Structural and Electrical Properties of TiO_2 Thin Film Derived from Sol-gel Method using Titanium (IV) Butoxide

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Abstract

Fabrication of titanium dioxide (TiO_2) 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_2 thin film. The TiO_2 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_2 thin film was heated at 500°C. The roughness and the crystalline phase of TiO_2 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_2 thin film.

Keywords: structural properties, electrical properties, TiO_2 thin film, titanium butoxide.

1. INTRODUCTION

Titanium dioxide (TiO_2) has been investigated by many researcher because of their numerous application in the various industries. A transparent TiO_2 thin film can be applied for coating such as for a self-cleaning glass and solar cell application. TiO_2 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_2 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_2 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_2 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_2 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_2, 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_2 structure [6]. Fernando Gordillo Delgado *et. al.* also reported that the crytallinity of TiO_2 thin film depend on the growth condition and the number of layer TiO_2 colloidal coated [7]. C.Su *et. al.* then claimed that TiO_2 thin film is sensitive to heat treatment. The anatase phase was formed when at growth temperature between $400^{O}C$ to $700^{O}C$ and then after $700^{O}C$ the rutile phase was formed. Furthermore, it has been reported that the anatase structure formed influences the photo catalytic activity of TiO_2 thin film [8]. Therefore, in general the property of TiO2 thin film is strictly depended on growth condition and materials.

In the present research, synthesis of TiO_2 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_2 gas for drying purpose.

2.2. TiO_2 solution

Using a sol-gel technique, TiO_2 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_2). 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:

$$Ti(OR)_4 + H_2O \rightarrow Ti(OR)_3(OH) + ROH,$$

$$Ti(OR)_4 + Ti(OR)_3(OH) \rightarrow Ti_2O(OR)_6 + ROH.$$

The reaction stops with the inclusion of two water molecules:

$$Ti(OR)_4 + 2H_2O \rightarrow TiO_2 + 4ROH.$$

2.3. TiO_2 thin film

The TiO_2 solution then was coated onto substrate by using spin coating technique. After that, the sample was heated at $100^{O}C$. The process of coating and heating was repeated in different times. The process repeated represents the number of layer of TiO_2 thin film. As-prepared sample was carried to annealing process at $500^{O}C$ in 1 hour.

2.4. Characterization

2.4.1. X-ray diffraction (XRD)

The nanostructured TiO_2 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_2 thin film.

2.4.2. Atomic force microscope (AFM)

The nanostructured TiO_2 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_2 thin film. We scan the TiO_2 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_2 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:

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

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_2 thin film was measured by surface profiler (Alpha Step IQ-KLA Tencor). Figure 1 shows the overall experimental produce used in this research.

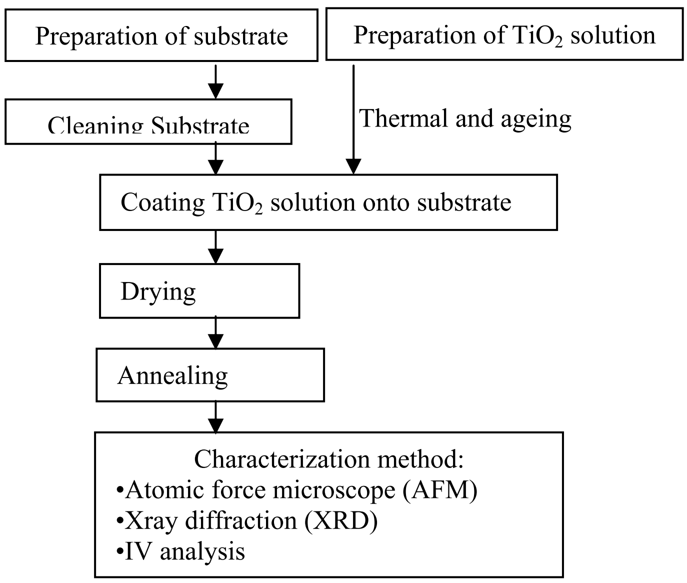

Figure 1. Experimental procedure.

3. RESULT AND DISCUSSION

3.1. Effect of annealing process

Figure 2 shows the XRD spectra of TiO_2 thin film before and after the annealing process at 500°C for 1 hour. The TiO_2 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_2 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_2 thin film after the annealing process is better than before the annealing process.

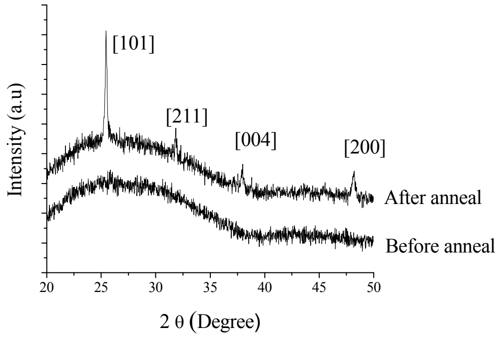

Figure 2. XRD spectra of TiO_2 thin film before and after annealing process.

