnO	(013)
	67.9412	0.6471	1.3786	14.8	1.3782	ZnO	(112)
600	31.7309	0.3235	2.8177	25.5	2.8137	ZnO	(100)
	34.3824	0.2647	2.6062	31.4	2.6035	ZnO	(002)
	36.2059	0.2976	2.4790	28.1	2.4754	ZnO	(101)
	47.5000	0.4212	1.9126	20.6	1.9110	ZnO	(012)
	56.5294	0.3680	1.6267	24.5	1.6245	ZnO	(110)
	62.8529	0.4315	1.4774	21.6	1.4772	ZnO	(013)
	67.9812	0.3918	1.3779	24.5	1.3782	ZnO	(112)
	69.0520	0.3941	1.3591	24.5	1.3582	ZnO	(201)
800	31.7059	0.2353	2.8199	35.1	2.8137	ZnO	(100)
	34.3529	0.2353	2.6084	35.3	2.6035	ZnO	(002)
	36.1765	0.2941	2.4810	28.4	2.4754	ZnO	(101)
	47.5294	0.3718	1.9115	23.3	1.9110	ZnO	(012)

800 pulses

	56.5294	**0.3831**	**1.6267**	**23.5**	**1.6245**	**ZnO**	**(110)**
	62.8235	**0.3924**	**1.4780**	**23.7**	**1.4772**	**ZnO**	**(013)**
	68.0213	**0.3918**	**1.3771**	**24.5**	**1.3782**	**ZnO**	**(112)**
	69.0120	**0.2941**	**1.3598**	**32.8**	**1.3582**	**ZnO**	**(201)**

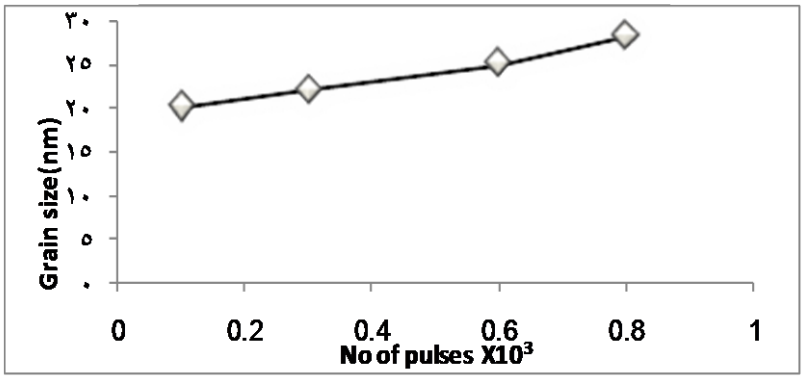


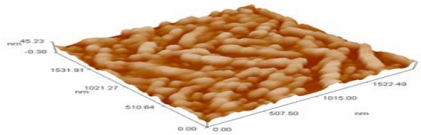
Figure (4): Grain size as a function of laser pulses (100, 300, 600 and 800).

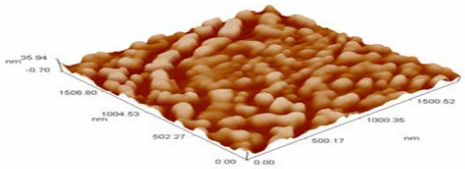
3-2Atomic Force Microscope Analysis

The AFM images of pure ZnO and 3% Fe doped ZnO thin films deposited on glass substrate at temperatures of(150)ºC at different laser pulses(100,300,600and 800)as shown in figures(5),(6) respectively, the laser energy is fixed at 900 mj, also pressure at 10^{-2} mbar , it can be seen from table (3) that the crystalline of the films improves and the crystalline size becomes larger with increasing No.oflaser pulses. Also the degree of surface roughness increases. From the topographic images, it can be seen that the average grain size increases with increasing No.of laser pulses.It is clear from the figures (5)and(6) that the films had a good and uniform surface homogeneity which give a good indicator for deposition of Fe over nano spikes of ZnO.

