Effect Adding PVA Polymer on Structural and Optical Properties of TiO_2 Thin Films

Arwa Fadil Saleh*, Ahmed Mousa Jaffar*, Najim A. Samoom** and Marwa Wailed Mahmmod**
* Department of Physics, College of Science, Al- Mustansiriyah University, Baghdad-Iraq.
** Iraqi Ministry of Sciences and Technology.
E-mail: ahah1986_12_14@yahoo.com.

Abstract

Thin films of titanium dioxide TiO_2 pure and TiO_2:PVA polymer were prepared using chemical spray pyrolysis technique on glass substrate preheated at (350 °C) for TiO_2 pure, and at (160 °C) for TiO_2:PVA. with spray rate 3sec./1min, and thickness (250nm). The investigation of (XRD) indicates that structural of TiO_2 pure and TiO_2: PVA thin films they are polycrystalline and XRD investigation is anatase titanium dioxide, intensity of <101> is more than the intensity of < ٠٠٤ >, <200> and <105> for TiO_2 and TiO_2:PVA thin films. The optical properties measurement explain the effect of adding PVA on Transmittance, absorptance, refractive index, absorption coefficient and electronic transitions of prepared thin films. and their results observed that filling of PVA caused increase in optical properties generally.

Keywords: titanium dioxide TiO_2, chemical spray pyrolysis, PVA, optical and structural properties, thin films.

Introduction

Recently conjugated polymers (cps) and inorganic compounds have been intensively investigated for the applications devices as light emitting diodes, photodiodes, sensor smart microelectronic and photovoltaic (cells) [1,2,3]. TiO_2 have the outstanding proportion of high refractive index (N2.5), excellent transmittance in visible as well as high electrical and chemical stability. It has been studied extensively for using in optoelectronic device [4,5] TiO_2 was used as electron accepting material because of its non-toxic and abundance availability to indentify physical and structural properties of semiconductor material, the scope of thin films has enabled this opportunity to study semiconductors through the preparation of films [6], because of easily breaking the thin film which is does not exceed only microns thick it is deposited on certain substrate ,such as glass, silicon ,and alumina[7]. TiO_2 is found naturally as white material, in three forms of crystalline, Rutile (tetragonal), Anatase (tetragonal), and Brokite (orthorhombic)[8], TiO_2 films can be prepared by different techniques, such as thermal evaporation in vacuum deposition (TEVD), chemical vapor deposition (CVD), pulse laser deposition (PLD) chemical spray pyrolysis deposition (CSPD) and other method[9,10,11]. Polyvinyl Alcohol (PVA) is a white and granular, it is soluble in hot water but insoluble in cold water and common organic solvents for many applications[12], this polymer chose in this research because of its relative ability for preheating (comparing with other polymers) to deposited on glass. Polyvinyl Alcohol is prepared in water solutions on evaporation of water, transparent films are formed which have high tensile strength and tear resistance[6], PVA polymer has a melting point of 180°C[13] and it has a molecular weights (26,300, 72,000 and 30,000) g/mol[14]. The aim of this research is study adding PVA polymer on some structural and optical properties of TiO_2 thin films which prepared by chemical spray pyrolysis technique.

Experimental Work

TiO_2 were prepared by chemical spray pyrolysis technique, which spraying an aqueous solution of titanium chloride $TiCl_3$, which prepared with (0.1 ml/ mol) by dissolving in distilled water (50 ml) of (H_2O), then the resulting solution was sprayed on clean preheated glass substrate at (350°C). TiO_2 thin films were formed according to equation[15]:

$$2TiCl_3 + H_2O \rightarrow Ti(OH)_2Cl_2 + TiCl_4$$

$$Ti(OH)_2Cl_2 \rightarrow \downarrow TiO_2 + \uparrow 2HCl \text{ .... (1)}$$

The resulting films were transparent, white yellowish coulor, stable free from pen holes and have good adhesive property .measured by Two method weight and micro balance. The selected thickness were (250nm).

