Synthesis of Nano-TiO2 Thin Films by Sol-gel Dip-coating Method

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Abstract

Synthesis of titanium dioxide (TiO_2) Thin film on three microscope glasses using sol-gel method has been studied intensively. The starting materials were titanium(III)chloride, Ammonium Hydroxide. The components were mixed together to form the sol. Then, at 50℃ heating and ageing was applied to form stable sol-gel . Every glass substrate dipping in sol-gel beaker for period time (1,3,5)min respectively, for obtaining different thickness films. To evaluate the performance of films, After annealing at 500℃, the crystallinity of the films was determined by using the x-ray diffractometer (XRD). The change on the surface morphology was observed using Atomic Force Microscope(AFM). Finally, Optical properties measurements Absorbance (A) and transmittance(T)) for (TiO_2) films were studied by UV-Visible spectrometer.
analysis on the films. It has been successfully shown that the anatase crystalline phase was observed when the TiO_2 thin film was annealing at 500°C. The roughness and the crystalline size of TiO_2 thin film changed with the thickness. The minimum grain size(6.92) nm for thickness 1.2µm UV-visible studying that absorption is maximum at UV spectrum (opaque) and the transmittance is maximum at the visible spectrum

Keywords: sol-gel, TiO2 thin films, Structural properties, Optical properties, Surface morphology.

تصنيع أغشية رقيقة نانوية من ثنائي اوكسيد التيتانيوم باستخدام طريقة محلول-هلام بطريقة الطلاء بالتغطيس.

الخلاصة

تم تحضير اغشية رقيقة من مادة ثنائي اوكسيد التيتانيوم باستخدام تقنية محلول هلامي بطريقة الطلاء بالتغطيس رسبت طبقة رقيقة على شرائح مجهر زجاجية باستخدام تقنية سول- جل المكثف. استخدمت المواد الاولية لتحضير سول- جل من ثلاثي كلوريدالتيتانيوم وهيدروكسيد الامونيوم . خلطت المكونات لتشكيل السول ويتم الخلط بدرجة حرارة 50 درجة مئوية لتشكيل سول-جل.
غطست ثلاثة شرائح زجاجية لفترة متفاوتة من (1-3-5) دقيقة في مادة المحضرة للحصول على اغشية بأسماك مختلفة. تم تقييم أداء الافلام المحضرة بعد التلدين بدرجة 500 درجة مئوية . تم تحديد التبلور باستخدام جهاز حيود الاشعة السينية ولوحظ التغير في ميرفولوجية السطح باستخدام مجهز القدرة الذرية.

اخيراً درست الخصائص البصرية من امتصاص ونفاذية للغشاء المحضر باستخدام مطياف الاشعة فوق البنفسجية –المرئية. ومن تحليل الاغشية اظهرت نجاح تبلور طور antatag عن تلدين بدرجة 500 درجة مئوية خشونة السطح والحجم الحبيبي لغشاء ثاني اوكسيد التيتانيوم تغير مع تغير السمك. أقل حجم حبيبي 6.92 نانومتر لسمك 1.2مايكروميتر. وأعظم امتصاص عند منطقة الفوق البنفسجية وأعظم نفاذية في المنطقة المرئية.

INTRODUCTION

The sol-gel technique is an attractive and versatile method that can be relatively easily applied to a range of materials. It can be utilized to fabricate ceramic coatings from solutions by chemical means. The sol-gel technique has also been shown to improve the mechanical properties of the coatings as a result of the nano-crystalline grain structure produced(1).

The sol-gel technique is chemical process to synthesis of inorganic or metal oxide materials i.e.Titanium oxide. In this process may be product in amorphous or crystalline phase(2). it involved three stages i) hydrolysis of the organometalic or metal salts group precursor ii) poly condensation iii)gel formation(polymerization) . It used for synthesis nanomaterial , bulk materials in addition to convenient for nano , thin, thick films depositing on substrates at lower temperatures(3) .

The advantages of sol-gel coating is that because of the small amounts of material required, the costs of precursors are relatively low. Sol-gel film deposition also offers the significant advantage over other films deposition techniques, such as homogeneity, stoichiometry control, purity, Ease of possessing, lower temperatures and controlling the composition, and useable to coating an extensive and ununiform area substrate(4). Other methods requires major capital investment, such as chemical vapor deposition, physical vapor deposition, and sputtering, sol-gel route offers improvement in properties such as surface area, pore volume, and grain size by the careful control of chemistry[5].

