

Preparation of Titanium Dioxide (TiO₂) Via the Sol-Gel Process.

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Abstract

It had prepared Titanium Dioxide (TiO₂) by use of Sol-Gel, and with the use of Titanium Isopropoxide (TIP) in chemical construction (C₁₂H₂₈O₄Ti) with purity (98%), also from (Acetic Acid) which has chemical construction (CH₃COOH) with purity (99.5%), and also from (Ethanol) which has also chemical construction (C₂H₅OH) with purity amount (99.7%). These materials were prepared of (Aldrich Chemicals Company).

TiO₂ prepared and deposited on Indium Tin Oxide (ITO-glass) by using spin coating method with different speeds between (1000-5000) rpm to get thickness for the different thin film according to the speed, wherever the speed increased, the thickness becomes less and the opposite is right.

After the process of deposition preparing samples in programmed oven, the temperature started from the room temperature (R.T), then raised one degree for each minute and then settle up to 550 °C, and after a half an hour the temperature started to be down, and also a degree for each minute so as to reach the room temperature (R.T) in order to get on Antase phase.

Through out the examination of SEM, and XRD on the preparing samples, it had matched with what is previously prepared.

1- Introduction to the Sol – Gel Technology.

The sol-gel processing has low temperature chemical method used for production of inorganic oxide materials. Such a process may be used to yield a for of single and multi-component oxides as crystalline or amorphous form (Brinker and Scherer 1990). It is also used to give bulk materials but is suitable for thin film coatings production. The method of Sol – Gel helps oxide to be deposited on a substrate at much lower temperatures than traditional ceramic, (Twite and Bierwagon 1998).

There are many advantages involved in Sol – Gel during conventional methods concerning oxide (Saveninije 1998) materials which have the possibility of changing the film features extensively through altering the composition of the solution as well as in a relatively low process cost (Mandea et al 2007), (Carp et al 2004). In addition Sol-Gel overcomes the difficulties of producing a high quality dielectric semiconductor interface, and obtaining a stoichiometric ratio of elements and molecular homogeneity in multicomponent oxide film As for example, (Fujishima and Honda (1972), the Titanium Dioxide (TiO₂) belongs to an important material class because of its various uses in wide applications. (Oregon and Gratzal 1991), (Kubota et al 2001).

For example in solar cells as an electron-hole generator. TiO₂ thin film have been receiving much attention in the past as their chemical stability high refractive index and high dielectric constant allow their use as components in optoelectronic devices and sensor (Rancourt 1987), Fleisher et al 1999), Battiston et al 1994). There are many deposition techniques have been used to prepare them, such as

chemical vapor deposition, evaporation, reactive D.C. or diode or magnetron sputtering (Lobl et al 1994), (Martin et al 1994), ion beam techniques (Fernandez et al 1994), and sol-gel processes. The sol-gel processing are particularly efficient in producing thin, transparent, multi-component oxide layers of many compositions on various substrates, including glass (Brinker and Harrington 1981).

TiO₂ crystallizes in three types Anatase, Rutile, and Brookite (Landolt and Bornstein 1984), Rutile is being the most stable of the three types (Henrich 1985). To the author's knowledge, brookite has not appeared so far in thin film form and rutile has been extensively studied both theoretically and experimentally. Anatase, whose importance in solar cell technology has been recently increasing (Graetzel 1991), and the way in which its electronic properties differ from those of rutile (Furro et al 1994). This distinctness is in agreement with the study of the electronic and optical properties of thin anatase thin film (Tang et al 1994).

TiO₂ is an excellent material which shows most promising prospect in environmental purification, photoelectrochemical solar energy conversion and optical coating application (Fujishima et al 2000).

This is due to several properties such as remarkable activity, chemical stability, non-toxic (Raseshwar and Ibanez 1995), highly oxidative photogenerated holes, high energy conversion, highly transparent and high refractive index (Tryl et al 2000). Due to its high dielectric constant thin films of TiO₂ have also been studied for application as a gate insulator for Metal Oxide Semiconductor (MOS) device applications, with reduced leakage current (Paily et al 2002). This is an inherently n-type semiconducting material due to stoichiometric oxygen deficiency in the film structure, with a wide band gap typically 3.1 eV and a high index of refraction of about $n=2.6$, the TiO₂ anatase is an n-type semiconductor (Gugliemi et al 1992), Forro et al 1994).