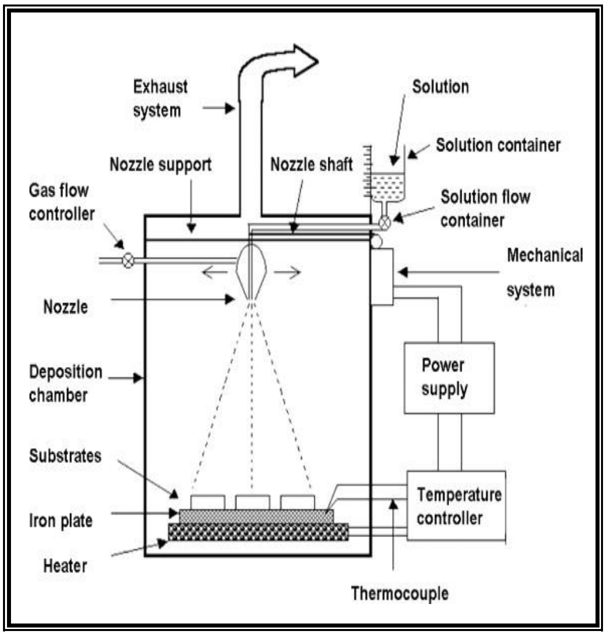


Fig.(1) Equipments of chemical spray pyrolysis system.

To prepare titanium dioxide doped polymer (poly vinyl alcohol) is added (0.065 g) of PVA to the distilled water and they solves exposure solution to heat with constant stirring and after confirmation of soluble polymer is added to the solution titanium chlorides $TiCl_3$ record advance and then sprayed on the slides glass and degree temperature 160 °C producing TiO_2:PVA with same thickness (250 nm).

Results and Discussions

A. XRD analysis: The crystalline structure for TiO_2 and TiO_2: PVA can be recognized by studying the phase of (XRD) for that material, when a beam of (XRD) from mono wavelength incident on film surface, will exhibit peaks on limit angels for each material because of reflecting of Bragg on parallel crystalline surface. XRD instrument is from type (Shimadzu 6000) made in Japan, with the following specifications are Target is Cuk_{α}, Wavelength is 1.5406 A, Current is 30 (mA.) and Voltage is (40 KV.). The XRD find that structural of TiO_2 thin film it is polycrystalline and XRD investigation is anatase titanium dioxide, intensity of <101> is more than the intensity of <٠٠٤ >,< 200> and <105> which agrees with (ASTM) card, for TiO_2 and TiO_2 :PVA, as shown in Fig.(2).

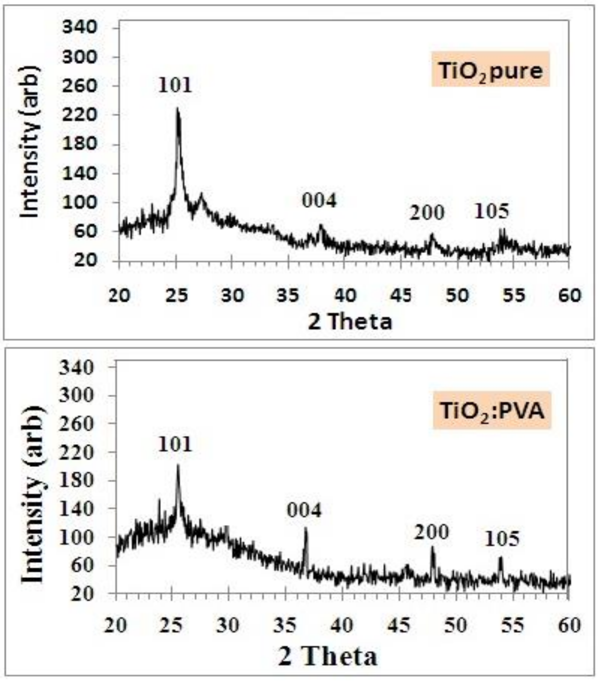


Fig.(2) XRD pattern of TiO_2 pure and TiO_2:PVA thin films.

