Investigation of structural, optical and electrical properties of TiO_2 and ZnO thin films

دراسة الخواص التركيبة ، البصرية والكهربائية لاغشية اوكسيد التيتانيوم وأوكسيد الخارصين النانوية.

Samer. Y. Al-Dabag[1] Ghuson. H. Mohammed[2a] Sudad. S. Ahmed[2b] Wasan. J. Tahar[1]

[1] University of Baghdad /College of Science for Women, Department of Physics, laser and electro optics .

[2a] University of Baghdad /College of Science ,Department of Physics/ thin film.

[2b] University of Baghdad /College of Science ,Department of Physics, laser and electro optics.

Abstract

This paper reports the investigation of structural, optical and electrical properties of TiO2 and ZnO thin films. The thin films were prepared by pulsed laser deposition (PLD) method using pulsed Nd:YAG laser at 1064nm wavelength and repetition rate 6Hz. Different pulse of shot (200, 500, 800) and different thickness of TiO_2 (150, 250, 400)nm, ZnO (250, 400, 550)nm. were used at constant energy (800 m J).

Morphology of the deposits materials were studied by Atomic Force Microscopy (AFM), results indicated that all thin films have nanoscale grain size around 90 nm.

The linear optical measurements showed that nanostructure (TiO_2 and ZnO) thin films have direct energy gap.

The Hall effect measurements confirmed that the nanostructure (TiO_2 and ZnO) thin films are n-type and the charge carriers concentration (n) were increased with increasing pulse shot. Hall mobility (μ_H) decreases with the increasing of pulse shot thin films.

Key words :PLD,ZNO,TiO_2 , Al, Nd:YAG

الخلاصة :-

في هذا البحث تم ترسيب مادة (TiO_2 , ZnO) بطريقة (ترسيب الليزر النبضي) باستخدام ليزر النيدميوم ياك النبضي ذي الطول الموجي 1064nm بمعدل تكرار 6Hz . استخدمت نبضات (200, 500, 800)ns عند طاقة ثابتة 800mJ

طبوغرافية السطح للمادة المترسبة تم دراستها ، حيث وجد من فحص مجهر القوه الذرية (AFM) أن جميع الاغشيه ألرقيقه ذات حجم حبيبي نانوي حوالي 90 نانومتر .

تم دراسة الخواص البصريه الخطية حيث اظهرت القياسات ان اغشية المواد النانويه (TiO_2 , ZnO) ذات فجوة طاقه مباشره ووجد انها تقل بزياده عدد النبضات المسلطه على الاغشية، كما وجد ان مادة الTiO_2كانت ذات امتصاصيه اعلى من مادة ZnO.

اظهرت القياسات للخواص الكهربائيه للاغشيه النانويه الرقيقه، من خلال حساب تاثير هول ان الغشاء من نوع n وان كثافة حاملات الشحنه تزداد بزيادة عدد النبضات وتحركية هول تقل بوضوح مع زيادة عدد النبضات .

1-1 Introduction

The metal oxides for beneficial many application not only because of its high mobility for better charge transport, but also due to its various nanostructures applied for the order heterojunction, which can efficiently improve the exciton dissociation. Therefore the performance of device can be improved significantly with the application of metal oxides(1).

The metal oxides such as TiO_2 and ZnO with a distinct advantage of controllable nanostructure(2) are commonly used in many application such as solar cell nanostructure metal oxides are first fabricated via various methods, . Since the mobilities of metal oxides are significantly higher than the organic materials (3).

In recent years, nano zinc oxide has found wide ranging applications in various areas due to its unique and superior physical and chemical properties compared with bulk ZnO(4), (ZnO is an n-typesemi-conductor(5)). The large specific surface area, high pore volume, nano structured properties, low cost and low toxicity of nano ZnO(4).

