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A Study the Effect of Zno Concentration and Annealing Temperature on the Structural and Optical Properties of Tio_2 Thin Films Prepared By Pulse Laser Deposition

Samar Y. AlDabagh[1], Kadhim. A. Aadim[2] , Thura tariq abbas[3]
[1]*Baghdad University, College of Science, Physics Department*
[2,3] *Baghdad University, College of Science for Women, Physics Department*

Abstract: *Nanostructure pure TiO_2 and TiO_2:ZnO thin films were synthesized via the pulse laser deposition (PLD) method. The effects of the ZnO concentration (2%,5%,7%) and annealing temperature (500°C) on structural, morphological and optical properties have been studied. XRD results showed that the pure TiO_2 films had amorphous structure at room temperature (RT) and after annealing at 500°C transformed to polycrystalline structure anatase and rutile phase. It can be see from AFM that the average grain size and roughness increases with increasing the dopant concentration of ZnO and annealing temperature. Optical properties investigation such as transmittance it found be decreases as ZnO concentrationis increased.*
Keywords*: TiO_2:ZnO thin films, X-ray diffraction, transmittance*

I. Introduction

Titanium dioxide (TiO_2) is used in a wide range of applications. It is cheap, high dielectric constant, non-toxic and chemically stable. Titanium is successfully used as implant material for dental. TiO_2 powder is used as white pigment in paint.[1] TiO_2 is a wide band semiconductor which exists in three crystallographic phases: rutile, anatase and brookite.The first two polymorphs have a tetragonal symmetry and due to their strong photocatalytic properties and stability have become materials of high scientific interest.[2] Zinc oxide is n–type semiconductor of wurtzite structure have a direct wide-band-gap semiconductor with a band gap of 3.37 eV, high excitonic binding energy (60)meV, high photoconductivity and important piezoelectric.[3] Both oxides TiO_2 and ZnO are classified as wide band-gap semiconductors and have similar band-gap energies. Titania (TiO_2) and ZnO are the two semiconductors attracting the most attention for applications in photocatalysis, gas sensors and solar cells.[4] The photocatalytic activity is based on the generation of electron/hole pairs and limited by the recombination of electron/hole pairs. A lot of methods, such as doping[5], metal modification[5]and coupling of composite semiconductors, have been investigated to decrease the recombination and increase the life time of separated electron and hole, and therefore to improve the photocatalysis properties.[5]There are many methods that can be used to prepare TiO_2 thin films with desired properties including sol–gel, sputtering, anodic oxidation, pulsed laser deposition PLD and spray pyrolysis.[9]In the present work, preparation of nanostructure TiO_2:ZnO thin films using laser ablation on glass substrates, and study the effect of ZnO concentrations (2%, 5%, 7%) and annealing temperature on the physical properties such as structural, absorption properties of TiO_2:ZnO.

Experimental work

The samples were prepared from pure TiO_2 and doped with ZnO targets films were grown by pulsed laser deposition on glass substrates kept distance of 2 cm from the TiO_2 target. The deposition was done by using a Q switched Nd:YAG laser at 1064 nm (800 shot and laser energy 900 mJ) and oxygen pressure was maintained at 5×10^{-2} mbar. All substrates were firstly cleaned in distilled water in order to remove the impurities from their surface, then cleaned in alcohol ultrasonically for 15 minutes subsequently dried prior to film deposition experiment. Then compress the mixture under 5 Tons (homemade compressor) to get the final pellet of TiO_2 pure and doped with (ZnO) of 2.5 cm diameter. The structural properties of the films were analyzed by X-ray diffraction (XRD) and Atomic Force Microscopy (AFM). The optical properties of the films were measured by a UV-VIS spectrometer in the wavelength range of (300- 1100) nm to determine the refractive index and energy gap for each sample.