2-Experimental Work

The three components were used in the preparation of the TiO₂ Sol-Gel films it can be explained as follows: - Titanium Isopropoxide (TIP) Ti[OCH(CH₃)₂]₄ purity 98%, Acetic acid CH₃COOH purity 99.5% and Ethanol CH₃CH₂OH purity 99.7-100% all chemicals were as supplied by Aldrich chemicals Ltd. TIP is a metal alkoxide, where metal alkoxides have the general formula M(OR)_n, where M=metal, R=alkyl group and n is the valence of the metal atom.

TiO₂ thin films are prepared by Sol-Gel spin-coating method using 50 ml of Ethanol and allowed to mix for 50 min, measure 5 ml of acetic acid with a pipette into Ethanol and stir by using a magnetic stirrer it for 5 min or at least 3 min, and measure 6.3 ml of TIP was added by pipette to a beaker containing a mixture of glacial acetic acid and ethanol that had been mixed for five minutes. The mixture was continually stirred using a magnetic stirrer addition and for a further two minutes after addition of the precursor. The Sol concentration was altered in order to assess the effects of ratios and concentration.

The effects of altering molar ratios of acid: TIP on thickness and absorption properties of the films were investigated. The Sols manufactured due to the method described above were immediately used to produce coating on the various substrates. Such as silicon or ITO-glass.

Thin films of TiO₂ were deposited by spin coating method using a standard photoresist spinner (Model 4000 Electronic Micro System). Glass slide coated with transparent conducting indium tin oxide (ITO) films were used as substrates.

These were thoroughly cleaned in Millipore water and neutral detergent for 10 min using an ultrasonic bath and then propanol was applied for further 10 min in the ultrasonic bath (type MXB14 sonic continuous of time from 0.1 to 99.9 min size 14 litter at temperature setting range 5-80 °C) (Grant) . Put the solution in to a convenient glass flask and seal it well. This sealing should keep the solution from contaminated air.

Finally the substrates were spray rinsed by deionized water and then dried out with nitrogen gas. For electrical measurements, TiO₂ films were spun coated onto the cleaned ITO-coated slides with a spinning speed between 1000 and 5000 rpm.

Before applying the solution onto the ITO slides a small section of the ITO electrode was masked in order to prevent the solution covering the whole area thus allowing electrical contacts to be made to the base ITO electrode as shown in figure (1).

A furnace type, (CAUTION) was used in this work which has a temperature range of (25-1000 °C). Put all sample in the furnace program at rang of (room temperature (R.T)-550 °C. As shown in figure (2).

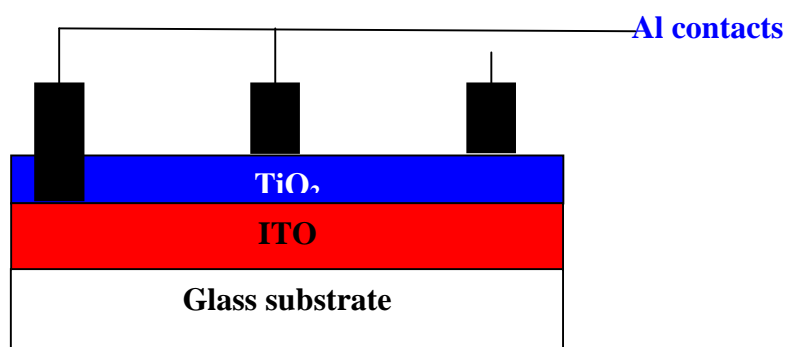


Figure (1) a schematic diagram of device structures with spin coating TiO₂ thin film.



Figure (2) photograph of the furnace type (CAUTION) using in this work

3- Results and Discussion

3.1- Scanning Electron Microscope (SEM)

It was found that the factors that affected the overall Sol stability and lifetime include considerable emphasis of acetic acid and Titanium Isopropoxide (TIP), and the steps mentioned for Sol preparation. The influence on Sol stability on deleting the reaction that modifying acetic acid was an immediate precipitation and films produced from this Sol were inhomogeneous. A strong initial exothermic reaction and fast gelatin resulted from Pre-reacting the TIP with the acetic acid. On the addition of this mixture to the remains of the solvent gel were left on equipment mentioned which had catastrophic influences on the accuracy of the volume added. Film supplied from Sol of this kind were also inhomogeneous and contained small clusters of TiO_2 . These could be seen under the SEM illustrated in figure (3). The TiO_2 consists of fine particles with a diameter of several tens nanometer (Yan-Sun et al 2006).