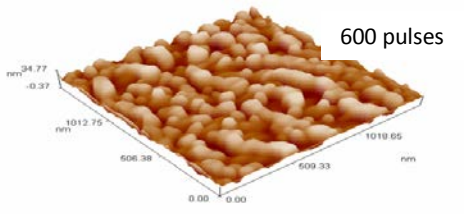
Table (3): The obtained results from AFM Analysis for pure ZnO thin films at different laser pulses

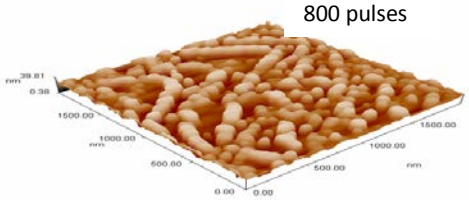
No. of pulses	AFM of plane grain size (nm)	Roughness (nm)	RMS roughness (nm)
100	71.31	5.2	5.96
300	80.12	5.27	6.02
	82.74		
	91.31		



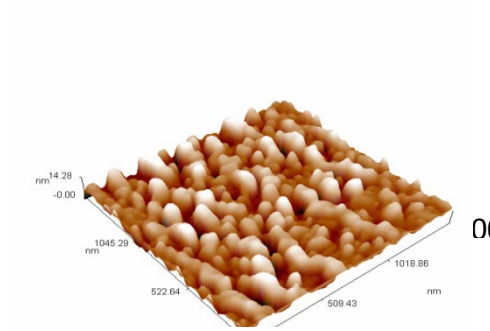


100

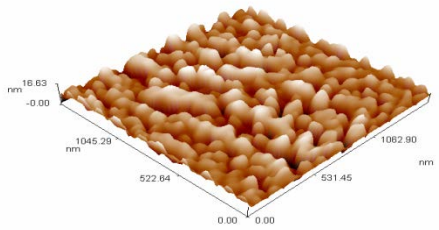




300

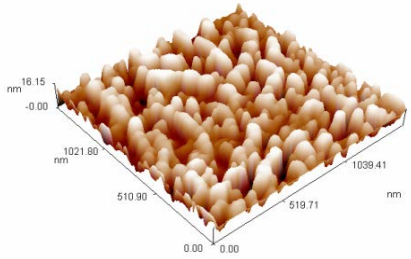


ZnO at 00100

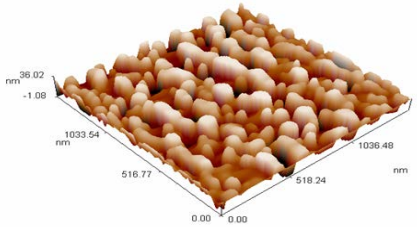


800

Figure(5):Three-dimensional AFM of nanostructure pure different laser pulses



100



300

800

600 pulses

Figure(6):Three-dimensional AFM of nanostructureZnOdoped with (3%wt)Fe films at different laser pulses

Table (4): The obtained results from Analysis AFM ZnO doped with 3%Fe thin films at different laser pulses

No. of pulse	AFM of average grain size (nm)	Roughness(nm)	RMS roughness(nm)
100	73.72	2.64	3.23
300	86.72	2.85	3.52
600	67.87	3.83	4.47
800	77.59	8.76	10.2

100 pulses

3-3Optical Properties

The UV-VIS spectrum of pure ZnO and ZnO doped with 3%Fe at laser pulses is shown in figures (9)and(10), respectively. It could be seen that the average transmittance in the visible spectrum region was decreased with the increasing laser pulses. This indicates that the pure ZnO films and ZnO doped with Fe films have good absorption characteristics in UV rang. In consistent with the increasing of the surface roughness promoting the increase of the surface scattering of the light.