Lattice constancies (a) and (c) can calculate from the following equation:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \text{ .... (2)}$$

XRD pattern is observed characteristics diffraction peaks corresponding to the <101>, <004>, <200> and <105>The values which measured by XRD instrument of diffraction angle (2θ), interplaner spacing (d) and Full Width at Half Maximum (FWHM) are shown in Table (1) which it emerged adding PVA polymer enhanced the structural properties of TiO_2 thin films that means the degree of crystalline increases because the molecules of TiO_2 come close together.

Table (1)
Some structural properties for TiO_2 pure and TiO_2:PVA thin films.

substrate	hkl	d A°	2θ	FWHM (β)	$D_{ave.}$ A°	a A°	c A°
TiO_2 pure	101 004 200	3.52125 2.37769 1.89835	25.2721 37.8063 47.8792	0.9233 0.5917 0.7000	1.5723	3.7906	9.5107
TiO_2:PVA	101 004 200 105	3.49702 2.47889 1.87732 1.69990	25.4502 36.2081 48.4497 53.8501	0.1636 0.1962 0.1083 0.1150	8.5829	3.7172	9.9155

B. Optical properties

(1) Transmittance and Absoptance

The transmittance and absorptance of prepared films were measured using (UV-1650PC Shimadzu software 1700 1650, UV-Visible recording Spectrophotometer), (Phillips), Japanese company in the wavelength range (300-850 nm), it is found the transmittance decreasing with add polymer that behavior is vice versa with absorpance behavior as in Fig.(3), which means the PVA polymer enhancement the TiO_2 thin films absorptance, this attributed that when adding PVA to TiO_2 solutions these molecules fills the vacancies between polymer chains.

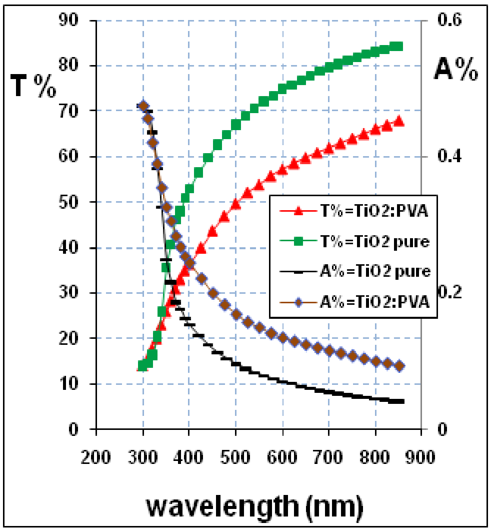


Fig. (3) Transmittance and absorptance of TiO_2 pure, TiO_2:PVA thin films.

(2) Absorption coefficient (α)

The absorption coefficient (α) of thin films prepared was calculated in the fundamental absorption region from the relation [7]:

$$\alpha = 2.303\frac{A}{t} \quad \text{...} (3)$$

Where: A : absorptance of the thin film.
t : thickness of thin film, which is 250 nm.

Fig.(4) shows the relation of absorption coefficient as a function of incident photon energy for TiO_2 thin films. The figure shows the high variation. Also we can evidently see that TiO_2 thin films have high value of absorption coefficient ($\alpha > 10^4$ cm^{-1}) which leads to increasing the probability of occurrence direct transitions. From the same figure we can notice an increasing in absorption coefficient when we add PVA. This is due to the formation of localized levels near the edge of connection, that means this decreasing could be attributed to the changes in the particle size distribution function of formed thin films.