Both of TiO_2 and ZnO are used in solar cell because of their similar optical and electrical properties. These two metal oxides are transparent to visible light, due to their respective wide band gaps of 3.2 eV and 3.37 eV, only absorbing in UV range of solar light. Their high electron affinity, which stems from the position of their conduction bands, allows them to match with the Lowest Unoccupied Molecular Orbital (LUMO) of almost all organic semiconductors. This high exciton binding energy in TiO_2/ZnO-organic photovoltaic device allows efficient exciton emission at room temperature. In general the mobility of metal oxides is much higher than of the organic semiconductor. (6,7)

In this work ,we report on the growth of (TIO_2 :ZnO)deposit by PLD method using Nd:YAG laser using pulsed Nd:YAG laser at 1064nm wavelength and repetition rate 6Hz . The deposits were characterized by AFM to observe the surface structure ,Uv-visible to investigate the optical properties and hall effect to examined the electrical properties of the films

1-2 Experimental Work

During this work pulse laser deposition (PLD) is used to prepare TiO_2 and ZnO nanoparticals. The experimental setup of PLD-system consist of laser source and deposition chamber which include inside it the target, the substrate and the vacuum system

- **Laser Source**

Nd: YAG Laser was used for the deposition of TiO_2 and ZnO nanopartical at different pulse of shot (200, 500, 800) mJ and (energy, frequency, wavelength)constant at each pulse: = 800mJ, = 6Hz, = 1064nm respectively

- **Target preparation**

TiO_2 and ZnO powder from (Dr. Zuhair/ P.H.D Genetic Engineering ND Bio Technology/ AL-BASHEER for laboratory materials/ Baghdad/ Iraq) with high purity 99.9 % powder was pressed under 5 ton as show in figure (1)

Figure (1): The target before and after being ablated by the laser(2.5 cm diameter and 0.4 cm thickness)

- **Substrate preparation**

substrates were used for depositing thin films by laser ablation. These are glass plates. glass slides of 3 x 2 cm^2 area were used in this work.

- **Electrodes Deposition**

Aluminum electrodes were evaporated on the surface of TiO_2 and ZnO thin films using thermal evaporation tequipment through a mask giving sensitive area as illustrated in figure (2)

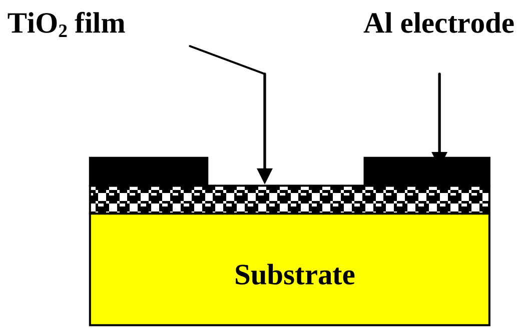


Figure (2): Al electrodes deposited on the surface of TiO_2

Characterization Measurements

The surface roughness and topography of deposited thin films are studied by (AFM) Atomic Force Microscopy. The optical features of the films were investigated by UV-Visible spectroscopy and the electrical testing of the film were investigated by hall effect

1-3 Result and desiccation

1-3-1 Structure measurement
1-3-1-a Morphology Analysis :

The surface morphology of the TiO_2 and ZnO nanoparticals was investigated using atomic force microscopy (AFM). The value of roughness and grain size were calculated from the height values in AFM image using the commercial software.

Figure (3-1A), (3-1B), (3-1C), (3-2A), (3-2B) and (3-2C) show two-dimensional and three-dimensional of (AFM) images of TiO_2 and ZnO thin films deposited at various pulse of shot(200, 500, 800)ns (respectively. Average grain size of the particles is in nanoscale . Average grain size and surface roughness values were listed in Table (1) . It can be noticed that the average grain size and roughness increase with increasing of No. of pulse because of increasing the thickness of the film and this is can be explain to create the localized state in the structure of the film.

Table (1): *Grain size and surface roughness of nanostructure TiO_2 and ZnO nanoparticals at different pulse of shot.*

No. of shot	*Average grain size (nm) (TiO_2)*	*Average grain size (nm) (ZnO)*	*Roughness (nm) (TiO_2)*	*Roughness (nm) (ZnO)*
200	**93.57**	**94.15**	**3.61**	**2.11**
500	**95.66**	**96.75**	**5.02**	**3.44**
800	**97.48**	**100**	**8.89**	**7.34**

