Structural and Optical properties of SnO_2 doped ZnO thin films prepared by Pulsed Nd:YAG Laser Deposition

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Abstract

In this work the thin films of ZnO were deposited at room temperature and were doped with different concentrations of SnO_2 thin films wich equal (x=0,0.2,0.4,0.6,1).The deposition process was carried out on glass substrates with a technique (PLD) that included the use of wave length equal to (1064nm) and the energy its amount(400 mj) and the pulses number used (200 puls). The structural properties and optical properties of as-deposited films were transported out using (XRD), UV–vis and AFM .The effect of SnO_2 content on these Characteristics was investigated properties by (XRD) show The thin films for ZnO have a hexagonal system, with wurtzite type Polycrystalline and numerous peaks [(100), (002), (101), (012) and (110)] respectively, were show. Moreover AFM investigation appears no clefts in the created layer. The optical properties related to the transition and absorption spectra of thin films prepared using the near-infrared UV spectrometer. The results appear that (T) of Zinc oxide film in visible domain reachs nearly 34.45%,Optical band gaps were found to be (2.54, 2.34, 2.33, 2.25 and 2.10) eV for different concentration of SnO_2 (X=0,0.2,0.4,0.6and1) wt% respectively. At (500 nm) extinction coefficient and the refractive index were determined

Keywords: (ZnO)x-1(SnO_2)x pulse laser deposition(PLD) growth, (AFM) ,(XRD) and Optical properties.

الخصائص التركيبية والبصرية لأغشية اوكسيد الزنك المشوبة باوكسيد القصدير الرقيقة باستخدام الترسيب لليزر Nd:YAG النبضي

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الخلاصة

تم ترسيب أغشية اوكسيد الزنك الرقيقة عند درجة حرارة الغرفة بتراكيز مختلفة من اوكسيد القصدير wt.% (0 , 0.2, 0.4, 0.6,1) =x . على قواعد زجاجية بواسطة تقنية الترسيب بالليزر النبضي باستخدام ليزر Nd–YAG ذو (طول موجي 1064 نانومتر) و(طاقة قدرها 700ملي جول)و(عدد نبضات 200 نبضة)، الخصائص التركيبة والبصرية للاغشية التي تم ترسيبها أجريت (باستخدام حيود الأشعة السينية و مجهر القوة الذري و مطياف الأشعة فوق البنفسجية). تم دراسة تأثير تركيز اوكسيد القصدير على هذه الخصائص .أثبتت نتائج حيود الأشعة السينية بان اوكسيد الزنك يمتلك طبقة رقيقة من الكريستالات من نوع wurtzite مع نظام سداسي وضهور العديد من القمم عند اسطح الانعكاس [(100) ، (002) ، (101) ، (012) و (110)] على التوالي ،كما تم دراسة الخواص البصرية للأغشية الرقيقة عن طريق تحليل طيف (النفاذية و الامتصاصية)وتم ايجاد فجوة الطاقة البصرية للاغشية التي تم تحضريها وكانت تساوي (2.25 ,2.33 ,2.34 ,2.54 و 2.10) الكترون فولت بتراكيز مختلفة من اوكسيد القصدير wt.% (0 , 0.2, 0.4, 0.6,1) =x على التوالي ,عند طول موجي 500 نانومتر تم حساب معامل الخمود و معامل الانكسار

Introduction

Transparent Conductivity oxides have recently raised a lot of interest in optoelectronics [1]. Transparent conductivity oxides are substances that exhibit higher visual permeability in the visible area, less paper resistance and higher electrical conductivity, Zinc Tin oxide is a class of (three-oxide) known for its fixed Characteristics under standard conditions. The mobility is high compared to its binary counterparts These materials are therefore perfect applications of (photovoltaic catalysts for solar cells, field-impact transistors (heterogeneous diodes and binary interfaces), light-emitting diodes and gas detectors [2-5]. Thin films are produced by various methods like (PLD), magnetic sputtering, MOCVD and also pyrolysis of spray)[6-9] . Tin oxide is a quadruple structure with n-deficient semiconductors