It was proved that the Mixing the TIP with a pre - acidified solution was a more accurate way and reduced cloudiness in Sol as see by Yoldas (Yoldas et al 1984). This procedure was taken into consideration for producing TiO_2 .

This procedure was adopted for the production of all TiO_2 . In contrast the sol-gel show a different structure on a microscopic scale because of the multiple coating processes a high porosity is reached within the whole layer, showing a slightly more compact material close to the substrate and thus a gradient of the pore distribution.

Such morphology has advantageous for efficient electrochemical cells because a fast and ionic charge transport can in part, prevent recombination losses. Furthermore the sol-gel shows larger particles with a size of 100 nm, few have a size of up to 200 nm. Thus an increase of the particle size should lead to a lower dye adsorption and to less efficient solar cell (Sebastion et al 2003).

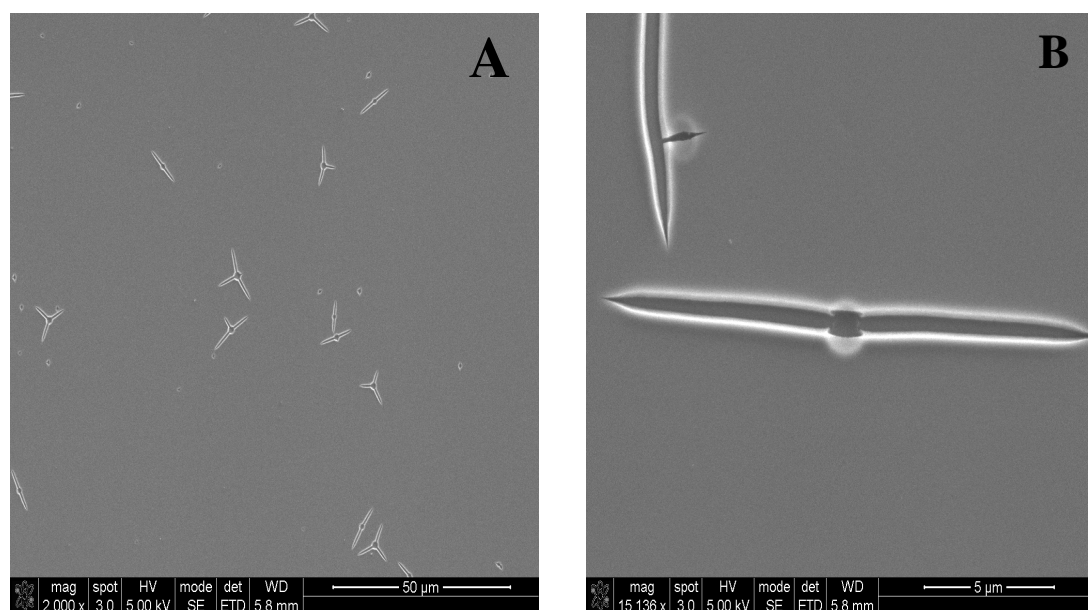


Figure (3) The SEM Micrographs of TiO_2 film surface, (A) at 50 μm magnification, (B) at 5 μm magnification.

3-2- X-Ray Diffraction

X-Ray Diffraction (XRD) analysis was carried out on TiO_2 thin films deposited at 2000 rpm and typical diffraction patterns are shown in figure (4).

Figures (4) are instances of the X-ray diffraction patterns taken from Sol residues heated 550°C . As a result it can be concluded that the increase in the heat treatment temperature to 550°C made a gradual crystallization of the material to the anatase component. The amorphous phase of TiO_2 was gained from Sol that did not submit to heat treatment. The rutile and brookite forms of TiO_2 were not see during the research. Figure (4) shows the X-ray diffraction patterns of a peak 25 and of a sol-gel layer. The peak 25 TiO_2 consists of anatase structure (Kheamrutai et al 2008).

