

# Structural and Electrical Properties of TiO<sub>2</sub> Thin Film Derived from Sol-gel Method using Titanium (IV) Butoxide

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## Abstract

Fabrication of titanium dioxide (TiO<sub>2</sub>) thin film on microscope glass using sol-gel method has been studied intensively. The starting materials were titanium (IV) butoxide, ethanol, acetic acid, triton x-100, hydrochloric acid and deionized water. The materials were mixed together to form the sols. Then, the heat and ageing treatment was applied to form stable sols. The sols were then spin coated on the glass substrate to form the homogenous and transparent TiO<sub>2</sub> thin film. The TiO<sub>2</sub> thin film was coated at several layers using specific conditions. To evaluate the performance of thin film, the crystallinity of the thin film was determined by using the x-ray diffractometer (XRD). The change on the surface morphology was observed using atomic force microscope (AFM). The electrical property of the thin film was determined by doing the current-voltage (I-V) analysis on the thin film. It has been successfully shown that the anatase crystalline phase was observed when the TiO<sub>2</sub> thin film was heated at 500°C. The roughness and the crystalline phase of TiO<sub>2</sub> thin film changed drastically with the growth conditions. Finally, the effect of film preparation to the film resistivity also showed a critical aspect where we should take into account during the preparation of TiO<sub>2</sub> thin film.

Keywords: structural properties, electrical properties, TiO<sub>2</sub> thin film, titanium butoxide.

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## 1. INTRODUCTION

Titanium dioxide (TiO<sub>2</sub>) has been investigated by many researcher because of their numerous application in the various industries. A transparent TiO<sub>2</sub> thin film can be applied for coating such as for a self-cleaning glass and solar cell application. TiO<sub>2</sub> solar cells (Dye-sensitized solar cells: DSSCs) were an extensive research due to low cost, easily fabricated, environmentally benign and have relatively high energy conversion efficiency [1]. Because of its numerous electrical, optical and chemical properties, TiO<sub>2</sub> is also used in a wide range of application such as catalysis, optical coatings, gas sensors and many more. It has been reported that TiO<sub>2</sub> porous film plays a key role in the enhancement of photoelectric conversion efficiency of DSSCs. Therefore, many scientists focus their researches on this particular subject [2,3,4].

There are number of methods have been employed to fabricate TiO<sub>2</sub> thin films, including reactive sputtering, chemical vapor deposition, and sol-gel process. The sol-gel technique offers many advantages over other deposition techniques due to the use of very simple and inexpensive equipment. Novel morphologies can be obtained and novel physical properties may be expected depending on the structures which are not produced by the usual processes. This simple method has also advantages to produce TiO<sub>2</sub> thin films in a relatively shorter processing time at lower temperatures. The rheological properties of sols and gels can give rise to the formation of films and thus considerably increase the anisotropy of the material and its chemical reactivity [5].

However, it is very important to study the evolution of different physical and chemical properties of TiO<sub>2</sub>, prepared by a suitable technique which is effective for controlled modification. N.Wetchakun *et. al.* claimed that the annealing process influence the nanosize of TiO<sub>2</sub> structure [6]. Fernando Gordillo Delgado *et. al.* also reported that the crytallinity of TiO<sub>2</sub> thin film depend on the growth condition and the number of layer TiO<sub>2</sub> colloidal coated [7]. C.Su *et. al.* then claimed that TiO<sub>2</sub> thin film is sensitive to heat treatment. The anatase phase was formed when at growth temperature between 400°C to 700°C and then after 700°C

the rutile phase was formed. Furthermore, it has been reported that the anatase structure formed influences the photo catalytic activity of TiO<sub>2</sub> thin film [8]. Therefore, in general the property of TiO<sub>2</sub> thin film is strictly depended on growth condition and materials.

In the present research, synthesis of TiO<sub>2</sub> thin film using titanium (IV) butoxide by spin coating method is intensively studied. The influence of the processes recipe to the structural and electrical properties is investigated.