In this work we chose the sol-gel technique it's one Chemical deposition methods that is widely adopted owing to its cost effectiveness and large area applicability. Titanium dioxide (TiO_2)is an excellent material because of wide applications such as EHP generator in soller cell[6]. photocatlysis [7], gas sensor[8]. TiO_2 has three crystalline structures or phases : anatase (tetragonal) , rutile (tetragonal) and brookite (orthorhombic). every structure have special properties and applications.[9,10] .In the present work, highly transparent and conductive TiO_2thin films were prepared by sol-gel technique

Experimental Work

TiO2 thin films were prepared by using $TiCl_3$(aqueous, 15%) as the precursor with NH_4OH (aqueous, 25%) to prepare the appropriate solution, 120ml of NH_4OH (aqueous, 25%) was added to 40 ml of $TiCl_3$ by drop wise with constant stirring For 2h as figure(1) .The pH of the solution was increased from 2 to 10.5 The solution was light violet in color and this changed to blackish violet with increasing PH. After 30 min of vigorous stirring at room temperature, a dark violet clear solution was obtained. The homogeneous solution was left under ambient conditions. It became muddy and changed in color from dark violet to whitish and colloidal occurred after some time. The three glass substrates were washed with distill water and detergent in an ultrasonic bath for 30 min then, with acetone for 10 min. The substrates dried by a blower. then, immersed vertically in the chemical sol –gel for(one , three, five) min. in order to obtain different layers. as figure (2). According to the solution components, the precipitate was expected to be TiO_2 or TiO_2-based hydrates. After appropriate deposition thicknesses, the substrate was dried at room temperature without any further treatment. Experiments were performed for different deposition times. All symbols had been putted in the cylinder furnace (carbolit) type and programmed at 500C as shown in figure.

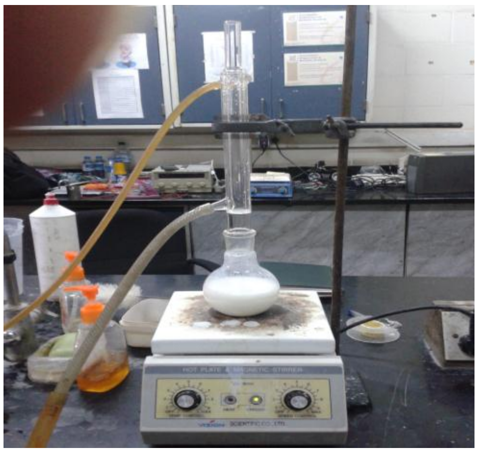


Figure (1) show reactor for synthesis of TiO_2 sol-gel

Figure (2) show dipping of glass substrates for different time

Results and Discussion

X-Ray Diffraction Measurements.

The crystalline phase of synthesized nano-TiO2 films was analyzed by XRD and their XRD patterns are shown in Figure(3) . The crystalline pure antase phase was confirmed by (101), (103), (004) diffraction peaks comparison by stander anataseTiO_2(PDF21-1272) and (110) diffraction peak with stander rutile (PDF21-1272) . The average crystallite size of the particles was calculated from XRD (110) peak of anatase TiO_2 by applying Scherrer's formula [11] .

$$D = \frac{0.9\lambda}{\beta Cos\theta} \qquad \dots (1)$$

where λ is the X-ray wavelength B is the full width at half maximum(FWHM) in radians, and θ is the angular position of the peaks The patterns reveal that the effects of thickness on grain size with thickness increased were shown in Table(1) of thickness (1. 2)µm , Table(2) of thickness (2.3)µm , Table(3) of thickness (3.5)µm .The thickness of (3.5)µm showed appearing peak of rutile phase. Moreover, antase phase. . Whereas the symbols were annealing under 500°C, with no annealing showed amorphous structures.