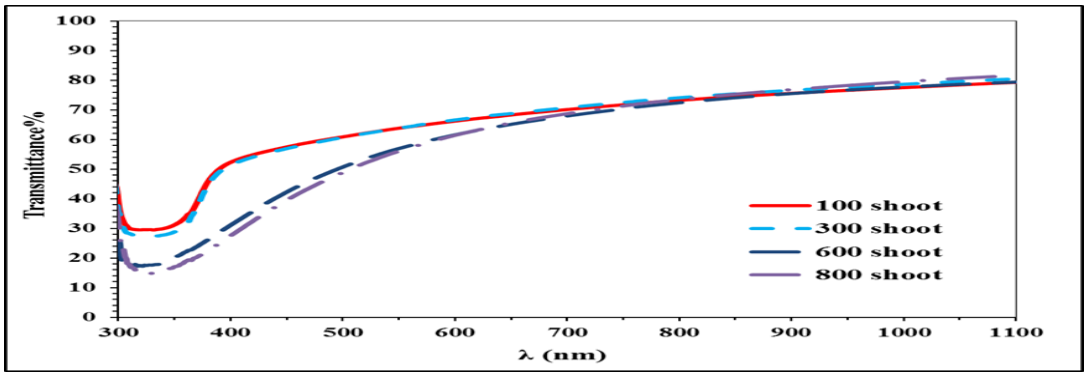


Figure (9):-Transmittance spectrum of pure ZnO thin film at different laser pulses

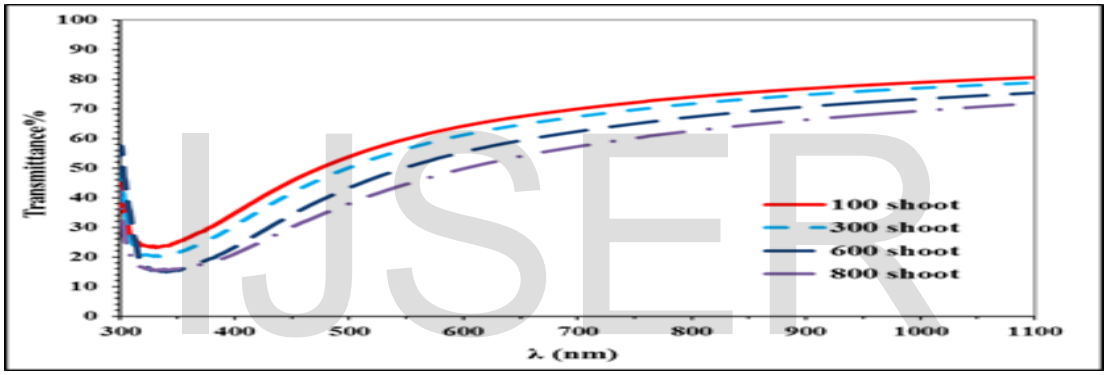


Figure (10):- Transmittance spectrum of ZnOdoped with 3%Fe thin film at different laser pulses

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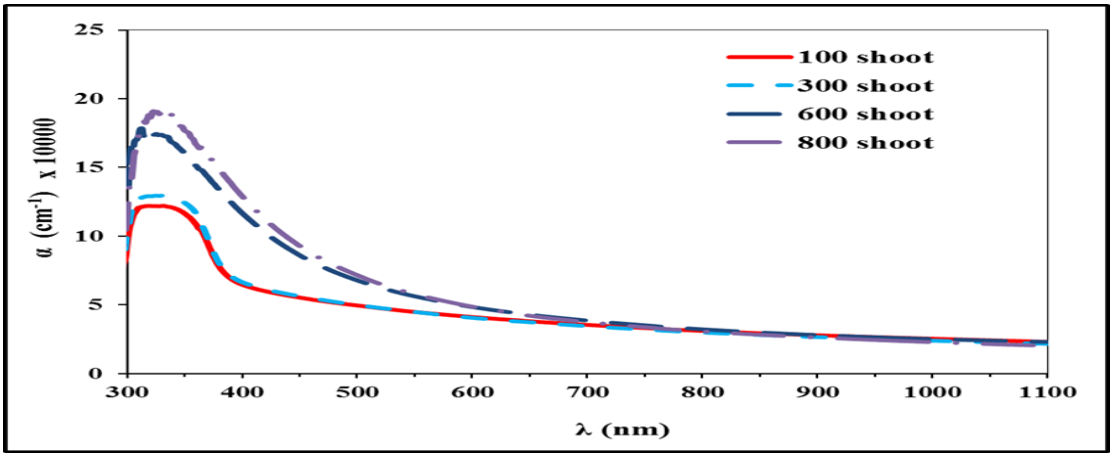

Figure (11):-Absorption coefficient of pure ZnO thin film at different laser pulses (100,300,600,800) .