## 2. EXPERIMENTAL

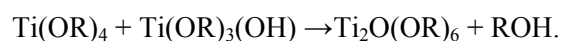
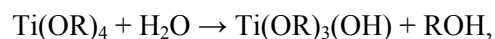
### 2.1. Substrate

In this experiment the substrate used is microscope glass. The glass substrate was first treated with acetone, methanol and distilled water in ultrasonic bath for 10 minutes each. Then, the substrate was blow with N<sub>2</sub> gas for drying purpose.

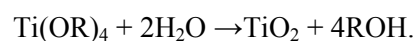
### 2.2. TiO<sub>2</sub> solution

Using a sol-gel technique, TiO<sub>2</sub> thin film was prepared by mixing titanium (IV) butoxide, glacial acetic acid, ethanol, deionized water and triton x-100. In order to investigate the influence of amount of solvent, the amount of ethanol was varies for 20% and 70%. In this technique, titanium butoxide was used as precursor, glacial acetic acid as a chelating agent, ethanol as a solvent and deionised water as a function of adding the oxygen (O<sub>2</sub>). Triton X-100 used acts as a stabilizer to avoid precipitation in solution and at the same time used to increase the conductivity of films.

The hydrolysis and the polycondensation of titanium alkoxides proceeds according to the following scheme:



The reaction stops with the inclusion of two water molecules:



### 2.3. TiO<sub>2</sub> thin film

The TiO<sub>2</sub> solution then was coated onto substrate by using spin coating technique. After that, the sample was heated at 100°C. The process of coating and heating was repeated in different times. The process repeated represents the number of layer of TiO<sub>2</sub> thin film. As-prepared sample was carried to annealing process at 500°C in 1 hour.

### 2.4. Characterization

#### 2.4.1. X-ray diffraction (XRD)

The nanostructured TiO<sub>2</sub> thin film was characterized used Bruker D8 Advanced at room temperature. The measurement was obtained at 2θ degree equipped with Cu Kα radiation. This characterization provide precise information about crytallinity phases and crystallite size of nanostructured TiO<sub>2</sub> thin film.

#### 2.4.2. Atomic force microscope (AFM)

The nanostructured TiO<sub>2</sub> thin film was characterized with atomic force microscope (AFM XE-100) at room temperature. With non-contact cantilever and non-contact mode, this characterization method promises a non-destructive testing. Other than that, it also capable to give the information about grain size and roughness of nanostrutured TiO<sub>2</sub> thin film. We scan the TiO<sub>2</sub> thin film of area 500 nm x 500 nm.

#### 2.4.3. IV analysis

Current-Voltage (IV) measurement was performed to investigate the electrical properties of nanostructured TiO<sub>2</sub> thin film. The IV measurement was performed with using 2-point probe connected to a source meter (Keithley 2400). The data of IV characteristic was plotted with platinum (Pt) as the metal contact. From the IV curve, the information of resistivity can be obtained from the equation below:

$$\rho = \frac{V}{I} \frac{A}{L} \text{ (}\Omega \text{ cm)}$$

Where ρ is resistivity, V over I is calculated resistance, A is cross sectional area and L is distance between metal contacts. The thickness of the nanostructured TiO<sub>2</sub> thin film was measured by surface profiler (Alpha Step IQ-KLA Tencor). Figure 1 shows the overall experimental produce used in this research.

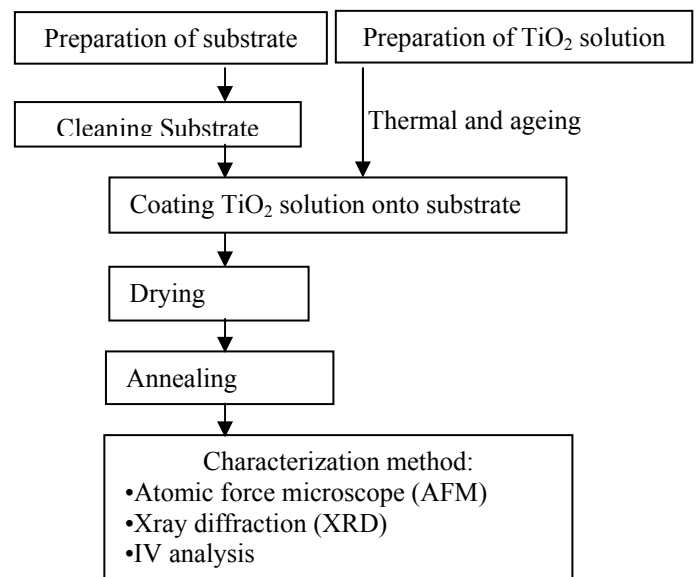


Figure 1. Experimental procedure.