.Note that there is a wide gap of (3.6ev). The high and detailed transparency of electricity leads to highly attractive applications in the spintronics device. Zinc oxide was introduced in high-range spectroscopy including the beneficial UV region and other properties like (low cost and stability in chemical environments) .The aim of the work is to know the effect of concentration on optical and structural properties of (ZnO)1-x(SnO2)x films Prepared by (PLD)Technique at RT

Experimental part

Sample preparation

Zinc oxide with high purity and Tin dioxide with high purity were mixed together at various concentration of x= (0, 0.2, 0.4, 0.6, 1) wt. %. The powder of precursors were blended together using a gate mortar for (one hour). It was compressed by hydraulic press operating at (6 Pa) in duration of (10min) Submitted pellets of (20 mm) in diameter and thickness reliance on the material amount ,usually weigh(3 gm).entails pellet of approximately (15 mm) of thickness

PLD and Thin Film Preparation

The $(ZnO)_{1-x}(SnO2)_x$ films were deposited on substrates made of glass and was deposition the films at (RT) using Pulsed Laser Deposited technique which include use Nd:YAG laser with (λ = 1064 nm) and at energy used (700 mJ)and repetition frequency equal to (6 Hz) and the number of pulses equal to (200 pulse) this method done under vacuum equal to (2.5 x 10-2 mbar)

Results and Discussion

X-ray diffraction results

The crystalline structure for $(ZnO)_{1-x}(SnO_2)_x$ known by studying the phase of (XRD) For these materials. Figure (1) appear the XRD patterns.It was received for $(ZnO)_{1-x}(SnO2)_x$ thin films prepared at RT

with thickness equal to(200 nm)and various concentration of (x= 0, 0.2, 0.4, 0.6 and1) wt. %. The XRD pattern of Zinc oxide (ZnO)film feigned by using(PLD) Technique on glass substrate as shown in Fig (1) the peaks of films for ZnO agree to the peaks of standard ZnO (JCPDS 96-901-1663), ZnO have a hexagonal system with wurtzite type polycrystalline, It can note two peaks for polycrystalline Hex. ZnO phase for pure ZnO located at 34.3192°and 34.3192°. with hkl[(100), (002), (101), (012) and (110)] respectively. According to (ICDD) the structure of SnO_2 thin film films appeared (polycrystalline tetragonal) . The analysis Checks the reflection surfaces [(110), (101), and (211)].The films were crystallized with a powerful peak at (110) direction congruent to a diffraction angle of 26.4568°. this means that this plane is passable for crystal growth. Figure (1) appears the XRD pattern of ZnO: SnO_2 thin films deposited at Room Temperature and various x content , also noted from this figure that The films era polycrystalline with (Tetragonal structure) for (x=0.4) with peaks at planes [(110)and(101)] for SnO_2.The structure become a mixture of (tetragonal and hexagonal) for (x=0.6) with peaks at planes[(110),(101), and (002)] for SnO2 and ZnO. At (x=0.2) The structure become (amorphous) as a due to increase the defects.

Table (1) gives the (FWHM (deg),grain size (nm) and interplaner distance (d)) For the prepared samples compared to the standard value as in the ASTM card or ICDD card ,The structure of $((ZnO)_{1-x}(SnO_2)_x)$ films has been exacted through using (XRD) to ensure the stoichiometry of our material . We can note that the values of (d and 2θ) are nearly is similar to that in the ASTM cards as listed in Table (1). by the Scherer's eq can calculated The mean grain size (G) of thin film [10]:

$G = 0.94 \lambda / \beta \cos\theta$ …(1)

Where λ is the wavelength

G is the average crystalline grain size

θ is the Bragg diffraction angle

β represents (FWHM) in radian .

The grain sizes (G) have been calculated using equations (1) and tabulated in table (1).