II. Results And Discussion:

2.1 structural properties

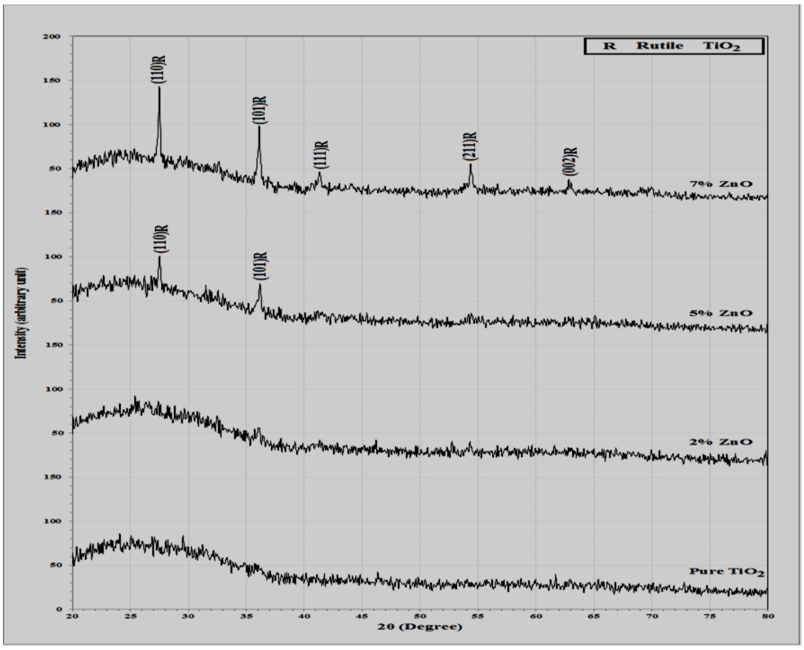
The crystal structure of pure TiO_2 and TiO_2 doped with ZnO at different concentration (2%,5%,7%) at RT and annealing temperature were investigated by XRD patterns. Figure(1-a) showed pure TiO_2 and TiO_2:ZnO (2%) are amorphous nature at RT. This nature changed to polycrystalline rutile phase of TiO_2:ZnO at

(5%, 7%) concentration. Figure (1-b) show pure TiO_2 and TiO_2 doped with different concentration of ZnO (2%,5%,7%) after annealing at 500°C for 3 hours, and it seems that the crystal structure of pure TiO_2 depend on annealing temperature, which can be transformed from amorphous phase to polycrystalline structure anatase and rutile phase identified by the (011)A,(110)R,(101)R,(111)R,(020)A,(211)R, which corresponding peaks to 2θ= (25.3°), (27.4°), (36.1°), (41.3°), (47.9°), (54.3°) respectively. When TiO_2 doped with ZnO at concentration 5% and 7% the anatase phase disappeared and rutile phase remain only and the intensity increase with the increasing of the concentration of ZnO.

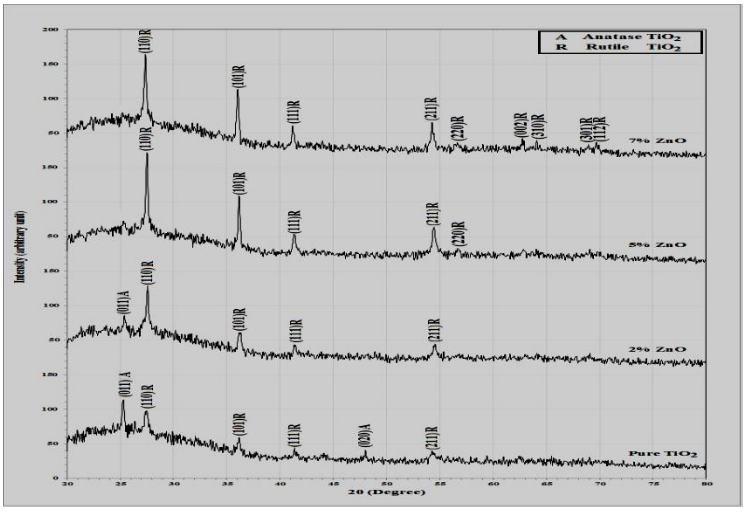
The crystalline size of deposited films were calculated using Scherrer's formula given by: [6]

G.s =$\frac{0.9\lambda}{\beta COS\theta}$……………………(1)

Where λ is the wavelength of X-ray used (1.54 A),β is the full width half maximum (FWHM) of the peak and θ is the Bragg 's angle.