## 3. RESULT AND DISCUSSION

### 3.1. Effect of annealing process

Figure 2 shows the XRD spectra of TiO<sub>2</sub> thin film before and after the annealing process at 500°C for 1 hour. The TiO<sub>2</sub> thin film was coated for 5 layers. After annealing process, the XRD peaks was shown at 25.3°, 37.8° and 48.06° correspond to the anatase peak at (101), (004) and (200) crystal planes of nanostructured TiO<sub>2</sub> thin film, respectively. In a previous report, it has been showed that the electronic and optical property of anatase phase was making it chosen for DSSCs rather than rutile and brokite phase [9]. Figure 2 shows that the TiO<sub>2</sub> thin film after the annealing process is

better than before the annealing process.

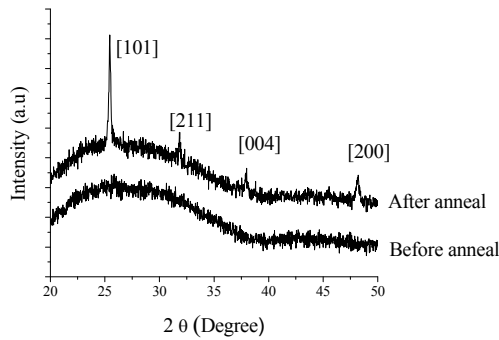


Figure 2. XRD spectra of TiO<sub>2</sub> thin film before and after annealing process.

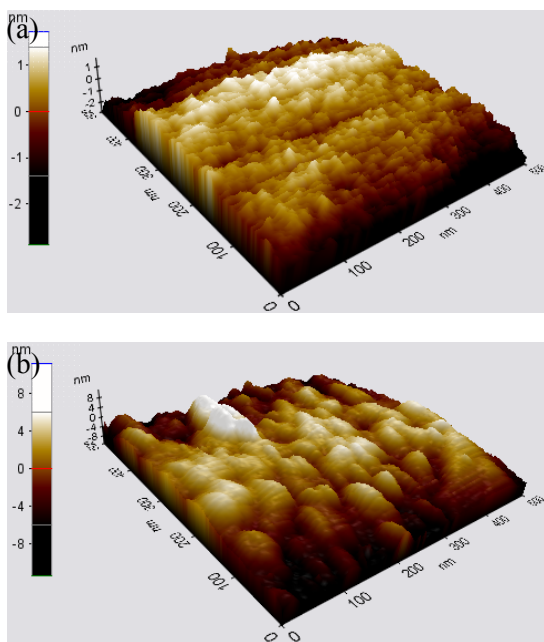


Figure 3. AFM image of TiO<sub>2</sub> thin film (a) before and (b) after annealing process.

Figure 3 shows the surface morphology of TiO<sub>2</sub> thin film before and after the annealing processes. The roughness of thin film increases from 0.341 to 1.690 after the annealing process. The increase in roughness is due to the existing of larger grain size of nanostructured of TiO<sub>2</sub> thin film which can be seen in figure 3 (b).

Table 1 : Resistance and resistivity of TiO<sub>2</sub> thin film before and after annealing process

	Before anneal	After anneal
Resistance (Ω)	5.00E+08	8.00E+07
Thickness (μm)	0.5	0.4
Resistivity (Ω . cm)	2.34E+04	3.20E+03

Table 1 shows the resistivity of TiO<sub>2</sub> thin film before and after the annealing process. It was noticed that the resistivity was decreased after annealing process as compared with as-prepared before annealing process. This may be due to the reason where after annealing process, the good crystallinity and nanostructure surface area obtained after the annealing and it promises much surface for electron passes through from one grain to another grain within the TiO<sub>2</sub> thin film.