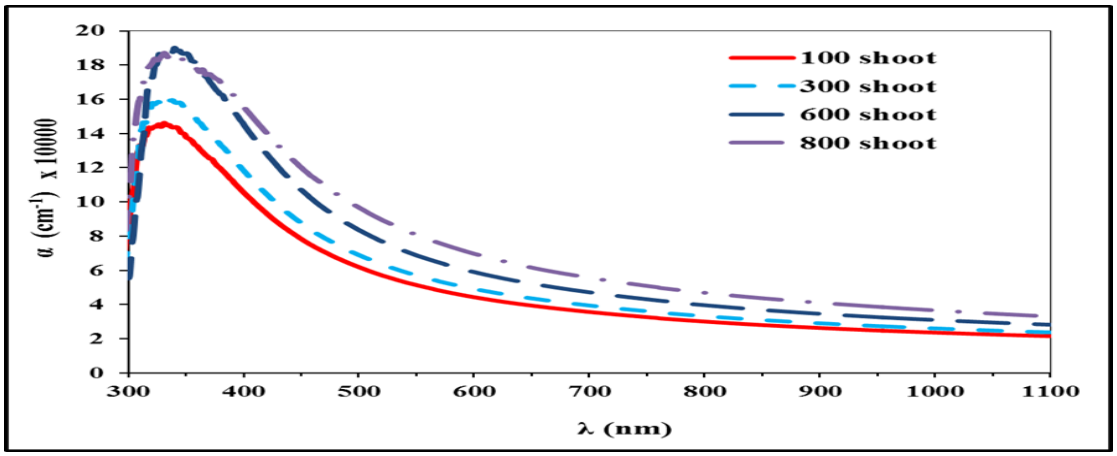

Figure (12):- Absorption coefficient of ZnOdoped with 3%Fe thin film at different laser pulses

It is observed that the absorption coefficient (α) increases with increasing the number of laser pulses as shown in figure(11) while the value of energy gap(Eg) decreases with the increasing number of pulses for all films

. This is due to the growth of grain size and the increase in defect states near the bands in turn decreased the value of Eg. A plot of $(\alpha h\upsilon)^2$ versus hυ for pure ZnO and ZnO doped with (3%) Fe thin films at differentlaser pulses is shown in figures (13) and(14).