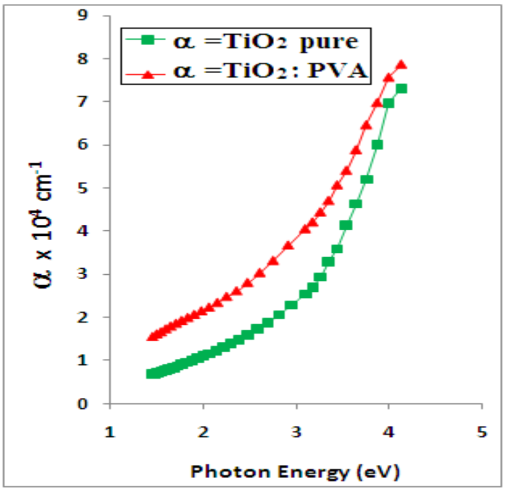


Fig.(4) Absorption coefficient of TiO_2 pure, TiO_2:PVA thin films.

(3) Refractive index (n)

The refractive index (n) of the prepared thin films was calculated according to the following equation [10].

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \quad \text{...} (4)$$

Where R: reflectance of thin film.

Fig.(5) shows the variation of refractive index (n) with photon energy of the prepared thin films. The increase may be attributed to higher packing density and the changes in the particle size distribution function of TiO_2 structural, this the enhancement of growth crystalline this attributed to the molecules of TiO_2 come close together when add PVA polymer[3,6].

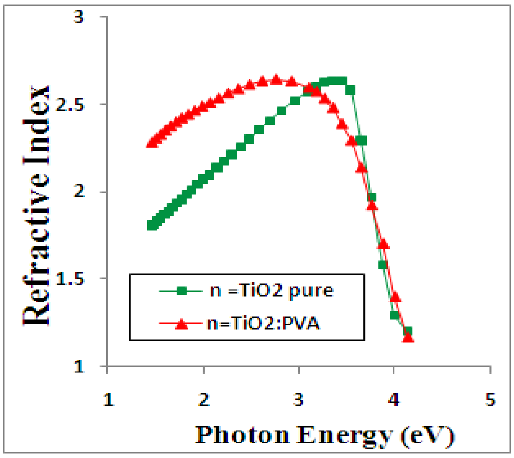


Fig. (5) Refractive Index of TiO_2 pure, TiO_2:PVA thin films.

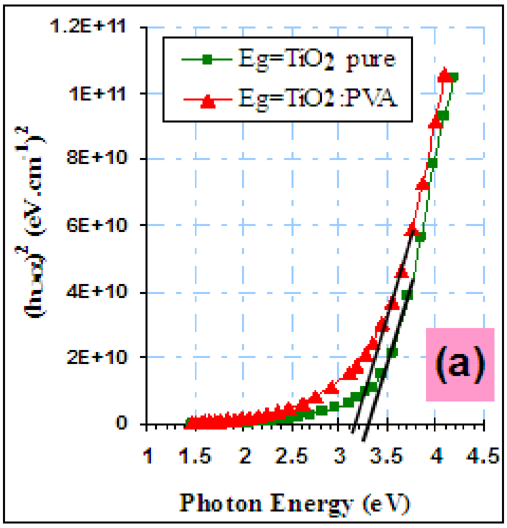
(4) Energy gap (E_g)

All electronic transitions for the prepared thin films were studied, the direct allowed energy gap in the fundamental absorption region of TiO_2 thin films was calculated from relation: [16]

$$\alpha h v = B\left(h v - E_g\right)^r \quad ....(5)$$

Where:
hυ: photon energy.
E_g: direct allowed energy photon.
B: constant depends on the type of transition.
r: exponential constant, its value depended on type of transition,
r =1/2 for the allowed direct transition.
r =3/2 for the forbidden direct transition.

Fig.(6-a) shows the relation of $(\alpha h\upsilon)^2$ against photon energy, from straight line obtained at high photon energy the direct allowed energy gap could be determined which was equal (3.195eV) at thickness (250nm), and Fig.(6-b) shows direct forbidden energy gap equal (3.052eV). The increase may be attributed to the improvement of growth crystalline that leads to crystallinity of anatase phase[17].