### 3.2. Effect of thickness

The thickness of nanostructured TiO<sub>2</sub> thin film can be control through controlling times repeating of coating TiO<sub>2</sub> solution onto substrate. The thickness of film were approximately 0.2 μm, 0.4 μm and 1.0 μm with 1, 5 and 10 layer of TiO<sub>2</sub> thin film, respectively. Under the XRD spectra, with increasing number of layer, the anatase peak of TiO<sub>2</sub> can be identified clearer. The crystallinity of TiO<sub>2</sub> was identified best at 5 layers and above (figure 4).

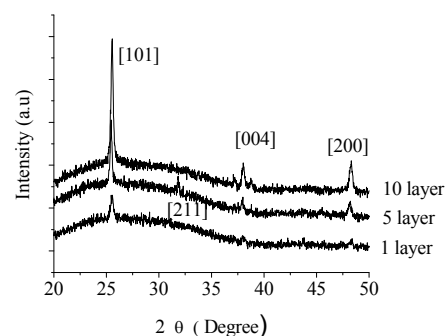


Figure 4. XRD spectra of 1, 5 and 10 layer of nanostructured TiO<sub>2</sub> thin film after annealing process.

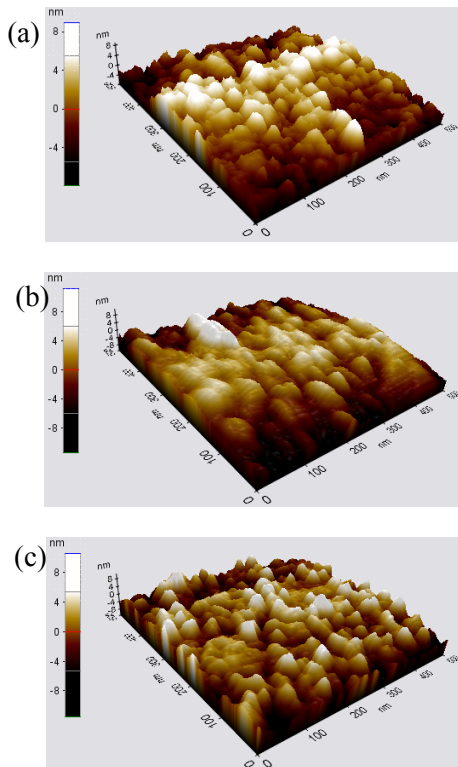


Figure 5. AFM image of (a) 1, (b) 5 and (c) 10 layer of TiO<sub>2</sub> thin film.

Figure 5 shows the surface morphology of TiO<sub>2</sub> thin film for different layers. The measured roughness was 1.574 nm, 1.690 nm and 1.794 nm for 1, 5 and 10 layers, respectively. The roughness of TiO<sub>2</sub> thin film increased with the thickness of TiO<sub>2</sub> thin film.

Table 2 shows the electrical properties of TiO<sub>2</sub> thin film for 1, 5 and 10 layers. With the increasing in the number of layer, the resistance and resistivity increased [11]. This is due to when we increase number of layer, the electron need to passes through the film with longer time to complete the circuit during the I-V measurement.

Table 2 : Resistance, sheet resistance and resistivity of 1,5 and 10 layer of TiO<sub>2</sub> thin film after annealing process.

	1 layer	5 layer	10 layer
Resistance (Ω)	5.00E+07	8.00E+07	8.00E+08
Thickness (μm)	0.2	0.4	1
Resistivity (Ω . cm)	1.00E+03	3.20E+03	8.00E+04

### 3.3. Effect of amount of solvent

One of the key parameter for TiO<sub>2</sub> thin film as an electrode in DCCS is that it needs to be transparent. This can be control by changing the concentration of sol. We varied the amount of ethanol solvent between 20% and 70% for this study. In general, we found that the TiO<sub>2</sub> thin film using 20% of ethanol was transparent compared to 70% of ethanol.