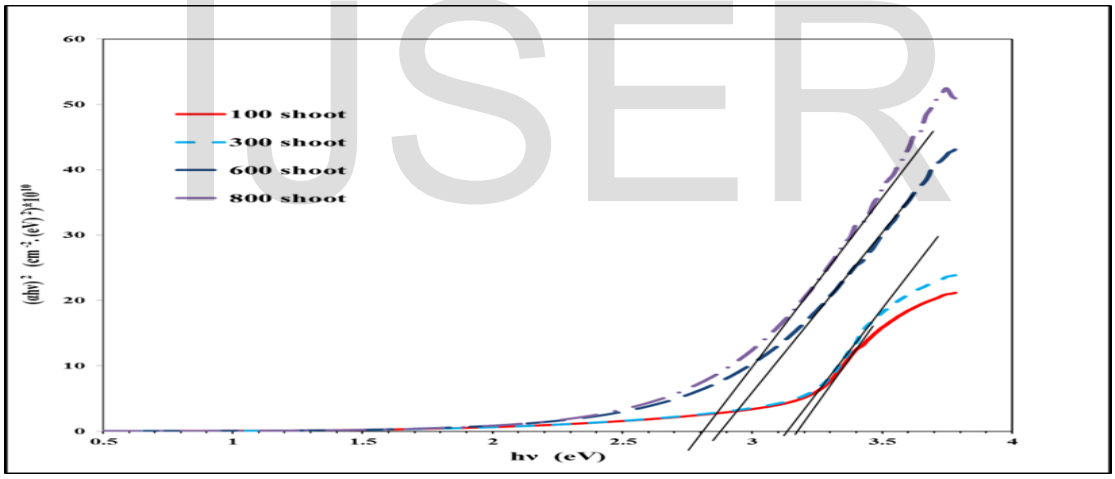

Figure (13): Energy gap of pure ZnO thin film at different laser pulses

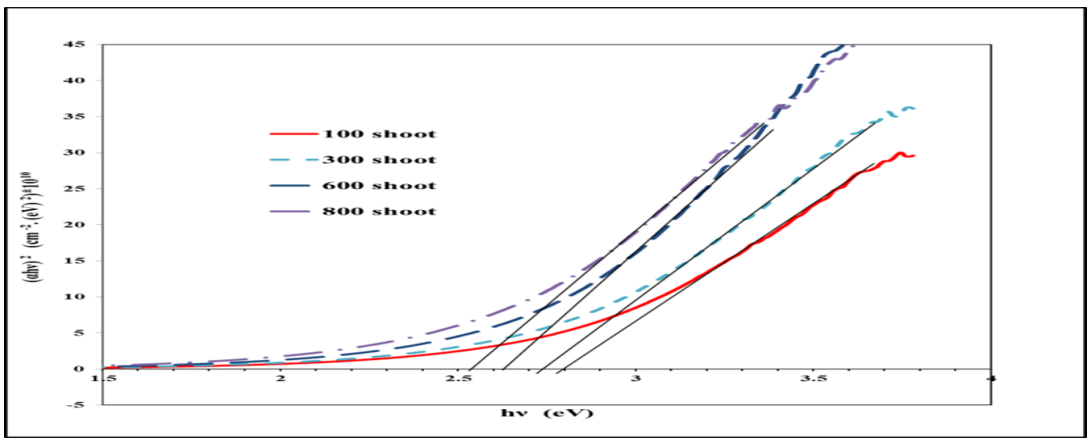

Figure (14):- Energy gap of ZnO doped with 3%Fe thin film at different laser pulses

The extinction coefficient, which is related to the exponential decay of the wave as it passes through the medium can be determined by using the following equation [13]:

$$k = \frac{\alpha\lambda}{4\pi} \quad \text{……..…….. (2)}$$

where λ: is the wavelength of the incident radiation.

The increase in the extinction coefficient values with increasing the No. of laser pulses is due to increase in the absorptions as shown in figures (15)and(16). Increased (k) with the increased number of pulses because increase in thickness of thin films.

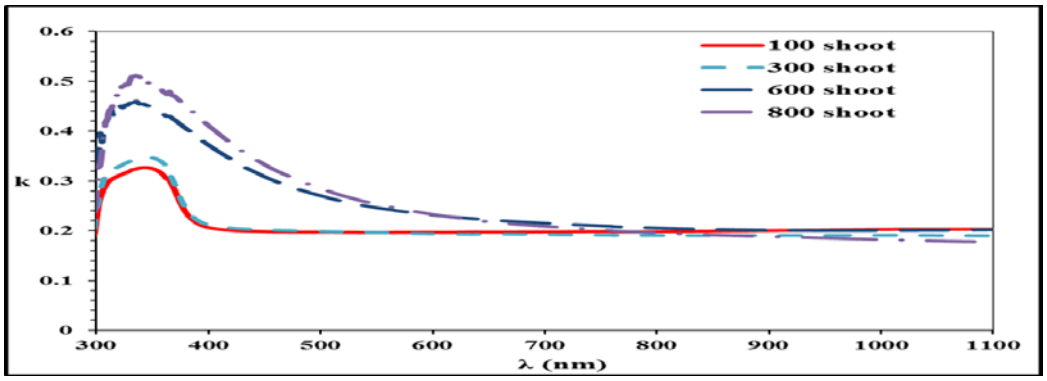

Figure (15):Extinction coefficient of pure ZnO thin film at different laser pulses.