Figure(1-a):XRD analysis of pure TiO_2 and TiO_2 : ZnO at different concentration (2%,5%,7%) at RT.



Figure(1-b):XRD analysis of pure TiO_2 and TiO_2: ZnO at different concentration (2%,5%,7%) at 500°C.

Table (1):The obtained result of the XRD of pure TiO_2 and TiO_2: ZnO at different concentration (2%,5%,7%) at RT.

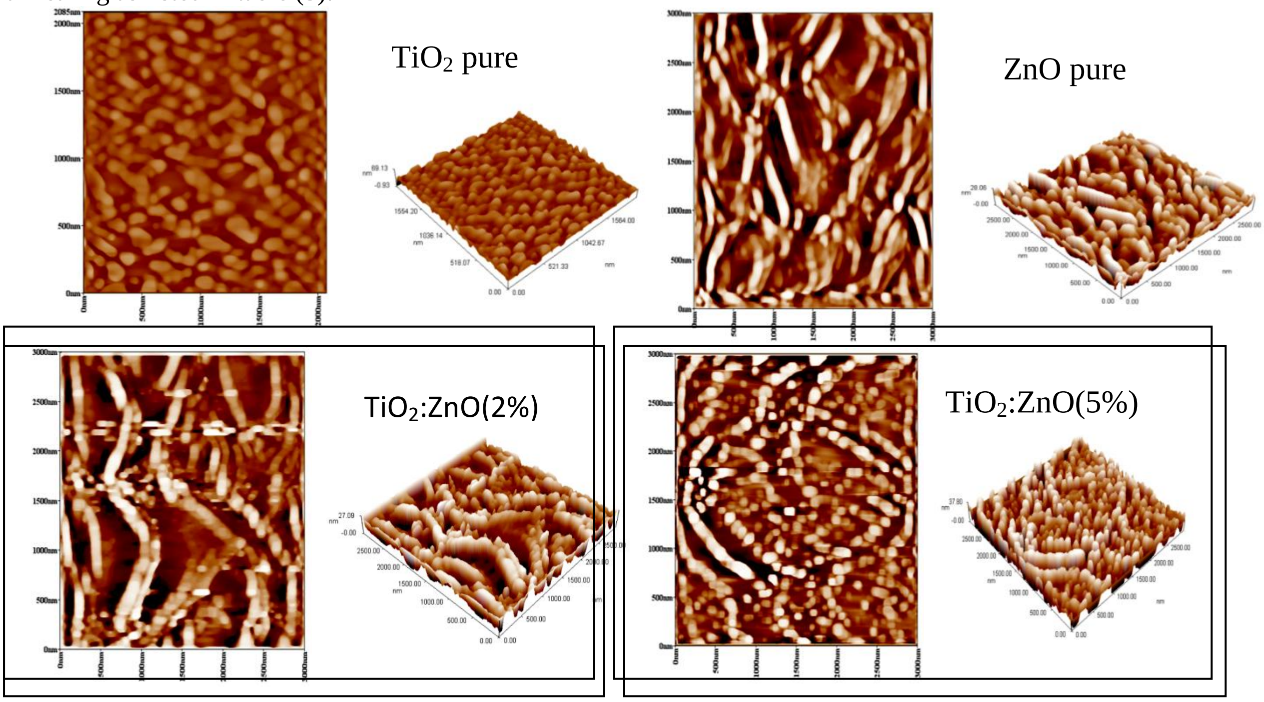
ZnO%	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std. (Å)	hkl
5	27.5068	0.4800	3.2400	17.0	3.2483	(110)
	36.1469	0.5000	2.4829	16.7	2.4871	(101)
	27.5227	0.1773	3.2382	46.1	3.2483	(110)