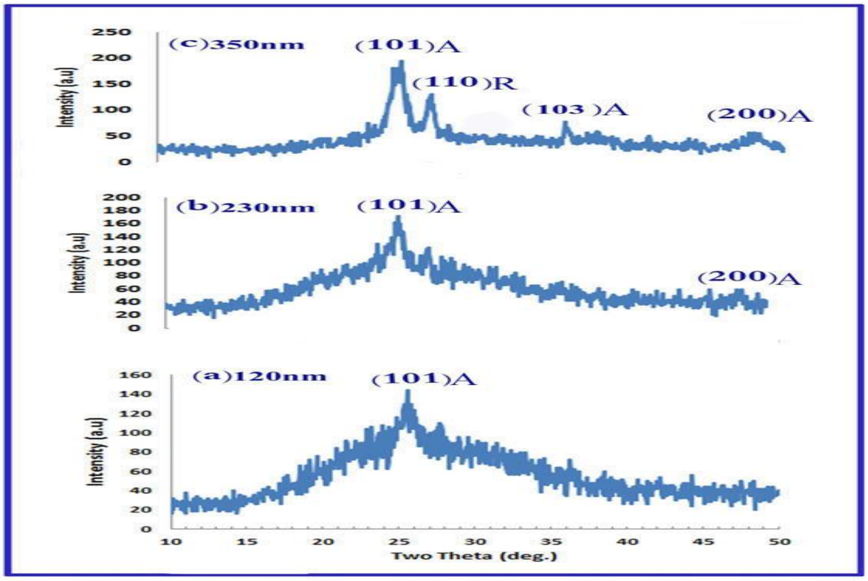


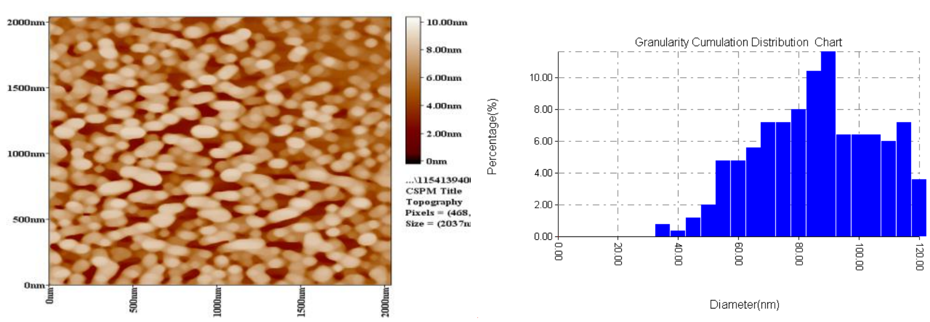
Figure (3) The X-Ray diffraction of TiO_2 thin films with deferent thickness.

Table (1) show the grains size of TIO_2 thin films of deferent thickness

Thickness(µm)	Average grain size(nm)
1.2	6.92
2.3	12.8
3.5	40.57

Atomic force Microscope (AFM) Measurements.

AFM shows, as evidence by the scanning process for an area with dimensions(2.037 ×2.037) μm^2. Films prepared and annealing at 500℃ clearly illustrated a change in surface morphology and roughness of TiO_2 films in figure (4) .The grain of the film can also be deduced form the AFM through histogram of the percentage of TiO_2 as a function of the grain size. The results indicated the growth of large grain size with increasing thickness and increased in the surface roughness.



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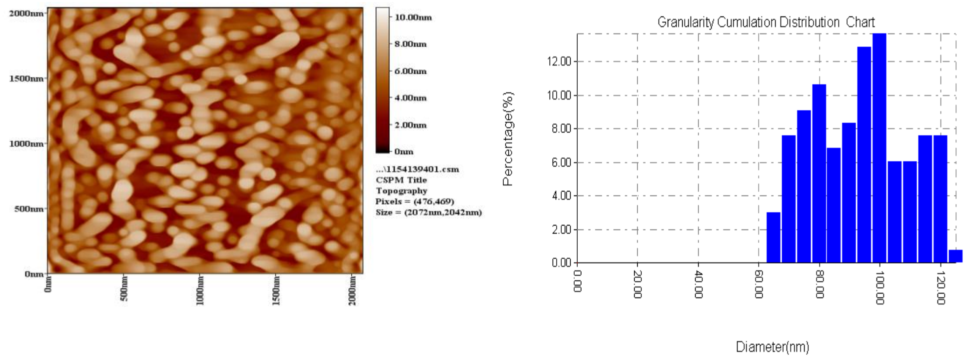