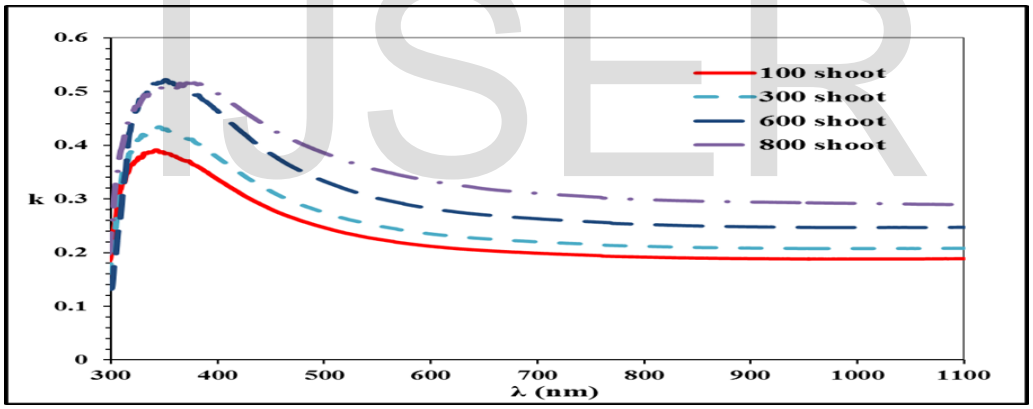

Figure (16):-Extinction coefficient of ZnO doped with (3w.t)Fe thin film at different laser pulses

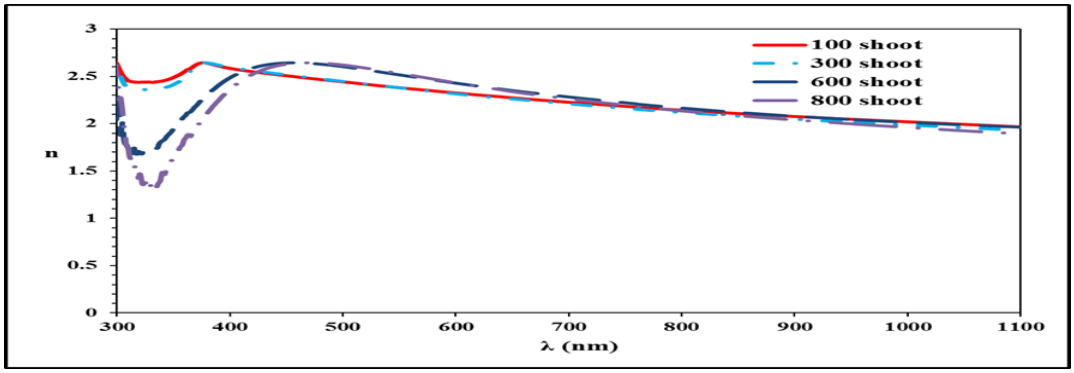

Figure (17):Refractive index of pure ZnO thin film at different laser pulses (100,300,600,800).

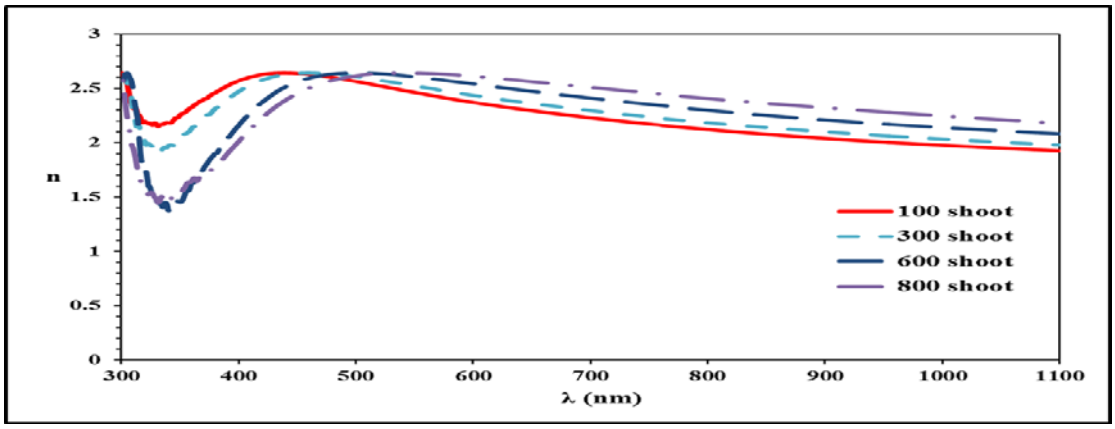

Figure (18):-Refractive index of ZnO doped with 3%Fe thin film at different laser pulses (100,300,600,800).