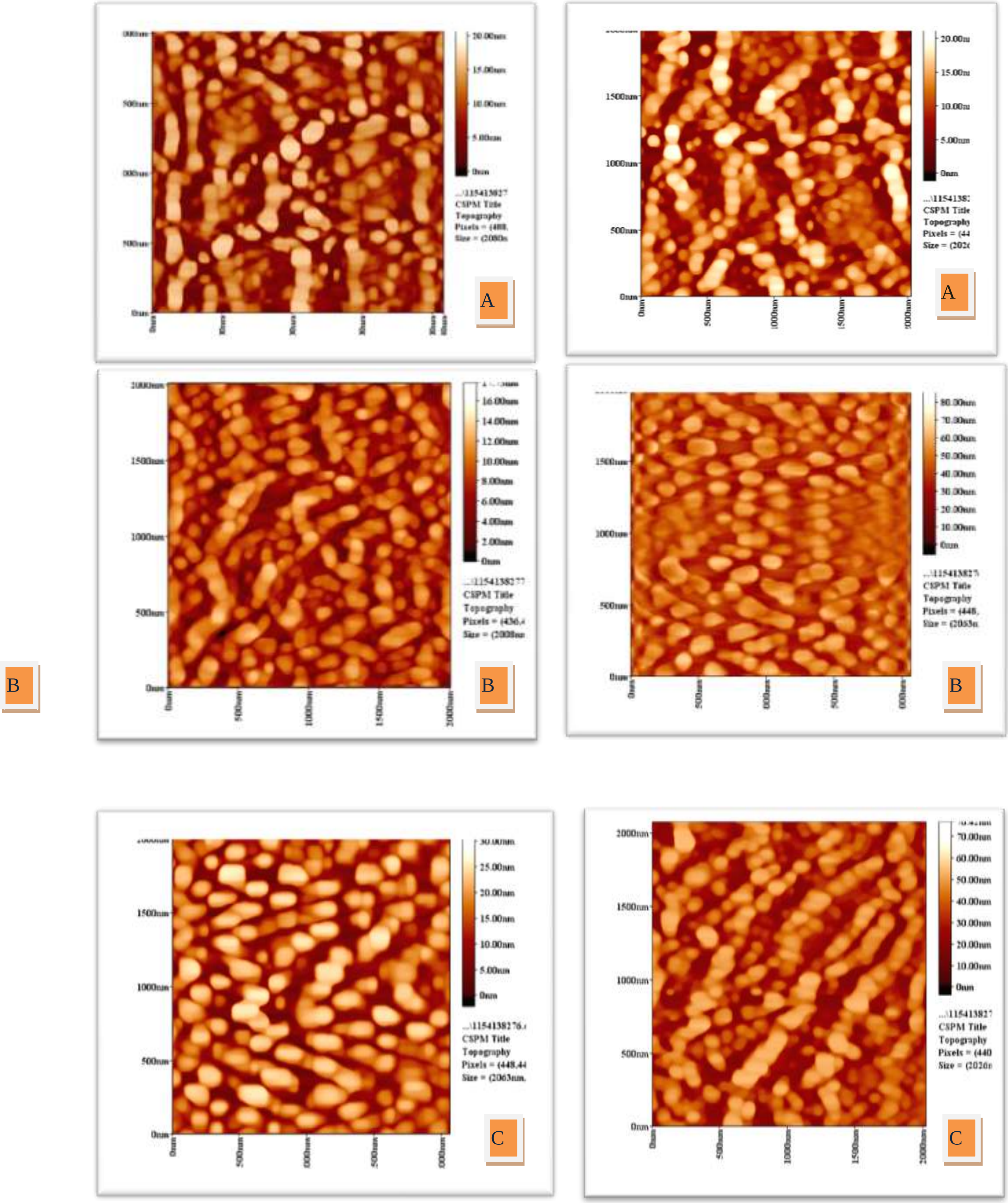