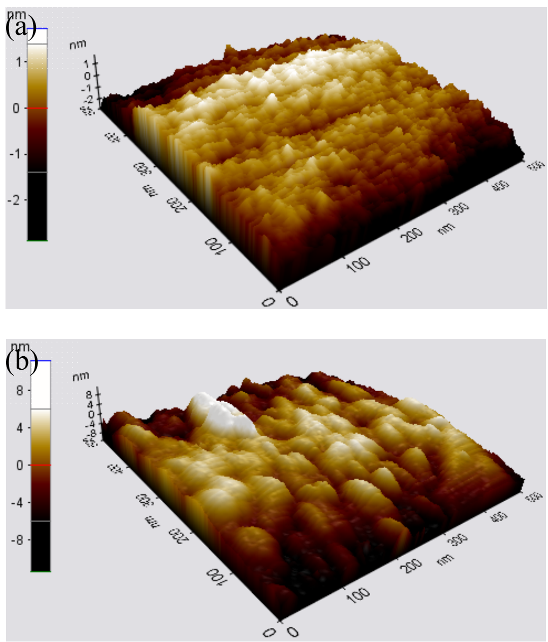

Figure 3. AFM image of TiO_2 thin film (a) before and (b) after annealing process.

Figure 3 shows the surface morphology of TiO_2 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_2 thin film which can be seen in figure 3 (b).

Table 1 : Resistance and resistivity of TiO_2 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_2 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_2 thin film.

3.2. Effect of thickness

The thickness of nanostructured TiO_2 thin film can be control through controlling times repeating of coating TiO_2 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_2 thin film, respectively. Under the XRD spectra, with increasing number of layer, the anatase peak of TiO_2 can be identified clearer. The crystallinity of TiO_2 was identified best at 5 layers and above (figure 4).

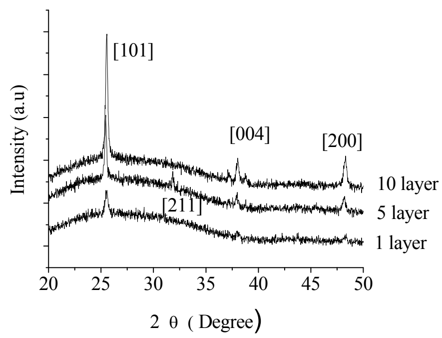

Figure 4. XRD spectra of 1, 5 and 10 layer of nanostructured TiO_2 thin film after annealing process.

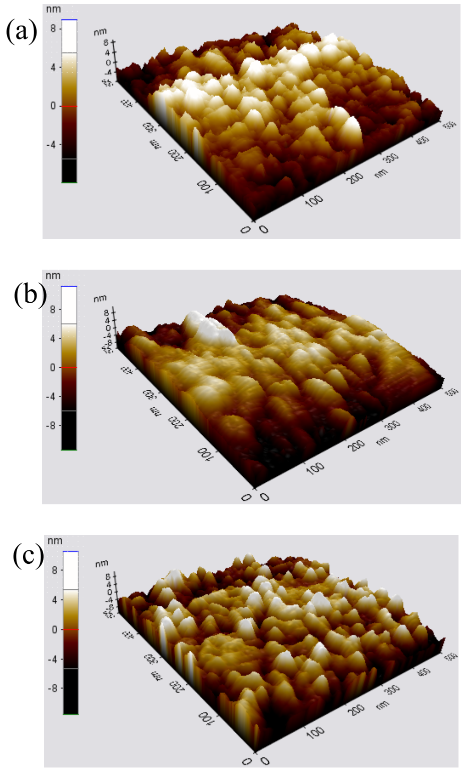

Figure 5. AFM image of (a) 1, (b) 5 and (c) 10 layer of TiO_2 thin film.

Figure 5 shows the surface morphology of TiO_2 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_2 thin film increased with the thickness of TiO_2 thin film.

Table 2 shows the electrical properties of TiO_2 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_2 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_2 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_2 thin film using 20% of ethanol was transparent compared to 70% of ethanol.