7	**36.1369**	**0.1866**	**2.4836**	**44.8**	**2.4871**	**(101)**
	41.3330	**0.2000**	**2.1826**	**42.5**	**2.1871**	**(111)**
	54.3680	**0.1567**	**1.6861**	**57.0**	**1.6874**	**(211)**
	62.8484	**0.1700**	**1.4775**	**54.8**	**1.4791**	**(002)**

Table (2):The obtained result of the XRD of pure TiO_2 and TiO_2: ZnO at different concentration (2%,5%,7%) at 500°C.

ZnO%	**2θ (Deg.)**	**FWHM (Deg.)**	**d_{hkl} Exp.(Å)**	**G.S (nm)**	**d_{hkl} Std.**	**hkl**
	25.3155	**0.3300**	**3.5153**	**24.7**	**3.5169**	**(011)**
	27.4901	**0.4067**	**3.2420**	**20.1**	**3.2483**	**(110)**
0	**36.1569**	**0.3800**	**2.4823**	**22.0**	**2.4871**	**(101)**
	41.3629	**0.3000**	**2.1811**	**28.3**	**2.1871**	**(111)**
	47.9858	**0.2867**	**1.8944**	**30.3**	**1.8925**	**(020)**
	54.3664	**0.4800**	**1.6862**	**18.6**	**1.6874**	**(211)**
	25.4368	**0.2933**	**3.4988**	**27.8**	**3.5169**	**(011)**
	27.5912	**0.2810**	**3.2303**	**29.1**	**3.2483**	**(110)**
2	**36.2268**	**0.3800**	**2.4777**	**22.0**	**2.4871**	**(101)**
	41.3929	**0.2800**	**2.1796**	**30.3**	**2.1871**	**(111)**
	54.5063	**0.4000**	**1.6822**	**22.3**	**1.6874**	**(211)**
	27.5354	**0.1973**	**3.2367**	**41.5**	**3.2483**	**(110)**
5	**36.1705**	**0.1925**	**2.4814**	**43.4**	**2.4871**	**(101)**
	41.3395	**0.2933**	**2.1823**	**28.9**	**2.1871**	**(111)**
	54.4339	**0.2650**	**1.6842**	**33.7**	**1.6874**	**(211)**
	56.7095	**0.3856**	**1.6219**	**23.4**	**1.6241**	**(220)**
	27.3913	**0.2714**	**3.2534**	**30.1**	**3.2483**	**(110)**
	36.0403	**0.2533**	**2.4900**	**33.0**	**2.4871**	**(101)**
	41.2130	**0.2400**	**2.1887**	**35.4**	**2.1871**	**(111)**
7	**54.2817**	**0.2573**	**1.6886**	**34.7**	**1.6874**	**(211)**
	56.6324	**0.4627**	**1.6240**	**19.5**	**1.6241**	**(220)**
	62.7249	**0.3085**	**1.4801**	**30.2**	**1.4791**	**(002)**
	64.1131	**0.2314**	**1.4513**	**40.5**	**1.4527**	**(310)**
	68.9717	**0.2314**	**1.3605**	**41.7**	**1.3599**	**(301)**
	69.7429	**0.4627**	**1.3473**	**20.9**	**1.3461**	**(112)**

The AFM images of pure TiO_2 and ZnO thin films and TiO_2:ZnO (2%,5%,7%) at room temperature shown in figure (2-a). The average grain size and roughness increases with increasing the dopant concentration of ZnO (2%,5%,7%) and after annealing at 500°C the average grain size and roughness for TiO_2 and ZnO pure and the doping increased as shown in figure (2-b). This result in good agreement with.[7] AFM study reveals that the roughness and average grain size of the film is dependent on the the dopant concentration before and after annealing as listed in table (3).