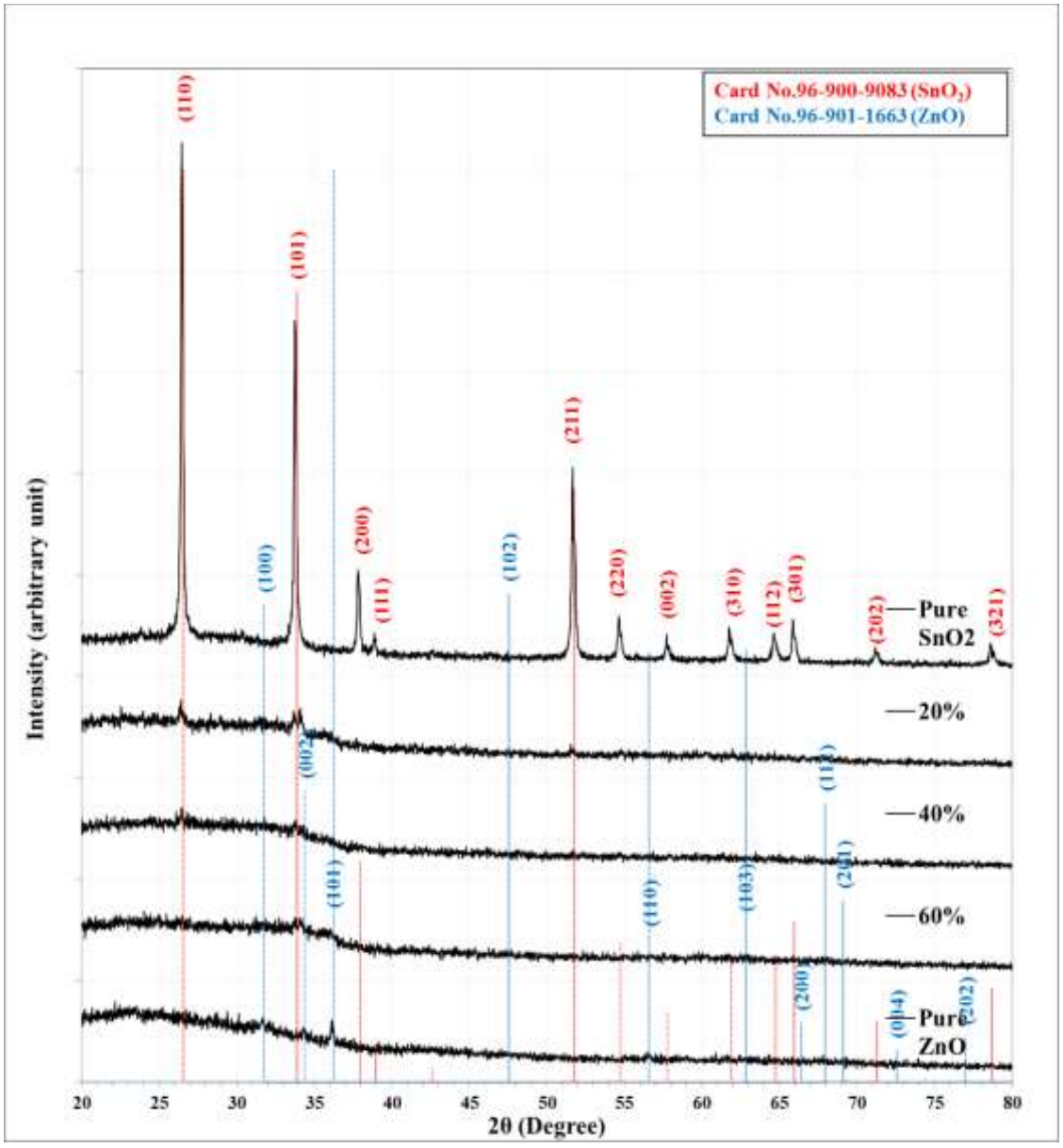

Figure (1) XRD pattern for $((ZnO)_{1-x}(SnO_2)_x)$ films prepared at RT and various concentration of SnO_2

Table (1).appears peaks, its Bragg's angle, FWHM and interplanar distance) of $((ZnO)_{1-x}(SnO_2)_x)$ thin films