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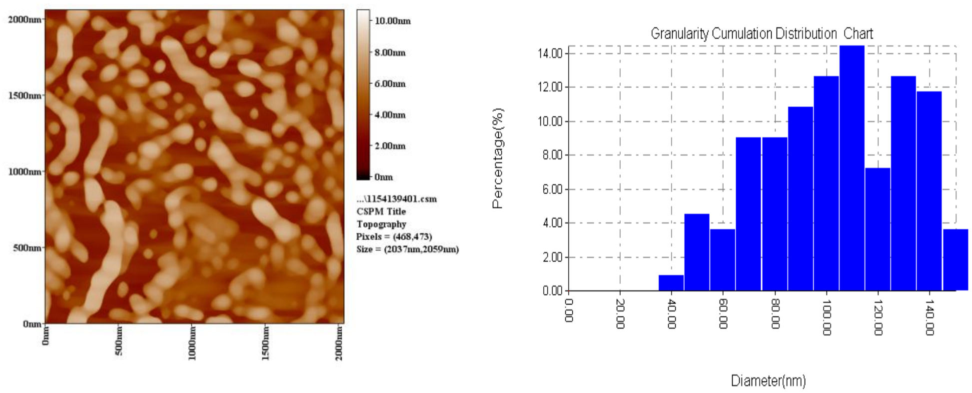

c

Figure (4) AFM images for TiO2 films with thickness a)1.2µm b) 2.3µm c) 3.5µm

The Optical Properties of TiO2 nano- Films

The optical properties of the deposited TiO_2 thin films on glass substrate at room temperature and with different thickness have been determined by study UV-Visible spectrum .

The Absorption Spectra

The absorbance spectra for TiO_2 in case of thin film at different thickness as shown in Fig. (5). At the visible spectrum absorption is minimum. At high wavelengths the incident photons do not have enough energy to interact with atoms, the photon will be transmitted when wavelength increases (photon energy decrease**.** and the absorbance was increased with thickness increased since grain size and crystallinity increased[12] .

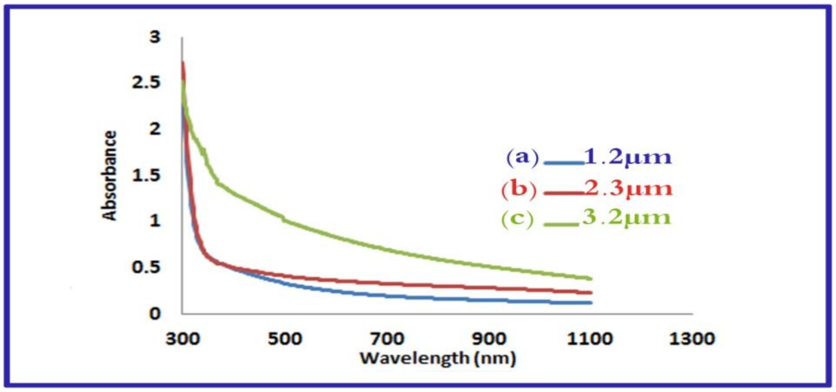

Figure (5) show The Absorbance versus wavelength for different thickness.

Transmittance Spectra

Figure (6) illustrates transmittance spectrum of TiO_2 films for different thickness. It is observed that maximum transmittance at (1.2µ) thickness for wavelength range (300-1100 nm) i.e. at visible region which is very suitable for solar cell. However, transmittance is inversely proportional with thickness, i.e., it decreases when thickness increases, transmittance decreases slightly with the increasing of film thickness. This behavior is attributed to the increase the number of atoms with the thickness that leads to the increase of the number of collision between atoms, which in turn, leads to the increase of absorbance and decreasing transmittance [13].