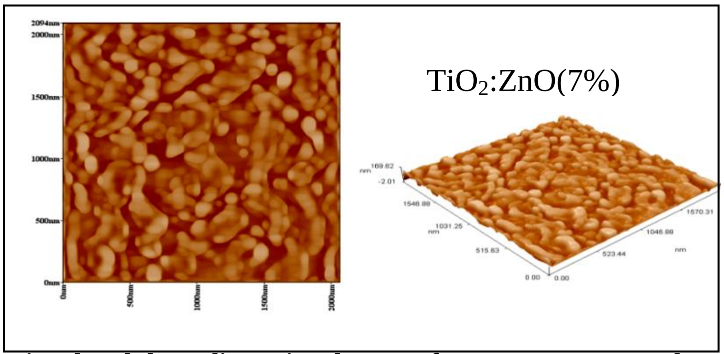


Fig (2-a):Two dimensional and three dimensional AFM of pure nanostructured and ZnO (2%, 5%, 7%) doped TiO_2 thin films at RT.

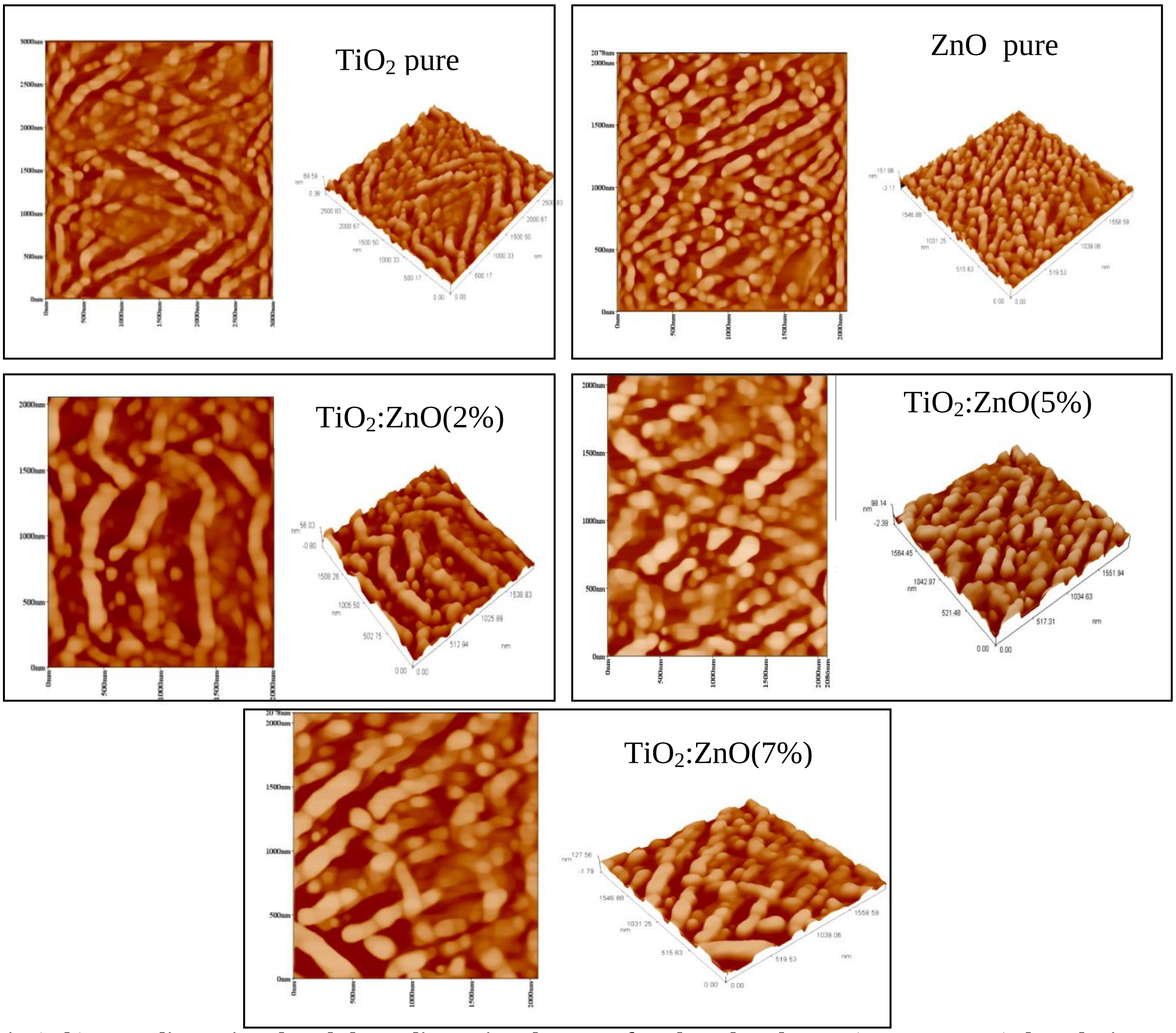


Fig (2-b):Two dimensional and three dimensional AFM of undoped and ZnO (2%, 5%, 7%) doped TiO_2 thin films at 500°C.

Table(3):Average grain size and roughness of nanostructure of undoped and ZnO (2%, 5%, 7%) doped TiO_2 thin films at RT and 500°C.

sample	average grain size (nm) at RT	RMS roughness(nm)at RT	average grain size (nm) at 500°C		RMS roughness(nm) at 500°C	
TiO_2	76.81	6.1	98.11		6.61	
ZnO	64.62	7.01	104.96		17.7	