Sample	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	hkl	d_{hkl} Std.(Å)	Phase	Card No.
ZnO	34.3192	0.3514	2.6109	23.7	(002)	2.6035	Hex. ZnO	96-901-1663
	36.1201	0.3514	2.4847	23.8	(101)	2.4754	Hex. ZnO	96-901-1663
0.2	Amorphous							
0.4	26.4129	0.3075	3.3717	26.5	(110)	3.3498	Tet.SnO_2	96-900-9083
	33.7921	0.4392	2.6504	18.9	(101)	2.6439	Tet.SnO_2	96-900-9083
0.6	26.4129	0.3514	3.3717	23.2	(110)	3.3498	Tet.SnO_2	96-900-9083
	33.7482	0.3514	2.6537	23.6	(101)	2.6439	SnO2	96-900-9083
	34.0996	0.4393	2.6272	18.9	(002)	2.6035	Hex. ZnO	96-901-1663
Pure SnO_2	26.4568	0.1757	3.3662	46.5	(110)	3.3498	Tet.SnO_2	96-900-9083
	33.7482	0.2196	2.6537	37.8	(101)	2.6439	Tet.SnO_2	96-900-9083
	37.8331	0.2636	2.3761	31.9	(200)	2.3686	Tet.SnO_2	96-900-9083
	38.8873	0.2635	2.3140	32.0	(111)	2.3087	Tet.SnO_2	96-900-9083
	51.6691	0.3074	1.7677	28.7	(211)	1.7642	Tet.SnO_2	96-900-9083
	54.6559	0.3074	1.6779	29.1	(220)	1.6749	Tet.SnO_2	96-900-9083
	57.7306	0.3074	1.5956	29.5	(002)	1.5932	Tet.SnO_2	96-900-9083
	61.7716	0.2636	1.5006	35.1	(130)	1.4981	Tet.SnO_2	96-900-9083
	64.6706	0.3514	1.4402	26.8	(112)	1.4388	Tet.SnO_2	96-900-9083
	65.8565	0.3514	1.4171	26.9	(301)	1.4149	Tet.SnO_2	96-900-9083
	71.1713	0.2635	1.3237	37.1	(202)	1.3220	Tet.SnO_2	96-900-9083
	78.6384	0.3075	1.2157	33.4	(321)	1.2147	Tet.SnO_2	96-900-9083

Atomic Force Microscope (AFM)

The morphology for surface of (ZnO:SnO2) thin films were prepared at various concentration deposited on glass substrate at RT has

been calculated by (AFM) . The three-dimensional topographic views of (AFM) images for films It is shown in Fig (2). AFM images reveal that the concentration rate has a strong impact on surface morphology. The films reveal a homogeneous surface made of pyramidal granules with sharp edges. The roughness of the ZnO pure film is measured to be (18.6 nm) and for(SnO_2pure) films is measured to be (3.13 nm).The average roughness and particles diameter average and (RMS roughness) increases with the increase of (SnO_2) ratio ,Which appears in the table, this result similar to [11]. this is due to the rearrangement of the atom in the film