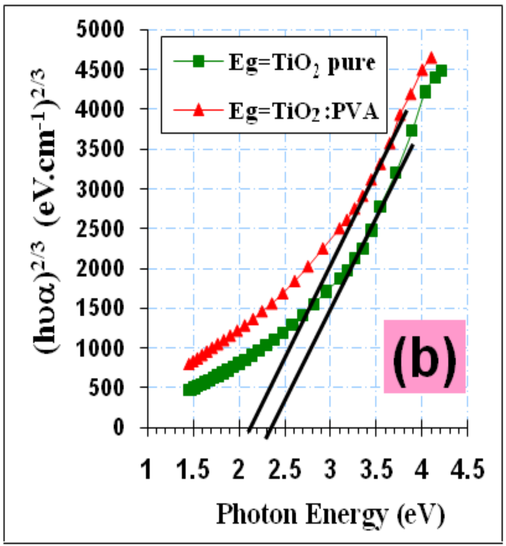


Fig. (6) electronic transitions of TiO_2 pure, TiO_2: PVA thin films. (a) allowed direct transition, (b) forbidden direct transition.

Table (2)
Optical constants of TiO_2 pure, TiO_2:PVA thin films.

Optical Constants	*TiO_2 pure*	*TiO_2:PVA*
T%	84.29	67.95
A%	9.02	16.7811
α	73100 cm^{-1}	78658.69 cm^{-1}
n_o	2.57	2.64
Allowed Energy Gap E_g	3.352eV	3.195 eV
Forbidden Energy Gap E_g	2.383 eV	2.011 eV

Conclusions

The following major conclusions be drawn from this work on the doped dependence on optical properties and the crystalline structure for TiO_2 and TiO_2: PVA prepared thin films:

1. XRD pattern is observed characteristics diffraction peaks which measured by XRD instrument of diffraction angle (2θ□, interplaner spacing (d) and Full Width at Half Maximum (FWHM), PVA enhances the general structural properties of TiO_2 thin films that means PVA increased tie-up of bonds between Ti and O atoms which means the molecules of TiO_2 come close together.
2. Prepared thin films have high values of absorption coefficient for the wavelength range (300-850 nm), It is increased when add PVA polymer.
3. Absorption and refractive index of TiO_2 thin films increase as film doped with PVA.
4. The direct allowed energy gap of TiO_2 and TiO_2 : PVA thin films was (3.195–3.052 eV) respectively, and forbidden energy gap was (2.109–2.383 eV) for TiO_2 and TiO_2 : PVA thin films respectively. This means the PVA decreased the energy gap of TiO_2 .

From enhancements for structural results, absorption and electronic transitions for optical properties of TiO_2 thin films prepared, can be using it as benefactor of solar cells after adding PVA polymer.

References

[1] Jae-Yeol Lee, W.Y.Lee, Duck-Kyun Choi, Jei Oh. "*Structure and properties of Co doped TiO_2 thin films on Si (100) by pulsed laser deposition method"*, "J.Ceramic Processing Res.", Vol.(7), No.(1), pp.(58-61), 2006.

[2] Doushita K. and Awahara T., *"Evaluation of Photocatalytic Activity by Dye Decomposition", "Journal of Sol-Gel Science and Technology"*, 22, 91–98, 2001.

[3] Ram A., *Fundamentals of polymer engineering*, Plenum Press, New York, p. 51, 1997.

[4] Donald. A.N., "*Semiconductor Physics and Devices*", Irwin, USA, 1992.

[5] Zhang C., Yuan X., Wu L., Han Y., Sheng J., "*Study on morophology of electrospun (poly vinyl alcohol) mats"*, Eur. Polym. J., 41, pp. 423-432, 2005.

[6] RADOIČIĆ M., ŠAPONJIĆ Z. V., MARINOVIĆ M. T. ,CINCOVIĆ, S. P. AHRENKIEL, BIBIĆ N. M. and NEDELJKOVI J. M., *"The influence of shaped TiO_2 nanofillers on the thermal properties of poly (vinyl alcohol)", "Journal of Serbian Chemical Society", 76* (0), pp.(1–23), 2011

[7] Chopra K.L., "*Thin films phenomena*", Mc.Graw-Hill, NewYork, 1969.