The anatase only structure is detected. This seems to be the reason for the comparable cell performances discussed above. Anatase TiO_2 is photochemical more active than rutile and brookite and has a larger bandgap 3.29 eV which prevents bandgap absorption of blue light by TiO_2 particles (Yoldas et al 1984). This guarantees that the dye only absorbs the incident visible light which enhances the overall yield. The amorphous phase of TiO_2 was obtained from Sol that underwent no heat treatment. The rutile and brookite forms of TiO_2 were not observed during the investigations (Kheamrutai et al 2008).

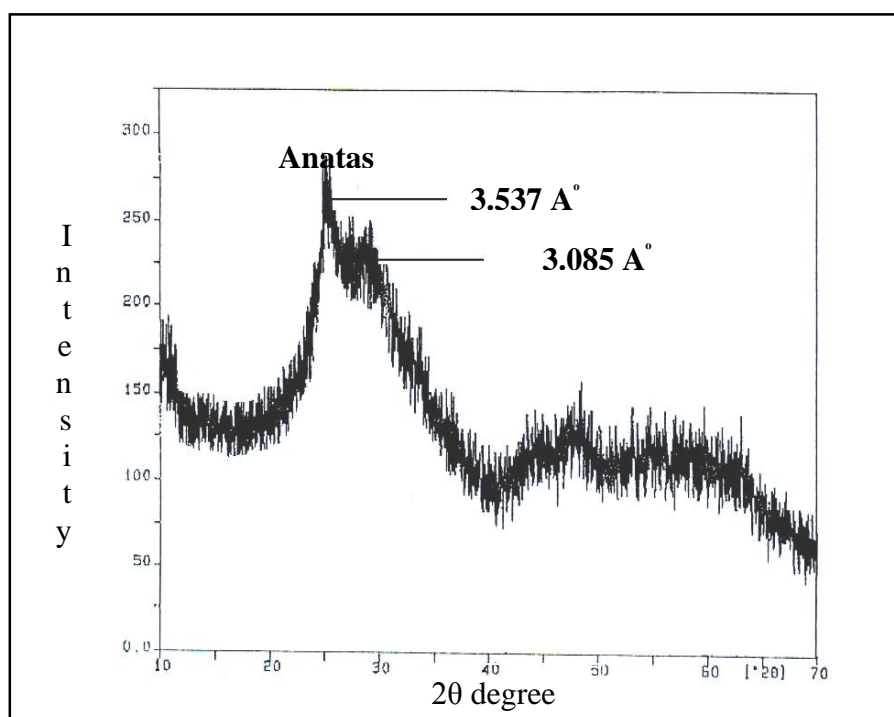


Figure (4). The X-ray diffraction of TiO_2 prepared by Sol-Gel at heating to 550°C .

3-3- Spectroscopic Ellipsometry

The measurements of Spectroscopic ellipsometry were investigated on TiO₂ films spin coated onto silicon substrates using a Woolam M-2000V that rotated compensator spectroscopic ellipsometry in the wavelength that rang from 370-1000 nm. The fixed degree of the angle of incidence is 70°. The experimentally measured ellipsometric spectra of $\Psi(\lambda)$ and $\Delta(\lambda)$ are suitable to be fulfilled by means of WVASE @ J.A. Woollam dedicated software that permits the extinction of optical parameters such as thickness (d) refractive index (n) and extinction coefficient (k) of all deposited layers (Woollam 2002).

A multilayer model component has been mentioned for the suitability of measured ellipsometry data. The model consists of Si substrate, SiO₂ layer representing a very thin native oxide layer 3 nm in thickness and the TiO₂ thin films. Cauchy model has frequently used for the extraction of the film parameters of adsorbed organic and bio-materials (Dalc 2002). This model has therefore been adopted in this research in order to determine the film thickness and optical constants of spun films of the TiO₂ (Nabok 2005).

The thickness (d), refractive index (n), and extinction coefficient (k) of the 2000 rpm spin speed are shown in table (1).

Table (1) Optical constants of spun films of TiO₂ obtained by fitting the measured $\Psi(\lambda)$ and $\Delta(\lambda)$ spectra.

d (nm)	n	k
64.37	2.354	0.037

The values of thin films were evaluated from ellipsometry data as a function of spin speed ω in the range 1000-5000 rpm and the results are shown in figure (5) on a logarithmic scale. Figure (6) illustrates the curve fitting obtained for TiO₂ film using Cauchy model and the obtained results of data fitting are summarized in table (1).