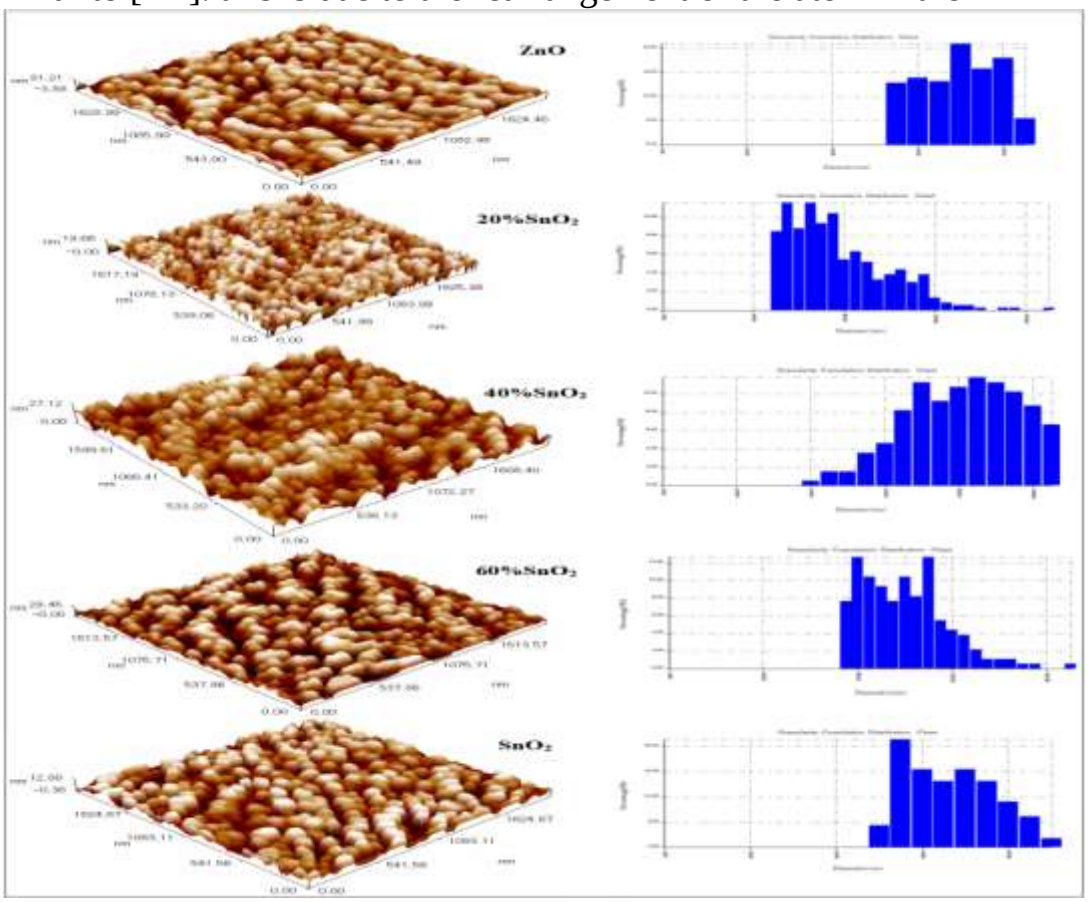

Figure (2) surface morphology for $(ZnO)_{1-x}(SnO_2)$ films analyzed by AFM prepared at RT at various concentrations of SnO_2

Table2: Consists of (Sample, Average Diameter, RMS the average of Roughness) for SnO_2:ZnO films prepared at various ratio and at RT

Sample	Average Diameter (nm)	RMS roughness (nm)	Roughness Ave. (nm)
ZnO	67.19	22	18.6
0.2	74.92	5.06	4.3
0.4	78.24	5.41	4.43
0.6	97.39	8.22	7.12
SnO_2	64.06	3.64	3.13

Optical properties Measurements

It Includes the study of optical properties of $(ZnO)_{1-x}(SnO_2)_x$ films, which deposited by (PLD) method with different concentrations. The Optical Variables which include(the absorbance, transmittance, absorption coefficient, the optical energy hole, extinction coefficient and refractive index) have been designed within the range (300-1100) nm.

Absorbance

The variation of absorbance as a function of wavelength at room temperature is shown in fig (3).The absorbance increase with increasing of SnO_2 content

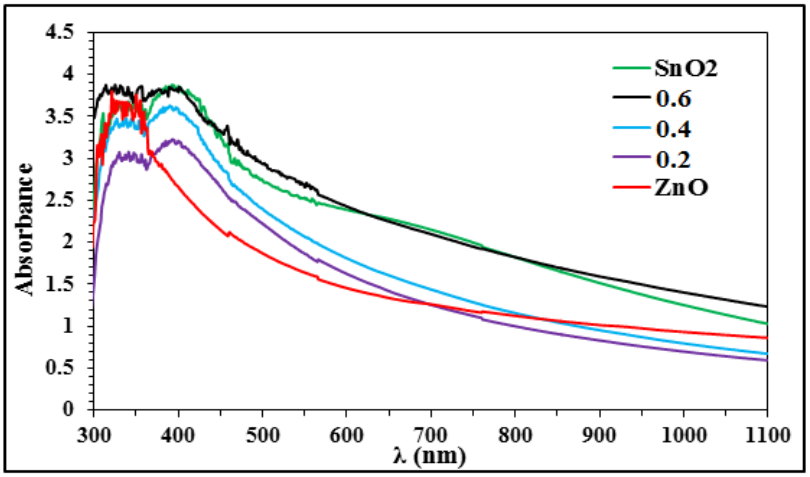

Fig (3) Absorbance versus λ for ((ZnO)1-x(SnO_2)x) films at R T and various concentrations of SnO_2

