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Effect of Annealing Temperatures on Surface Morphology and Electrical Properties of Titanium Dioxide Thin Films Prepared By Sol Gel Method

M.K. Ahmad[1, 4,*], M.L.M. Halid[1], N.A.Rasheid[1], A.Z. Ahmed[3], S. Abdullah[2] and M. Rusop[1, 2]

[1]Solar Cell Laboratory, Faculty of Electrical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia
[2]NANO-SciTech Laboratory, Faculty of Applied Sciences
Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia
[3]Institute of Research Development and Commercialization (IRDC)
Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia
[4]Faculty of Electrical and Electronic Engineering
University Tun Hussein Onn Malaysia, 86400 Batu Pahat, Johor, Malaysia
* Corresponding author: k_rul19@yahoo.com

Abstract: The effects of annealing temperatures on the surface morphology and the electrical properties of titanium dioxide (TiO_2) thin films prepared by the sol-gel method were studied. TiO_2 thin films were deposited on silicon substrates using the spin coater technique. By varying the parameters of the annealing temperatures, The TiO_2 thin films were deposited onto silicon substrates. Characterization was done using current-voltage (I-V) measurement and scanning electron microscopy (SEM). TiO_2 thin films were annealed at 300°C, 350°C, 400°C, 450°C and 500°C. The result indicated that the electrical properties of the TiO_2 thin films were changed with the increasing of the annealing temperature. As the annealing temperature increased, the resistivity decreased. The SEM investigation showed that the grain size of the TiO_2 increased with higher annealing temperatures. The results showed that surface porosity, electrical properties and surface morphology of TiO_2 could be affected by changing the annealing temperature.

Keywords: Titanium Dioxide Thin Film; Sol Gel Method; Electrical Properties.

1. Introduction

Many kinds of applications for metal oxide thin film have been discovered. Most of the applications are in electronics, solar cells, sensors, refractory, wear and corrosion-resistant coating. Titanium dioxide is a promising oxide material that has useful electrical and optical properties and also excellent transmittance of visible light [1-3]. The TiO_2 films were synthesized using the sol-gel method. This is of particular interest because of the advantages ensured by this method [4]. The crystallization and oxide film formation was affected by the thermal treatment of the modified sol-gel. Titanium Isopropoxide produced high hydrolysis and polycondensation rates and precipitated into condensed particles when combined with water. Chemical modification of alkoxides with different agents is very important in the sol-gel method. It can change the formation of new molecular precursors that can produce a wide range of new properties, a reported by Sanchez and co-workers [5, 6]. Chemical modification has a strong effect on parameters, such as particle size, morphology, porosity and etc. Two different methods of heat treatment are usually used. First is annealing each layer at a temperature sufficient for crystallisation of the film [7, 8]. Next is drying the titanium oxide film. The temperature was between 373 and 423K after the deposition of the last layer [9, 10]. Nevertheless, there are no publications comparing the result of these two kinds of heat treatment. In this study, titanium oxide films were obtained by the sol-gel method and TiO_2 thin films were deposited by using the spin coating method. The concentration and quantity deposition layer of the sol-gel is controlled while the annealing temperature using current-voltage (I-V) measurements using an Advantest source meter (R6243). The surface morphology and electrical is changed. The aim of this work is to prepare and study the influence of annealing temperatures in single layered TiO_2 thin films on silicon and glass substrate.

2. Experimental

Silicon and glass substrates were used as substrates. The silicon substrates cleaned with acetone, methanol, distilled water and hydrogen fluoride, followed by drying in an oven. The glass was also cleaned with acetone, methanol and distilled water, followed by drying in an oven. The TiO_2 solution was prepared by mixing the glacial acetic acid (5.5 ml), titanium (IV) Isopropoxide (5 ml) and triton X-100 (1 drop) with 2-propanol (10 ml). Deionised water (3 ml) was added to the solution drop wise while vigorously stirring the solution. The solution was heated at 50ºC and stirred for about 1 hour. The heating process increased the reaction process between the materials in the solution. Then the solution was continuously stirred for 24 hours at room temperature.The TiO_2 thin films were deposited on silicon and glass substrates by using the spin coating technique. Spin coating was set at the speed of 3000 rpm and nitrogen (N_2) gas at 60 psi. The TiO_2 solution was dropped 10 times onto the substrates and the TiO_2 thin films were dried in the oven at 100°C for 10 minutes. The dropping was done 10 times and drying process 1 time for the TiO_2 thin films. After that, the films were annealed at 300°C, 350°C, 400°C, 450°C and 500°C for 1 hour in the furnace without using any gases. The surface morphology of the TiO_2 thin films was observed by using a Scanning Electron Microscope (JSM-6380LA) at the same magnification. The electrical properties were measured by measurements were carried out at different temperatures (from 300ºC to 500ºC).