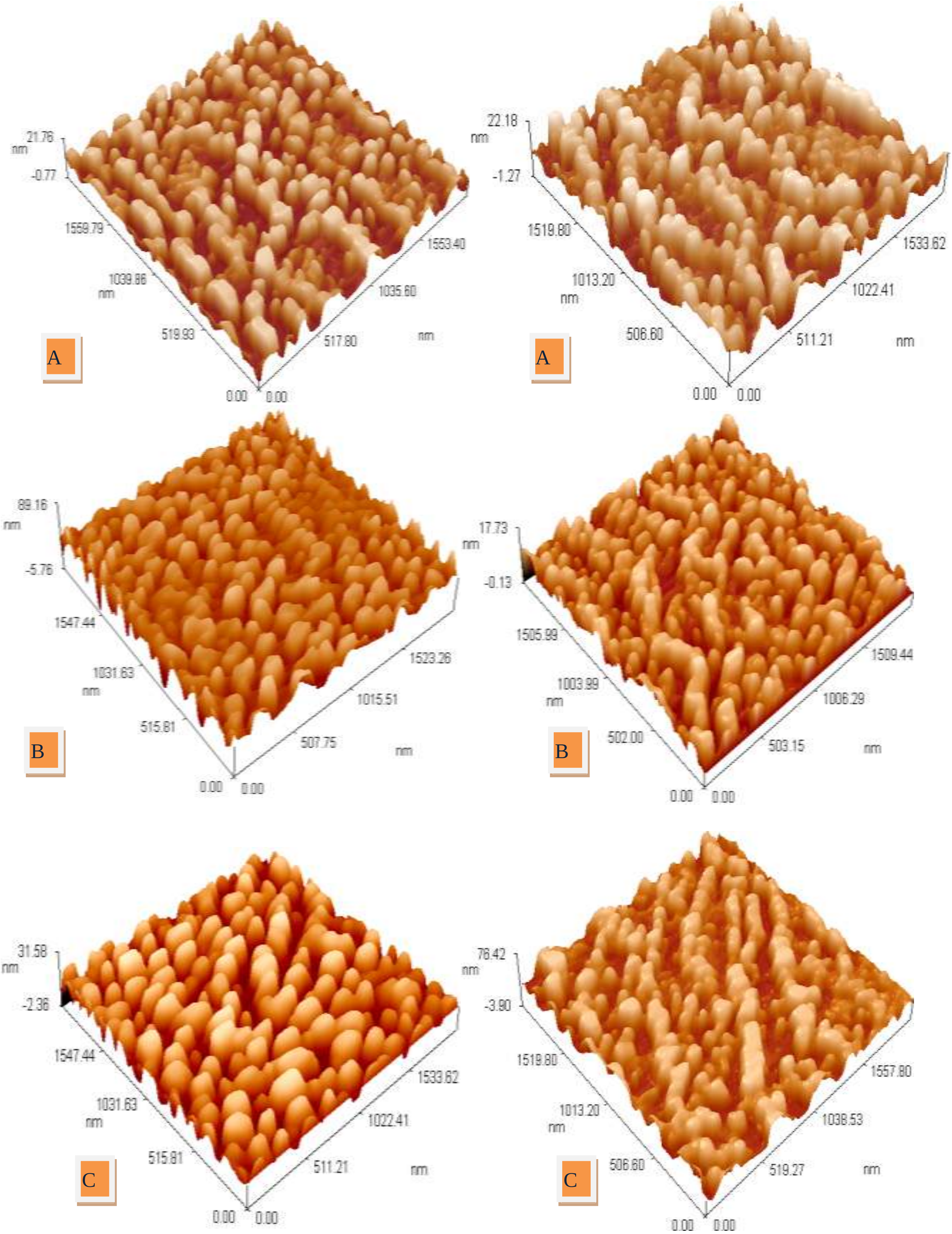