It can be noticed that the refractive index increases with increasing of No. of laser pulses as shown in the figures (17) and(18)respectively.This is due to the increase levels intensity of the energy in the optical energy that in turn serves as centers dispersion of rays falling gap increasing the reflectivity and thus increases the refractive index (n).

$$n=\left[\frac{4R}{(R-1)^2}-k^2\right]^{1/2}-\frac{(R+1)}{(R-1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where R is the reflectance and is given by the equation

$$R=\frac{(n-1)^2+K^2}{(n+1)^2+K^2} \quad \ldots\ldots\ldots(4)$$

The complex dielectric constant is given by the following equation[14] :

$\varepsilon=\varepsilon_r+\varepsilon_i=(n+ik)^2$……(5)

Where ε_r , and ε_i are the real and imaginary parts of ε and $(n+iK)^2$ is the complex refractive index. From equation (6) we obtain:

$\varepsilon r=n^2+k^2$ and $\varepsilon i=2nk$…..(6)

The variation of the real (εr) and imaginaryε_i) parts of the dielectric constant values versus wavelength in the range (300-1100)nm at different laser pulses are shown in figures (19),(20). The behavior of ε_r is similar to that of the refractive index because of the smaller value of k^2 compared with n^2 according to equation (2-13) and(2-14) while ε_i mainly depends on the k values equation(2-13)and(2-14). This behavior is inagreement with the results obtained by (A.Kamalianfar)[15].

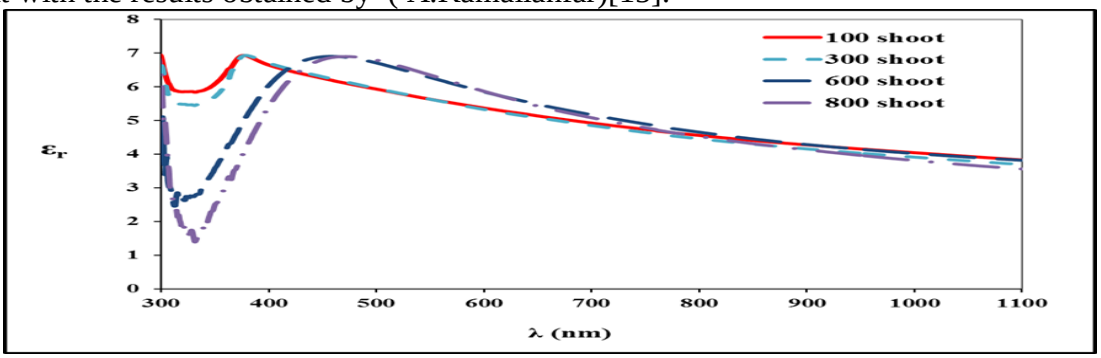

Figure (19):Dielectric Constantreal of pure ZnO thin film at different laser pulses

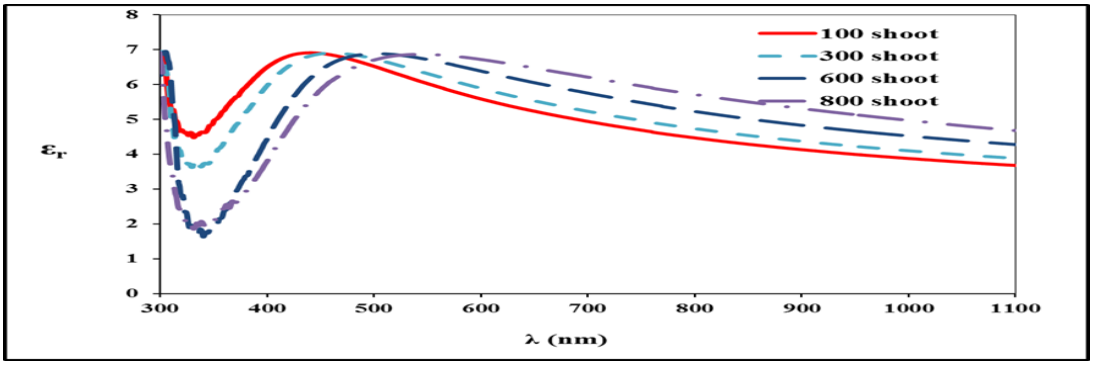

Figure (20):- Dielectric Constantrealof ZnOdoped with 3%Fe thin film at different laserpulses