[8] M.Landmann, E. Rauls and W, G, Schmidt, "*The electronic structure and optical response of rutile, anatase and brookite TiO_2,*" *J.Phys.: Condens. Matter*, 24, 195503, 2012.

[9] Chopra K.L., "*Thin Film Devices Application*", Plenum Press, New York, 1983.

[10] Eckortova L., "*Physics of Thin Films*", (plenum press), 1977.

[11] Hasan M.M., Hasseeb A.S.M.A., Saidur R., Masjuki H.H., "*Effect of annealing treatment on optical properties of anatase TiO_2 thin films*", "International Journal of Chemical and Bimolecular Engineering", Vol.1, pp.93-97, 2008.

[12] Chide B. T., AL-Wattar A. H., Al-Tememee N. A. A., Twej W. A., Hameed M. A., Ubaid A. Q., Sallman Q. M. and Redha A. B., "*Study the Effect of the High Voltage on The preparation of Polyvinyl Alcohol/ TiO_2 Nano Fiber by Electrospinning", "Iraqi Journal of Physics"*, Vol. 7, No.8, pp. 21- 24, 2009.

[13] Piorkowska E. and Galeski A. "*Thermal conductivity of polymers*", International Polymer Science and Technology, Vol.12, No.5. (1985).

[14] Koski A., Yim K., Shivkumar S.;"*Effect of molecular weight on fibrous PVA produced by electrospinning*"; Mat. Letter; 58; 493, 2004.

[15] Areej Adnan Hateef, Batool Daram Balawa, Arwaa Fadil Saleh and Marwa Wailed Mahmmod, *"Effect of the thickness on electrical properties of TiO_2 thin films, prepared by thermal chemical spray pyrolysis deposition"*, "International

Research Journal of Engineering Science, Technology and Innovation (IRJESTI)" Vol.(1), N(6), pp.(175-179), 2012.

[16] Nilens A.G., "*deep imparity in semiconductors*", Wiley -Interscience publication, 1973.

[17] Ristolainen N., Heikkilä P., Harlin A., and Seppälä J., "*Electro spun Nanofibers Prepared by two methods: in situ emulsion polymerized PVA/nanoTiO$_2$ and mixing of functional PVA with nanoTiO$_2$", "AUTEX Research Journal"*, Vol. (8), No. (2), 2008.

الخلاصة

حُضرت أغشية ثناني أوكسيد التيتانيوم الرقيقة النقية TiO_2 و المشوبة بالبوليمر TiO_2:PVA بأستعمال تقنية التحلل الكيميائي الحراري على قواعد زجاجية مسخنة، بدرجة حرارة ($350\ ^oC$) لتحضير أغشية ثناني أوكسيد التيتانيوم الرقيقة النقية TiO_2، و بدرجة حرارة ^oC ١٦٠ لتحضير الاغشية المشوبة بالبوليمر TiO_2:PVA بزمن رش ٣ ثواني لكل دقيقة، و بسُمك ٢٥٠ نانوميتر. فحوصات (XRD) بينت ان التركيب أغشية TiO_2 النقية و المشوبة بالبوليمر TiO_2:PVA بأنها متعددة التبلور polycrystalline نوع anatase و ان شدة <101> أكبر نسبياً من ,<105> <200>,<004> لكلا الغشائين النقي و المشوب بالبوليمر. كذلك تمت دراسة الخصائص البصرية للأغشية TiO_2 النقية و المشوبة بالبوليمر TiO_2:PVA حيث تم حساب الثوابت البصرية قبل و بعد إضافة البوليمر PVA كالنفاذية، الامتصاصية، معامل الانكسار، معامل الامتصاص، الانتقالات الالكترونية المباشرة المسموحة و الممنوعة، حيث بينت النتائج أن أضافة البوليمر PVA أثرت بصورة واضحة في زيادة الثوابت البصرية عموماً لأنه سبب في ربط الاواصر بين الذرات و ذلك ادى الى زيادة الخصائص البصرية و التركيبية أيضاً.