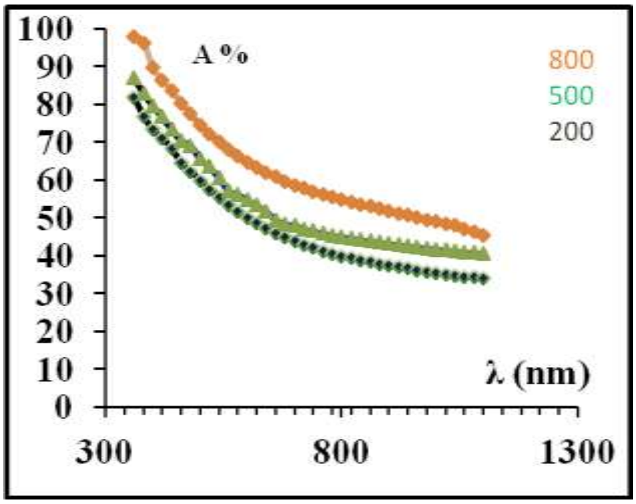
Figure (3-1): Two-dimensional AFM of images of TiO_2 (left) and ZnO (right) films deposited on galas plate with different pulse of shot {A(200), B(500), C(800)}.



Figure(3-2) : Three-dimensional atomic force microscopy images of nanostructure **TiO_2 (left) and ZnO (right) films deposited on galas plate with different pulse of shot {A(200), B(500), C(800)}**

1-3-2 Optical measurement
1-3-2-1 Absorbance spectrum:-

Figure (4) shows absorbance spectra for nanostructure (TiO_2 and ZnO) nanoparticals at different pulse of shot as a function of wavelength in the rang (300-1100). It can be observed that when the pulse of shot of the film increases; the absorption value is also increases because in the case of thicker film, more atoms are present in the film so more states will be available for the photons to be absorbed. At visible light region, the strong photo-absorption is presented in the wavelength 330 nm at each pulse.



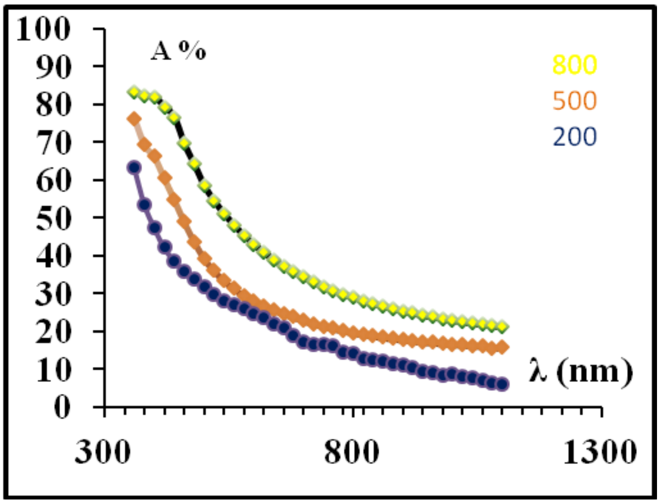
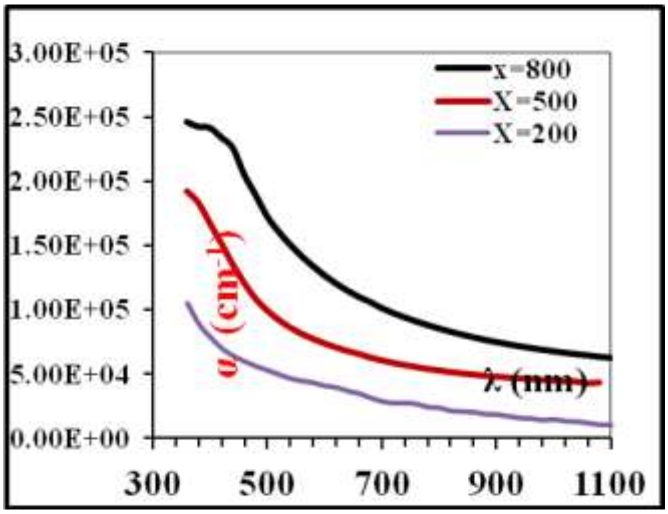


Figure (4) shows absorbance spectra for nanostructure (TiO_2(left) and ZnO (right)) thin films at different pulse of shot (200, 500, 800).

1-3-2-2 Absorption Coefficient (α):-

Figure (5) show the variation of (α) with wavelength (λ) for (TiO_2 and ZnO) nanoparticals. From this figure, it can be seen that the absorption coefficient (α) increases with increasing pulse of shot for investigated thin films.



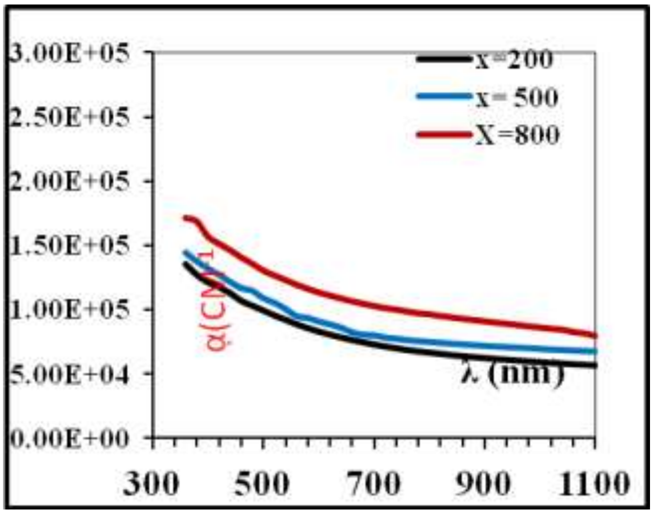


Figure (5): shows Absorption Coefficient for nanostructure (TiO_2(left) and ZnO (right)) thin films at different pulse of shot (200, 500, 800).