Transmittance

Figure (4) explain the transmittance spectra for ZnO at various concentration of SnO_2 .It can be noted that (T) pattern of all deposited films Increases with increase (λ). Also from Figure (4) and Table (3) show that the transmission values of $(ZnO)_{1-x}(SnO_2)_x$ thin films at (X= (0 , 0.2, 0.4, 0.6 and 1) wt. % are (38.45 %, 32.06%,29.28%, 22.29 % and 24.26 %), respectively. in the wavelength equal to (500 nm),We observe an increase in the permeability values of ZnO films and decrease with

increased concentration. The reason for this decrease is that the structural properties of the film properties are transparent and that the variables in the permeability are better dependent on the properties of the material films [11]. The decrease of T with the increase of SnO_2 content attributed to that the addition of SnO_2 to ZnO increases the density and consequently the samples because more opaque to the incident light.

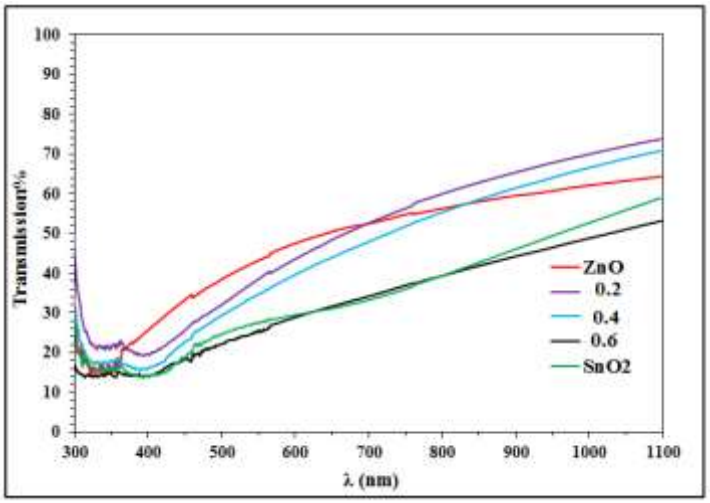

Fig (4): Transmittance spectrum as a function of λ for $(ZnO)_{1-x}(SnO_2)_x$ thin films at R T and various concentrations of SnO_2

Absorption coefficient

At the basic absorption area, the absorption factor (α) can be calculated by the following equation [12]

$$\alpha=2.303A/t \ldots\ldots\ldots\ldots (2)$$

Where(t) act the thickness and (A) is absorbance

Figure (5) appear the difference of (α) as a function of (λ) in the range from (300nm to 1100nm) at thickness (t=200nm) for concentration of x= (0 , 0.2, 0.4, 0.6 and 1) wt.% prepared at room temperature, We can view from the figure(5) and table (3) that (α) for $(ZnO)_{1-x}(SnO_2)_x$ films Increases with increase of the concentration SnO2 and values of absorption coefficient for $(ZnO)_{1-x}(SnO_2)_x$ films at (x=0 ,0.2,0.4,0.6 and 1)wt %, are

(215031cm^{-1},255944 cm^{-1},276337 cm $^{-1}$, 337746 cm $^{-1}$ and 315396 cm $^{-1}$) respectively. in the 500 nm wavelength.