TiO_2:ZnO(2%)	90.88	6.77	95.54		6.85	
TiO_2:ZnO(5%)	94.58	9.45	96.43		12.5	
TiO_2:ZnO(7%)	103.12	15.2	105.06		16.1	

3.2 optical properties

Figure (3-a) shows the optical transmittance of pure TiO_2 and ZnO (2%,5%,7%) doped TiO_2 thin films. It is clear that transmittance decreases as ZnO concentration is increased.

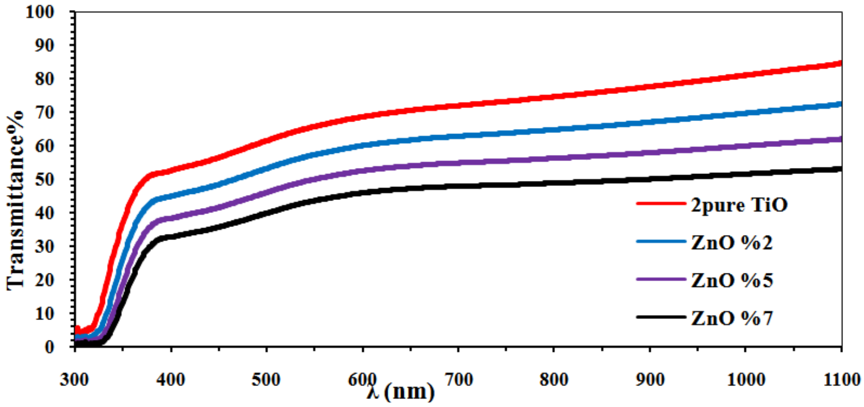


Fig (3-a):UV-VIS transmittance spectra of pure TiO_2 and TiO_2:ZnO (2%,5%,7%)thin films at RT.

Figure (3-b) shows the optical transmittance of pure TiO_2 and ZnO doped TiO_2 annealed at 500ºC. The optical transmittance increases with annealing temperature and decreases as the concentration of ZnO is increased.