1-3-2-3 The Optical Energy Gap (E_g):-

The value optical energy gap values (Eg) for (TiO_2 and ZnO) nanoparticale have been determined using Tauce. A plot the relation $(\alpha h\nu)^2$ versus photon energy (hν) and selecting the optimum linear part. The energy gap decreased with increasing pulse of shot of thin films. This is due to the increase the thickness of the films leads to increase of the density of localized states in the Eg which cause a shift the Eg to the lower values as shown in figure (6).

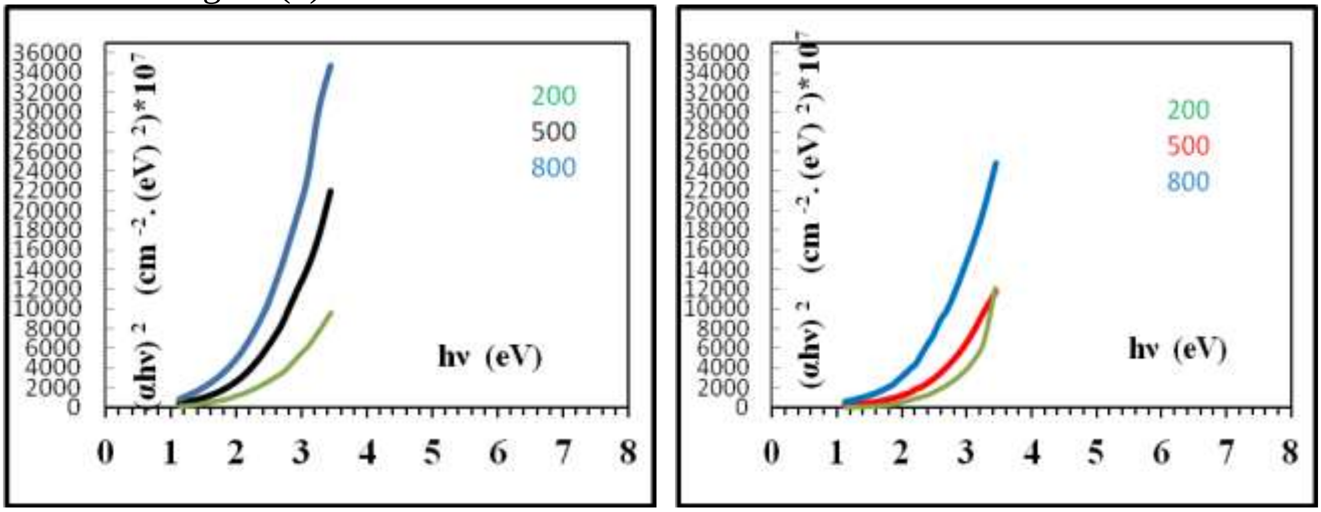


Figure (6): $(\alpha h\nu)^2$ as function of energy photon for different pulse of shot nanostructure(TiO_2(left) and ZnO (right)) thin films.

1-3-2-4 Optical Constants:

1-3-2-4-a Extinction Coefficient (K):-

Figure (7) illustrates variation of (K) as a function of wavelength for (TiO_2 and ZnO) nanoparticals. As shown in this figure that the variation of K versus λ is not systematic. The fall and rise in TiO_2 while ZnO the rise and fall in the extinction coefficient are due to the variation of the absorbance, with λ increasing. It is clear that the value of K increases with increasing No. of pulse as the same behaviors of α. According to eq. $K= \alpha\lambda/4\pi$.