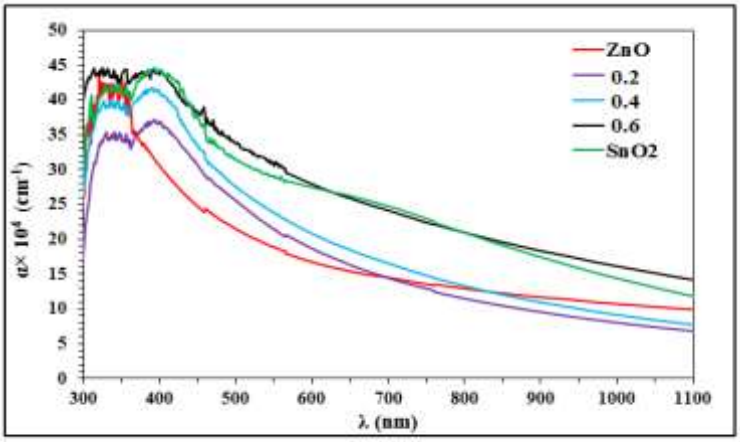

Fig (5) Absorption Coefficient Versus wavelength for ((ZnO)1-x(SnO_2)x) thin films at R T and different concentrations of SnO_2

Energy gap (E_g)

optical energy gap values for (ZnO)1-x(SnO_2)x by using the (Tauc eq) films were determined [13]

$$(\alpha h\nu) = A(h\nu - Eg)^{1/2} \quad \ldots\ldots(3)$$

Which is used to obtain the optical transition type using an $(\alpha h\nu)^2$ versus photon (hv) and the optimal linear selection. (Eg) of the portion at (αhv) 2 = 0 is appeared in Fig (6) The energy gap decreases when concentration increases ,The optical energy gap values of pure ZnO, pure SnO_2 and SnO2 doped ZnO was (2.54, 2.34, 2.33, 2.25 and 2.10)in (eV) for the concentration of SnO_2(X=0,0.2,0.4,0.6 and1) wt. % respectively. This is due to the increase of the density of localized states in the Eg , which cause a shift to lower values

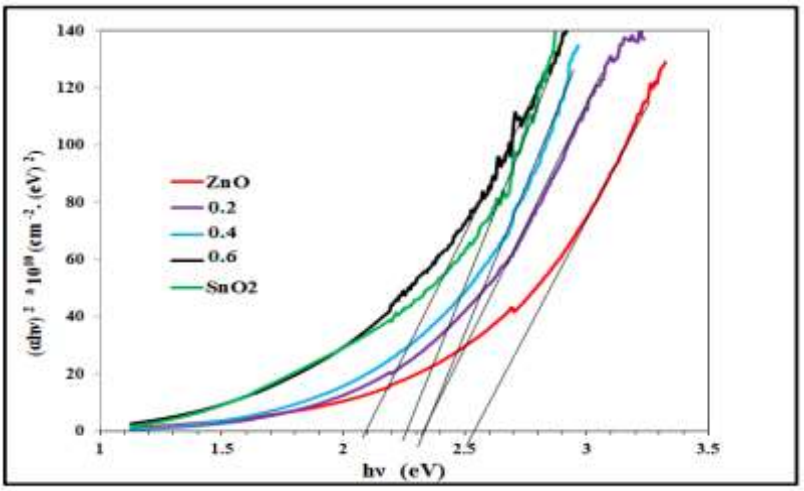

Fig (6): (αhv)2 as a function of hv for (ZnO)1-x (SnO_2)x thin films at RT and various concentrations of SnO_2

Refractive index (n) and Extinction coefficient

The complex refractive index (n *) is described by this relationship [16]

$$n^* = n - i K \quad \ldots (4)$$

Where (n *) is a complex refractive index, (n) represents the real part and (k) represents the imaginary part. We can also obtain the index refraction of samples from the following equation [16]

$$n = [(4R/(R-1)^2)-k^2]-(R+1)/(R-1)\ldots\ldots\ldots\ldots..(5)$$

Where R represents the reflectance and $k = (\alpha\lambda / 4\pi)$ is the extinction coefficient) (n) values were measured using Eq(5). The variation of (n) and the (k) with(λ) for the ZnO films at various SnO_2 concentrations is shown in Fig (7) and can observed from Figure (7) and Table (3) that the (n) decreases with increasing concentration of SnO_2 (from 1.927 to 1.738), The behavior of (k) can be ascribed to high absorption coefficient. And from Figure (8) and Table (3) it can see that the extinction coefficient increases with increasing the concentration of SnO_2 (0.856-1.256)