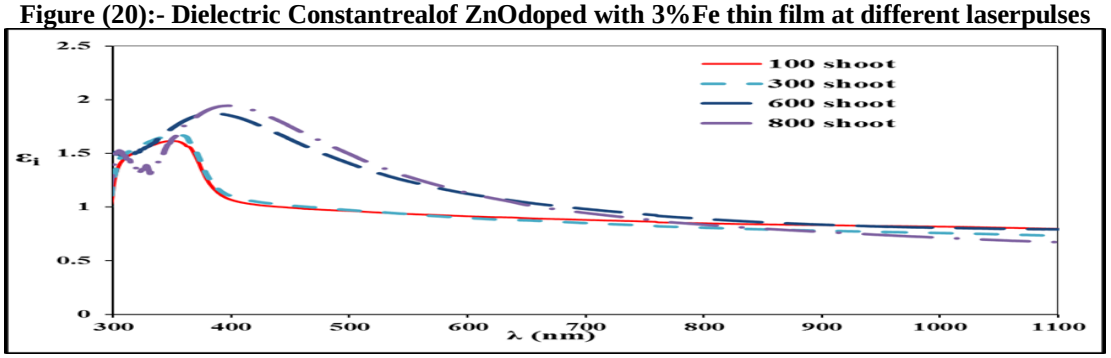

Figure (21): Dielectric Constantimaginary of pure ZnO thin film at different No. of laser pulses

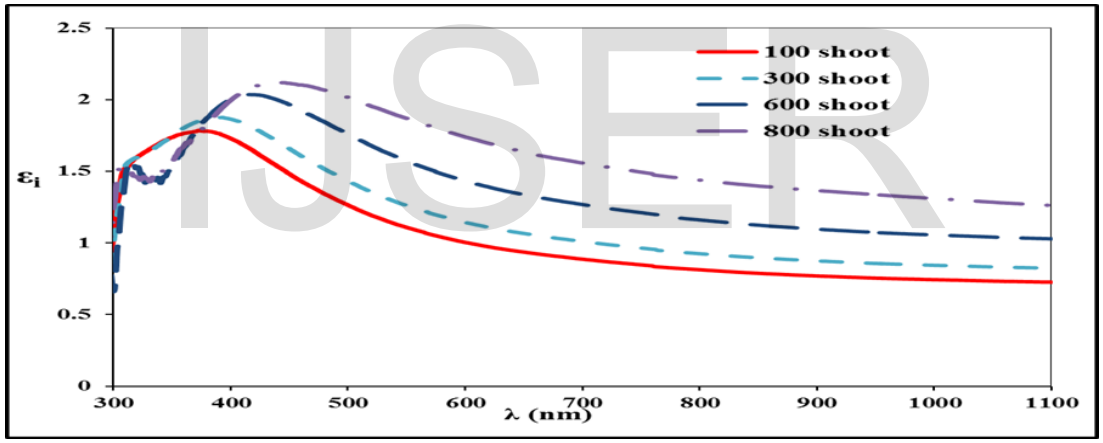

Figure (22):-Dielectric Constantimaginary of ZnOdoped with 3%Fe thin film at different No. oflaser pulses

Conclusions

The structure and optical and properties of pure ZnO and ZnO doped with Fe at different laser pulses obtained by PLD system are investigated. The results of XRD patterns showed that the un doped ZnO films are amorphous at 100,300,600 laser pulses and it became polycrystalline of wurtzite structure at 800 pulses and the ZnO doped with 3%Fe films were polycrystalline.Surface morphology pictures for the prepared films indicates that the average grain size and RMS roughness became larger with increasing no. of laser pulses. This result is nearly in agreement with Rajesh Kumar[16] and thin films have energy band gap decreased with increase no.of laser pulse while transmittance decreases with increasing no.of laser pulses.

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