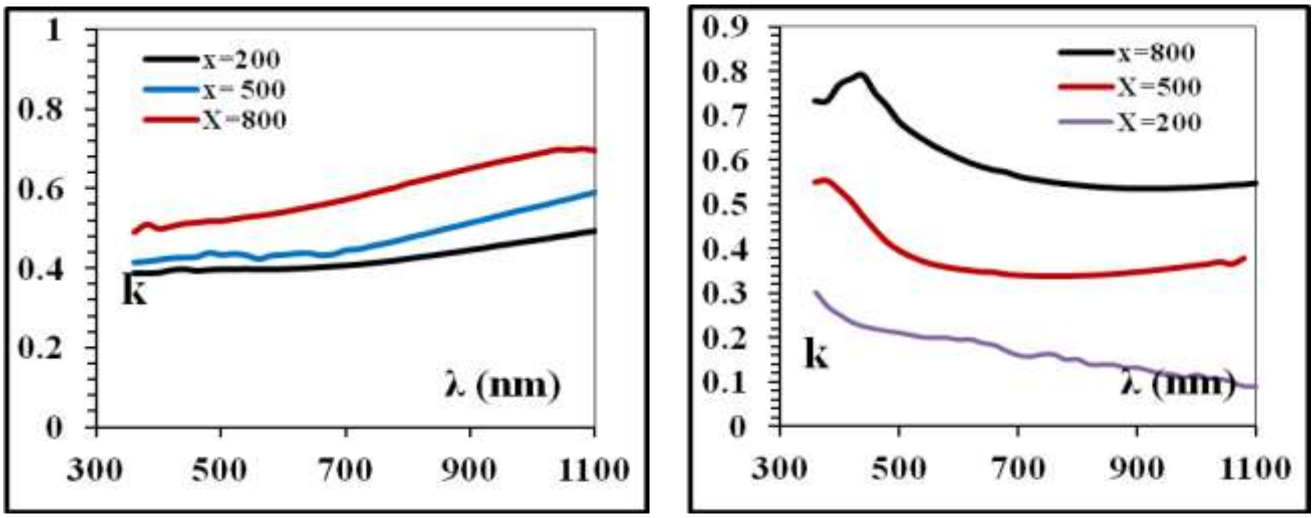


Figure (7) :Extinction coefficient as wavelength for different pulse of shot of nanostructure (TiO_2(left) and ZnO (right)) thin films

1-3-2-4-b Refractive Index (n) :-

The variation of n as a function of wavelength for nanostructure (TiO_2 and ZnO) nanoparticals at different λ as shown in figure (8). This can be explained that on the basis of that increasing the No. of pulse leads to increase the thickness of film and the make the film dense (high the more packing density) which in turn decrees propagation of velocity of light.

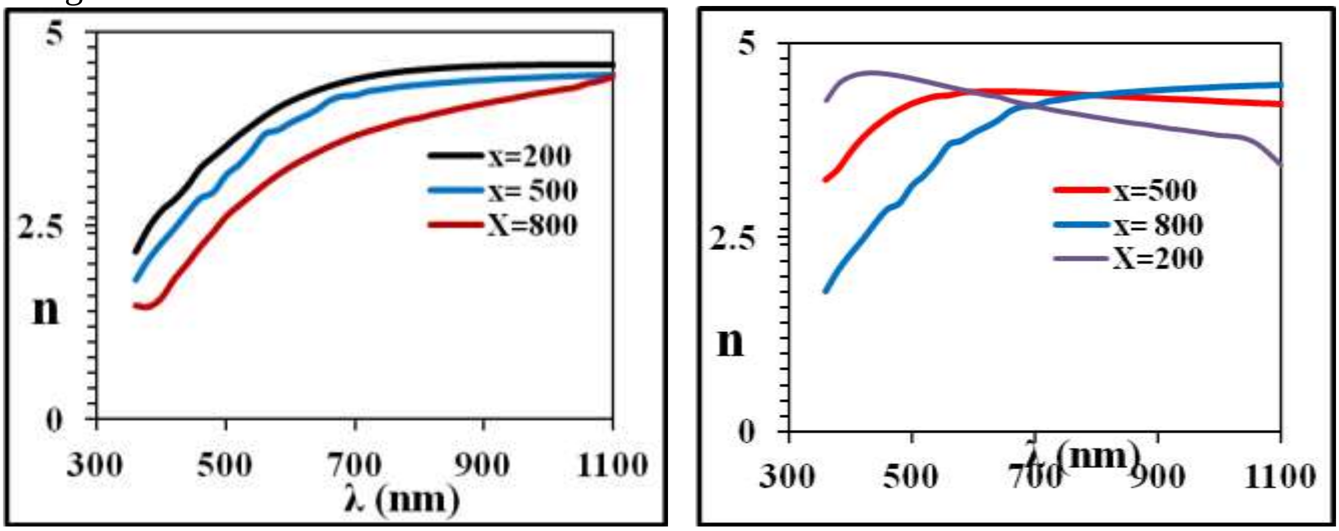


Figure (8): Refractive index as function of wavelength for different pulse of shot of nanostructure (TiO_2(left) and ZnO (right)) thin films