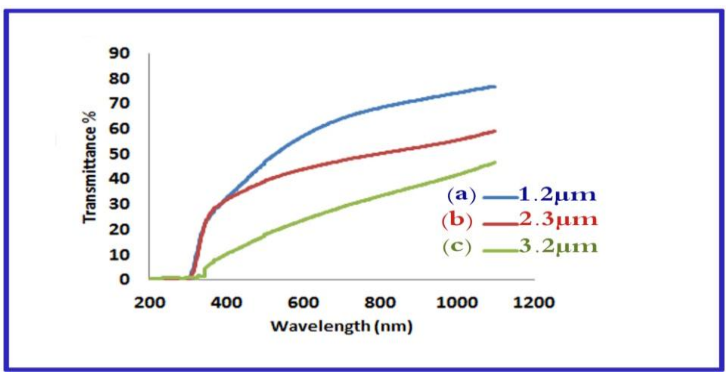

Figure (6) show The transmittance versus wavelength for different thickness

Refractive index

It has been shown in figures (7) refractive index as a function of wavelength of (TiO_2) films. It is increased with thickness increasing. It takes the values (2 , 2,1 , 2.2) , at wavelength 550 nm for film thickness(1.2, 2.3, 3,2)µm respectively. This increasing, probably, related to the enhancement of growth crystalline that is leaded to higher packing density and change in crystalline structure[14].

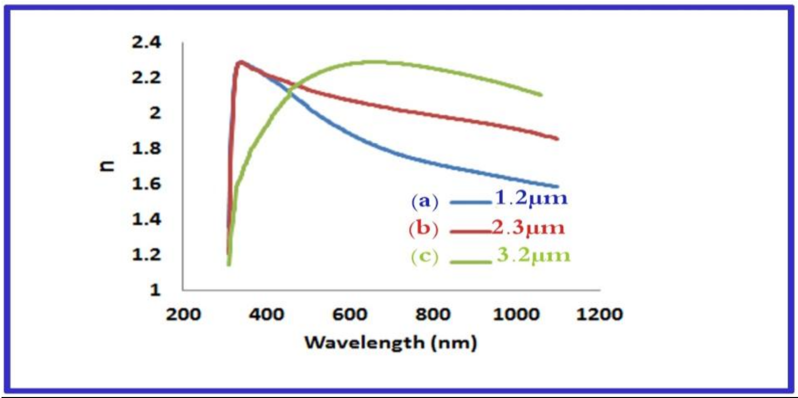

Figure (7)show the refractive index as function of wavelengths for TiO_2 thin films with different thicknes

Extinction Coefficient Measurements (K)

Figure (8) explains variation of (K) as a function of wavelength for (TiO_2) films with deferent thickness. Extinction coefficient works in the same way of absorption coefficient (α) , since they are connected by the relation[15], extinction coefficient decreasing with thickness increasing this attributed to increase of grain size and layers density .

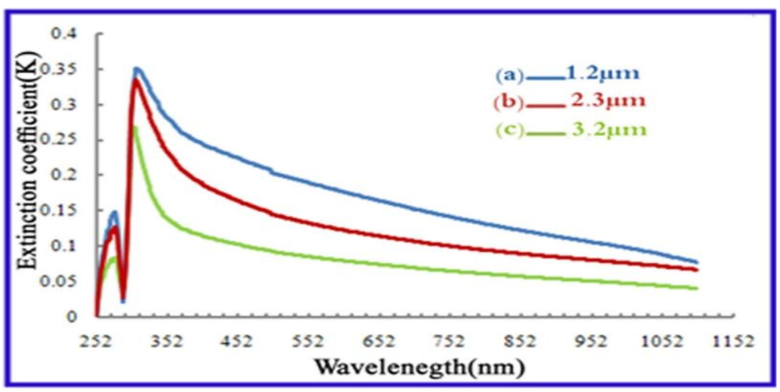

Figure (8) show the extinction coefficient as function of wavelengths for TiO_2 thin films with different thickness

Optical Energy gap measurements.

The optical energy gap was determined by using Tauc equation[16]. the relations are sketched between $(\alpha h\nu)^2$ and photon energy (hν),as in figure (9-a,b,c) explain allowed direct transition electronic. From table (2) and figures above-mentioned, it can be observed that (E_g) is decreasing with the increasing of thickness for all films. This is a result of the increasing in the carrier concentration, which effects in filling the bottom of the conduction band that leads to the decrease in the gab between (C.B.) level and (V.B.).