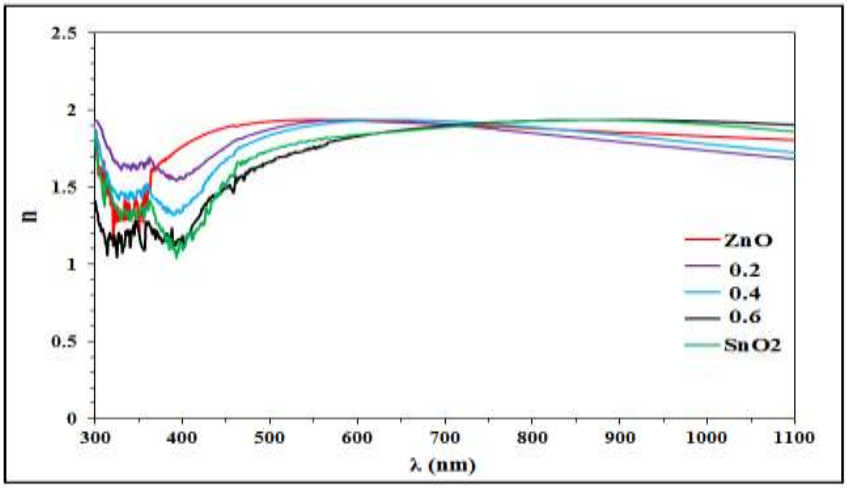

Fig (7): Refractive index as a function of λ for ((ZnO)1-x(SnO_2)x) thin films at R T and various concentrations of SnO_2

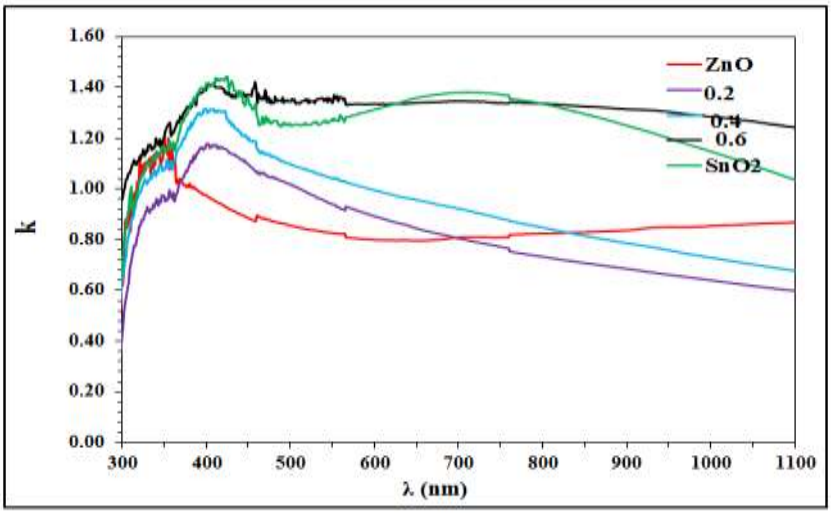

Fig (8): Extinction coefficient as a function of λ for ((ZnO)1-x(SnO_2)x) thin films at R T and various concentrations of SnO_2

Table(3) consist of ((T) for all films, (α) , (k), (n) and (Eg))in the wavelength equal to (500 nm) and with different concentration of SnO_2

X	T%	α (cm^{-1})	K	n	Eg(eV)
0	38.45	215031	0.856	1.927	2.54
0.2	32.06	255944	1.019	1.876	2.34
0.4	29.28	276337	1.100	1.836	2.33
0.6	22.29	337746	1.345	1.668	2.25
1	24.62	315396	1.256	1.738	2.10

Conclusion

In this work, pure zinc oxide films and mixed with tin oxides were deposited by pulse laser. The XRD study demonstrates that zinc oxide films have hexagonal system and polycrystalline wurtzite type.
The result of (AFM) shows that there are no cracks in the problem layer. The optical properties such as absorption and transition spectra were measured for thin films where The results show that the transmittance of the ZnO film in the visible domain reaches 34.45%. in the optical range were also calculated and found to be 2.54, 2.34, 2.33, 2.25 and 2.10 In eV for SnO_2 concentration (x=0, 0.2,0.4,0.6 and1) by weight. % Respectively.

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