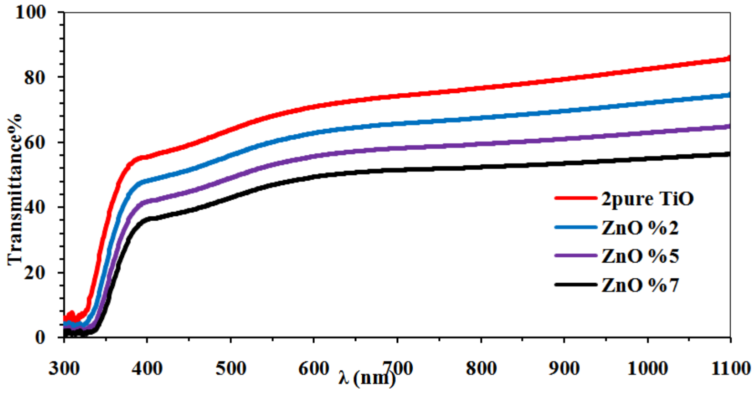


Fig (3-b) UV-VIS transmittance spectra of pure TiO_2 and TiO_2:ZnO (2%,5%,7%) thin films annealing at 500ºC.

TiO_2 has a direct band gap at room temperature as shown in figure (4-a) and the values of the band gap changes according to the preparation parameters and conditions. It can be observed that (Eg) decreased with the increasing of ZnO concentration.

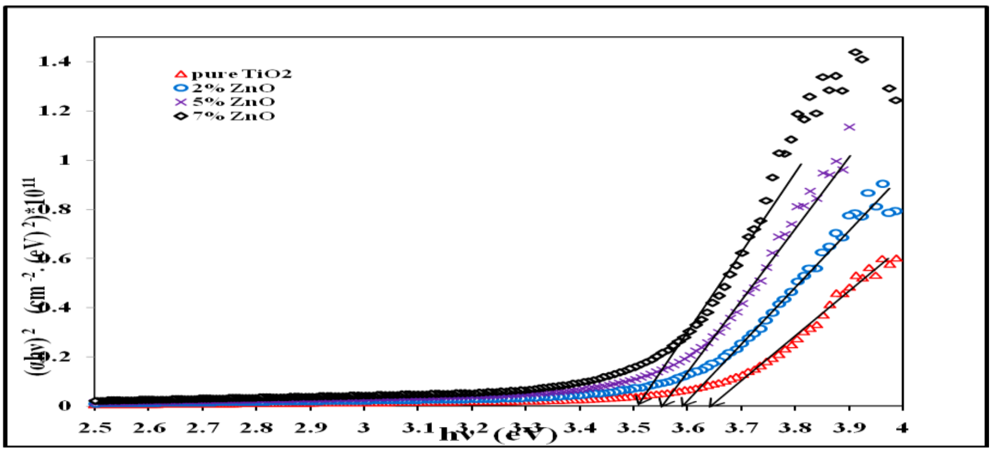


Fig (4-a) direct energy gap of pure TiO_2 and TiO_2:ZnO (2%,5%,7%) thin films at RT.

The energy band gap after annealing at 500ºC is shown in figure (4-b). It observed that E_g decreased after annealing. Can be attributed decrease energy gap to the increased size of particles in the films after annealing. These data are in good a greement with.[8]

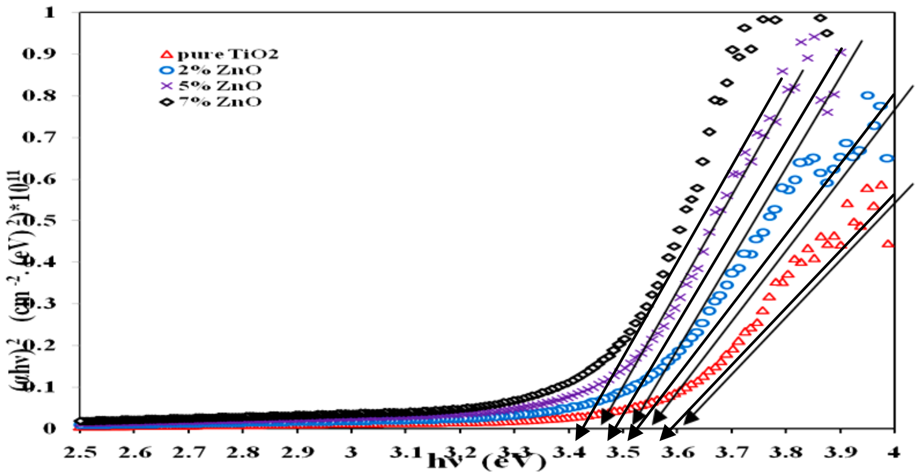


Fig (4-b)) direct energy gap of pure TiO_2 and TiO_2:ZnO (2%,5%,7%) thin films at 500ºC.