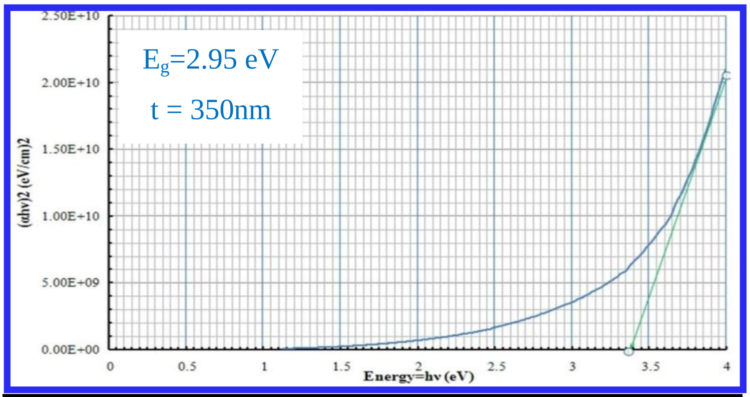

Figure (9-a) allowed direct electronic transitions of TiO_2 thin film a) 120nm

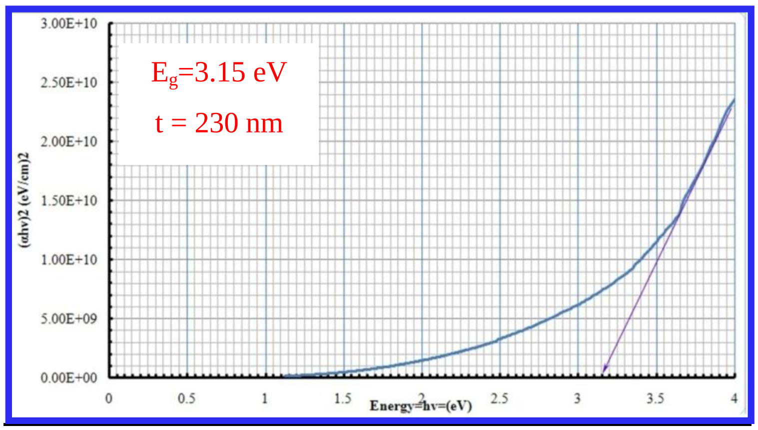

Figure (9- b) allowed direct electronic transitions of TiO_2 thin film b) 230nm.

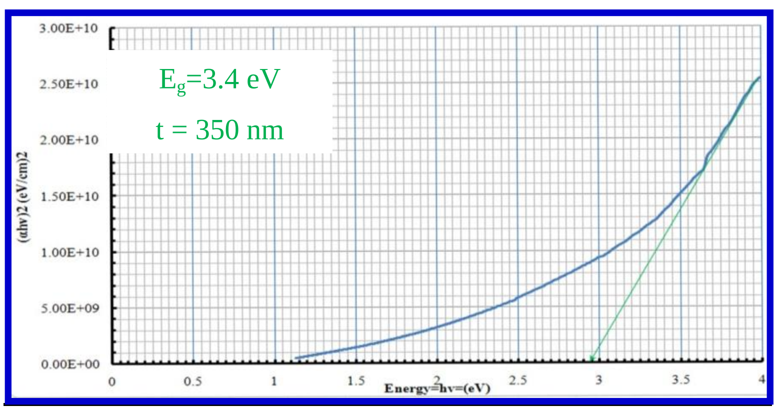

Figure (9-c) allowed direct electronic transitions of TiO_2 thin film.C) 120nm.

Table (2) shows direct energy gap for allowed transition for different thickness of TiO2 thin films.

Thickness (μm.)	**Allowed photon energy E_g (eV)**
1.2	3.41
2.3	3.15
3.5	2.95

Conclusions

Thin films of nano crystalline TiO_2 were prepared on glass substrates from an aqueous solution of $TiCl_3$ at room temperature using a simple and low cost-effective sol-gel method. The influence of the thickness on the structural, morphological, and optical properties was systematically investigated. Low-angle XRD and increasing of thickness led to polycrystalline TiO2 thin films of anatase phase. from AFM TiO_2 percentage and grain size histogram show increase percentage of TiO_2 particles with thickness increased. This may be attribute to agglomeration.

The simplicity of anatse TiO_2 thin-film deposition at room temperature is useful for direct fabrication of antireflection for solar cells, dye-sensitized solar cells, and gas sensors.

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