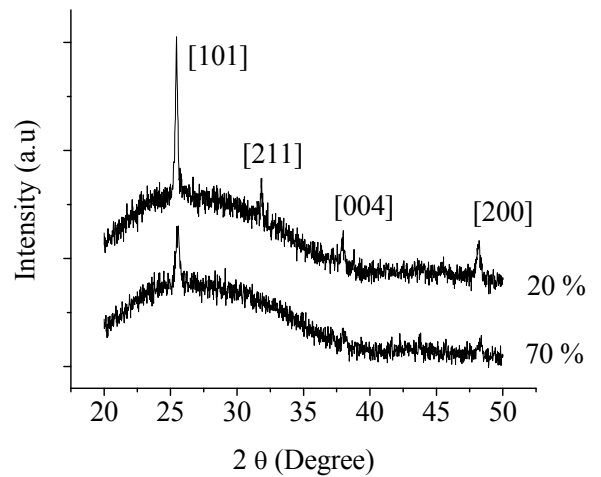


Figure 6. XRD spectra of 20% and 70% amount of ethanol.

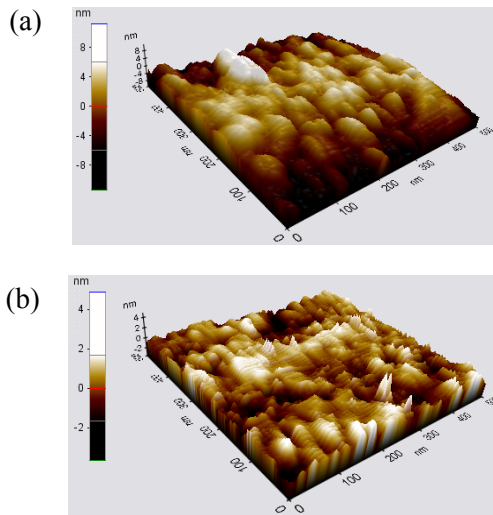


Figure 7. AFM image of (a) 20% and (b) 70% amount of ethanol

Figure 6 shows the XRD analysis of TiO<sub>2</sub> thin film using 20% and 70% of ethanol solvent. The peak of anatase TiO<sub>2</sub> is decreased with the increasing amount of ethanol. The XRD spectra of nanostructured TiO<sub>2</sub> thin film with 70% amount of ethanol shows single peak of anatase compared to nanostructured TiO<sub>2</sub> thin film with 20% amount of ethanol.

Figure 7 shows the AFM images of thin film prepared using 20% and 70% amount of ethanol. The roughness was 0.625 at 70% amount of ethanol. On the other hand, the roughness increased to 1.690 at 20% amount of ethanol.

Table 3 shows the electrical properties of TiO<sub>2</sub> thin film with 20% and 70% ethanol. The resistivity slightly increased when the 20% of ethanol was used. This is clearly understood from figure 6 where one can see a single phase structure of TiO<sub>2</sub> thin film. The single phase structure enhances the electron mobility thus improve the conductivity [10]. Therefore, the resistivity is lower at 70% of amount ethanol.

Table 3 : Resistance, sheet resistance and resistivity of 10% and 70% of TiO<sub>2</sub> thin film after annealing process.

	20% ethanol	70% ethanol
Resistance (Ω)	8.00E+07	5.00E+07
Thickness (μm)	0.4	0.458
Resistivity (Ω . cm)	3.20E+03	2.29E+03

## 7. CONCLUSION

We have successfully fabricated the TiO<sub>2</sub> thin film at various thickness and amount of solvent along with annealing process. The effect of the growth condition to the crystallinity, morphology and IV properties has been studied.

We found that the annealing process and the number of layer influence the crystallinity and morphology of TiO<sub>2</sub> thin film. The annealing process gives anatase phase of nanostructured TiO<sub>2</sub> thin film appears in XRD spectra. The anatase peak of nanostructured TiO<sub>2</sub> thin film can be identified clearer with increase number of layer.

Roughness of TiO<sub>2</sub> thin film is increase with annealing process and number of layer but decrease with increasing amount of ethanol.

The resistivity of TiO<sub>2</sub> thin film decrease with annealing process and amount of ethanol but increase with the number of layer deposited on nanostructured TiO<sub>2</sub> thin film.

Finally, we propose that the TiO<sub>2</sub> thin film is good to growth with annealing process, 5 layer and 20% amount of ethanol. However, further investigation on the optical properties of this TiO<sub>2</sub> thin film is needed.

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