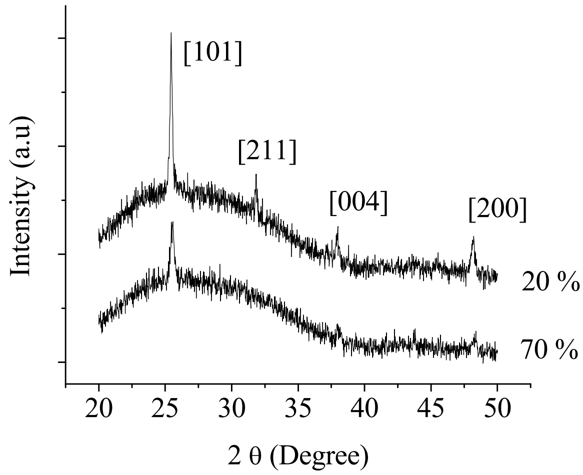

Figure 6. XRD spectra of 20% and 70% amount of ethanol.

(a)

(b)

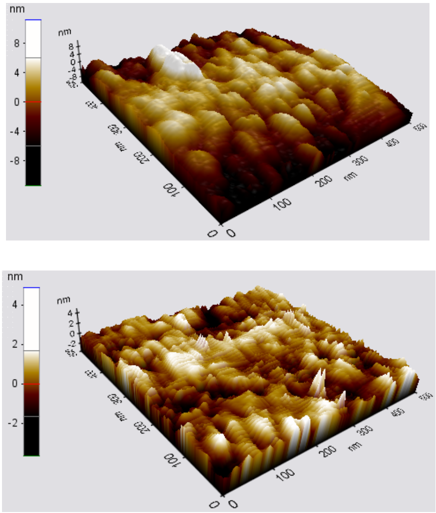

Figure 7. AFM image of (a) 20% and (b) 70% amount of ethanol

Figure 6 shows the XRD analysis of TiO_2 thin film using 20% and 70% of ethanol solvent. The peak of anatase TiO_2 is decreased with the increasing amount of ethanol. The XRD spectra of nanostructured TiO_2 thin film with 70% amount of ethanol shows single peak of anatase compared to nanostructured TiO_2 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_2 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_2 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_2 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_2 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 crytallinity and morphology of TiO_2 thin film. The annealing process gives anatase phase of nanostructured TiO_2 thin film appears in XRD spectra. The anatase peak of nanostructured TiO_2 thin film can be identified clearer with increase number of layer.

Roughness of TiO_2 thin film is increase with annealing process and number of layer but decrease with increasing amount of ethanol.

The resistivity of TiO_2 thin film decrease with annealing process and amount of ethanol but increase with the number of layer deposited on nanostructured TiO_2 thin film.

Finally, we propose that the TiO_2 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_2 thin film is needed.

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REFERENCES

[1] V. Thavasi a, V. Renugopalakrishnan, R. Jose, S. Ramakrishna , *Controlled electron injection and transport at materials interfaces in dye sensitized solar cells*, Materials Science and Engineering R 63 (2009) 81–99.

[2] Sancun Hao, Jihuai Wu, Leqing Fan, Yunfang Huang, Jianming Lin, Yelin Wei, *The influence of acid treatment of TiO_2 porous film electrode on photoelectric performance of dye-sensitized solar cell*, Solar Energy 76 (2004) 745–750.

[3] C. Legrand-Buscema, C. Malibert, S. Bach, *Elaboration and characterization of thin films of TiO_2 prepared by sol–gel process*, Thin Solid Films 418 (2002) 79–84.

[4] Bin Li, Liduo Wang, Bonan Kang, Peng Wang, Yong Qiu , *Review of recent progress in solid-state dye-sensitized solar cells*, Solar Energy Materials & Solar Cells 90 (2006) 549–573.

[5] N Naseri, M Amiri and A Z Moshfegh,, *Visible photoenhanced current voltage characteristics of Au : TiO_2 nanocomposite thin films as photoanodes*, J. Phys. D: Appl. Phys. 43 (2010) 105405 (8pp).

[6] N.Wetchakun, S.Panicchphant, Current Applied Physics, Volume 8, Issue 3-4, May 2008, Pages 343-346.

[7] Fernando Gordillo Delgado.et.al, Microelectronics Journal, Volume 39, Issue 11, November 2008, pages 1333-1335.

[8] C.Su, B.Y.Hong, C.M.Tseng, Catalysis Today, Volume 96, Issue 3, October 2004, Pages 119-126.

[9] Judy N. Hart, David Menzies, Yi-Bing Cheng, George P. Simon, Leone Spiccia, *"A comparison of microwave and conventional heat treatments of nanocrystalline TiO_2"* Solar Energy Materials & Solar Cells 91 (2007) 6–16.

[10] J. Nowotny, T. Bak and T. Burg, "*Electrical properties of polycrystalline TiO2· Thermoelectric power*", Journal of ionics, Volume 13, Number 3, 155-162.

[11] H.P. Deshmukha, P.S. Shinde b, P.S. Patil b, "*Structural, optical and electrical characterization of spray-deposited TiO_2 thin films*", Materials Science and Engineering B 130 (2006) 220–227.