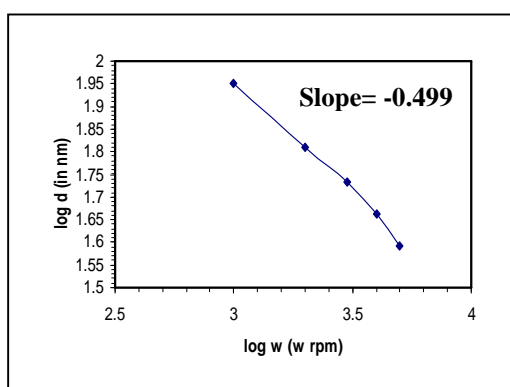
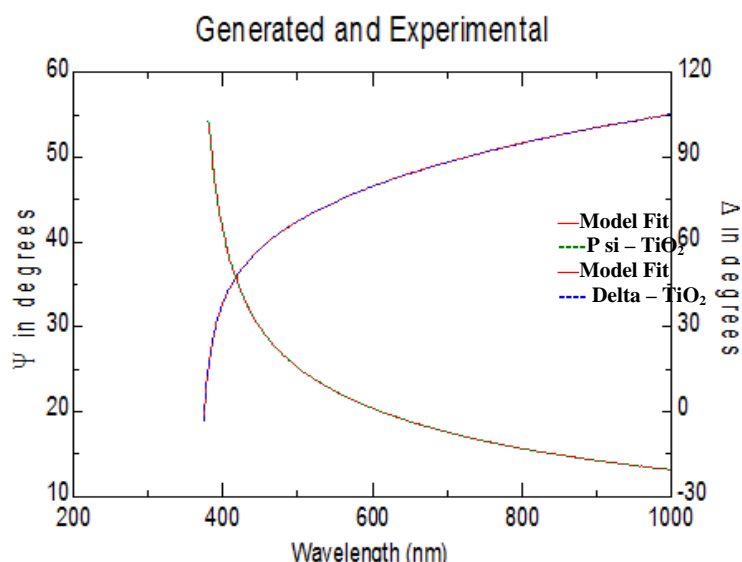


Figure (5) Thin films measured by ellipsometry plotted as a function of spin speed ω in the range 1000-5000 rpm.



The

curve fitting obtained for TiO_2 film.

Figure (6)

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تحضير (TiO₂) بترقية (Sol-Gel) Titanium Dioxide

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الخلاصة

في هذا البحث تم تحضير (Titanium Dioxide (TiO₂) باستخدام طريقة (SOL-GEL) وذلك باستخدام Titanium Isopropoxide (TIP) ذو التركيب الكيميائي $\text{Ti}(\text{OCH}_2(\text{CH}_3)_2)_4$ وبنقاوة مقدارها 98.1% وكذلك من (Acetic Acid) ذو التركيب الكيميائي CH_3COOH وبنقاوة 99.5% وكذلك من Ethanol ذو التركيب الكيميائي $\text{CH}_3\text{CH}_2\text{OH}$ وبنقاوة مقدارها 99.7% وكانت هذه المواد مجهزة من شركة (Aldrich Chemicals).

لقد تم تحضير TiO₂ و ترسيبها على ITO-glass بطريقة (spin coating) وبسرعة مختلفة تتراوح بين (1000-5000) للحصول على سمك للغشاء الرقيق مختلف وحسب السرعة حيث كلما زادت السرعة قل السمك والعكس بالعكس وبعد عملية الترسيب تم إدخال النماذج المحضرة في فرن مبرمج تبدأ درجة الحرارة من درجة حرارة الغرفة وبارتفاع درجة لكل دقيقة ومن ثم يستقر على 550°C وبعد نصف ساعة يبدأ بالهبوط كذلك درجة لكل دقيقة حتى يصل درجة حرارة الغرفة وذلك للحصول على طور (Antase) . ومن خلال إجراء الفحوصات مثل XRD و SEM على النماذج المحضرة تم مطابقتها مع ما هو محضر مسبقاً و حصلنا على نتائج جيدة.