1-3-3 Electrical measurement

1-3-3-1 Hall Effect Measurements:-

The Hall measurements is show in table (2) that includes Hall mobility, carrier type and concentration for nanostructure (TiO_2 and ZnO) thin films at different pulse of shot were measured from Hall coefficient (R_H) data and the conductivity.

Hall measurements show that the nanostructure (TiO_2 and ZnO) thin films are n-type i.e, the conduction is dominated by electron. The n_H was calculated by using the equation $\frac{(1)}{q \, x \, R_H}$. Were the q electron charge. The carriers concentration was increased with increasing of pulse of shot. It is also found that the mobility decreased with the increasing pulse of shot of thin films due to increase the carriers concentration.

Table (2) : Hall effect measurements of (TiO_2).

NO. Of shot	$\sigma_H x10^{-6}$ $(\Omega.cm)^{-1}$	$R_H\ x10^{10}$ (cm^2/C)	n_H (cm^{-2}) $x10^{11}$	μ_H $(cm^2/V.s)$ $X\ 10^2$	*Type of conductance*
200	1. 062	2.234	27.97	6.032	n-type
500	2.437	1.893	33.01	4.359	n-type
800	7.657	1.396	44.77	2.636	n-type

Table (3) : Hall effect measurements of (ZnO).

NO. Of shot	σ_Hx10^{-6} $(\Omega.cm)^{-1}$	R_H x10^{10} (cm^2/C)	n_H (cm^{-2}) $\times10^{11}$	μ_H $(cm^2/V.s)$ X 10^2	Type of conductance
200	1.539	6.256	9.99	4.169	n-type
500	2.383	3.580	17.4	3.053	n-type
800	4.251	1.774	35.2	1.899	n-type

Conclusion:

All thin films have grain sizes of the particles around 90 nm. The energy gap (Eg) of nanostructure (TiO_2 and ZnO) thin films were direct transition in the range (3.1 and 3.2) eV respectively. The absorption of TiO_2 is better than the ZnO thin films .Nanostructure (TiO_2 and ZnO) thin films were n-type from hall effect measurements.

References:-

1- T. Tachikawa, M. Fujitsuka, and T. Majima, *"Mechanistic insight into the TiO_2 photocatalytic reactions: design of new photocatalysts"*. The Journal of Physical Chemistry C, 111(14): p. 5259-5275. 2007.

2- L. Bozano, "*Temperature-and field-dependent electron and hole mobilities in polymer light-emitting diodes*". Applied Physics Letters, Vol. 74: p. 1132, 1999.

3- A. Arango, S. Carter, and P. Brock, "*Charge transfer in photovoltaics consisting of interpenetrating networks of conjugated polymer and TiO_2 nanoparticles*". Applied Physics Letters, Vol. 74, p. 1698, 1999.

4- G. Hamid Reza, S. Mahboobeh, S. Mohammad Ali, *"Synthesis of ZnO Nanoparticles by Spray Pyrolysis Method"*, Iran. J. Chem. Chem. Eng, Vol. 30 , No. 1, 2011.

5- S. Turner, S. M. F. Tavernier, G. Huyberechts, E. Biermans, S. Bals and K. J. Batenburg, "*Assisted spray pyrolysis production and characterization of ZnO nanoparticles with narrow size distribution*" J Nanopart Res, Vol. 12, p :615–622, 2010.

6- M. Lung, Y. Kuin, W. Chung, H. Yang, T. Fang and T. Chin, *"Effects of Post annealing on the Polymer Light-Emitting Devices PLED*", Japanese Journal of Applied Physics, Vol. 44, No. 10, pp: 7482-7484, 2005.

7- D. Olson, "*Hybrid photovoltaic devices of polymer and ZnO nanofiber composites Thin Solid Films*", Vol. 496, No. 1, pp. 26-29, 2006.