Table (4) the optical energy gap of pure TiO_2 and ZnO (2%,5%,7%) doped TiO_2 thin films at 500ºC.

Samples	Direct Eg (eV) *at RT*	Direct Eg (eV) *at 500ºC*
TiO_2	3.65	3.55
TiO_2:ZnO (2%)	3.6	3.5
TiO_2:ZnO (5%)	3.55	3.45
TiO_2:ZnO (7%)	3.5	3.4

Figures (5-a), (5-b) showed the refractive index increase at concentration ZnO (5%). The table (5) shows decrease in the refractive index with the increase in the temperature. This decrease is due to the decrease in reflectance with annealing, and the annealing impact on the morphology of the films and hence caused change in the refractive index.

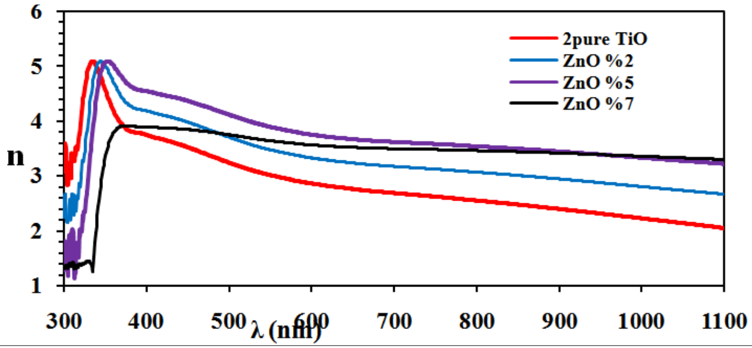


Figure (5-a)the refractive index as a function of wavelength of undoped and ZnO (2%, 5%, 7%) doped TiO_2 thin films at RT.

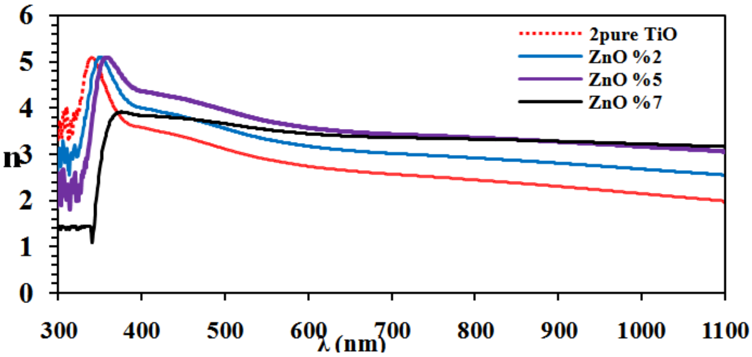


Figure (5-b)the refractive index as a function of wavelength of undoped and ZnO (2%, 5%, 7%) doped TiO_2 thin films at 500°C.

Table (5) the result of refractive index of pure TiO_2 and TiO_2:ZnO (2%,5%,7%) thin films at RT and at 500ºC.

Samples	*refractive index At RT*	*refractive index at 500ºC*
TiO_2	3.243	3.14
TiO_2:ZnO (2%)	3.709	3.1
TiO_2:ZnO (5%)	4.119	3.08
TiO_2:ZnO (7%)	3.749	3.05

III. Conclusion

All thin films nearly amorphous at room temperature turns to polycrystalline after doping with ZnO and pure TiO_2 turns to polycrystalline structure after annealing at 500ºC for 3 hours. The roughness increases with increasing the dopant concentration of ZnO and after annealing at 500°C. The optical energy gap of nanostructure TiO_2 and ZnO doped TiO_2 thin films were direct transition in the range (3.4 - 3.6) eV respectively.

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