3. Results and discussion

3.1 Surface morphology study

The TiO_2 thin films were observed in a Scanning Electron Microscope (SEM) to investigate their structure and surface characteristics. Microstructures of the sample after being annealed at different temperatures are shown in the figure below. For TiO_2 thin films deposited on silicon substrate (Figure 1a, 1b, 1c and 1d), the grain size of TiO_2 is large at higher annealing temperatures. It has been observed that TiO_2 thin film deposited on silicon substrate has less pore area on the surface area. Referring to Fig. 1b, the pore area is increased. In Fig. 1c, the porosity of TiO_2 thin film is improved. The porosity at 500ºC is the highest among the sintered temperatures. This shows that the surface area and pore volume decrease with the increase of annealing temperatures. The pore diameter increases due to increase in the crystal size of TiO_2 [11].

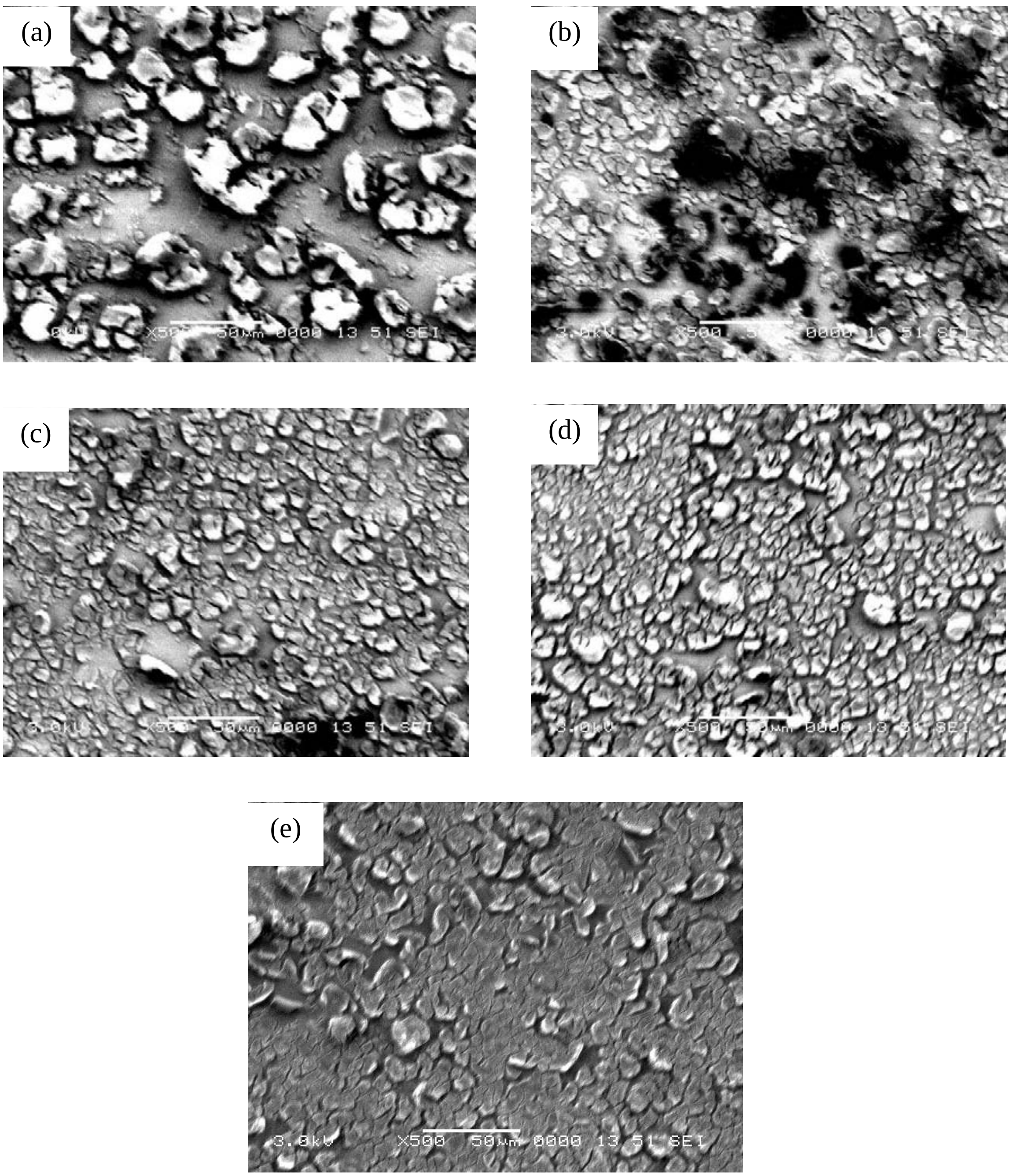

Figure 1. (a), (b), (c), (d) and (e) SEM image of TiO_2 thin film anneal at 300ºC, 350ºC, 400ºC, 450ºC and 500ºC using spin coater method at speed of 3000 rpm on silicon substrate respectively.

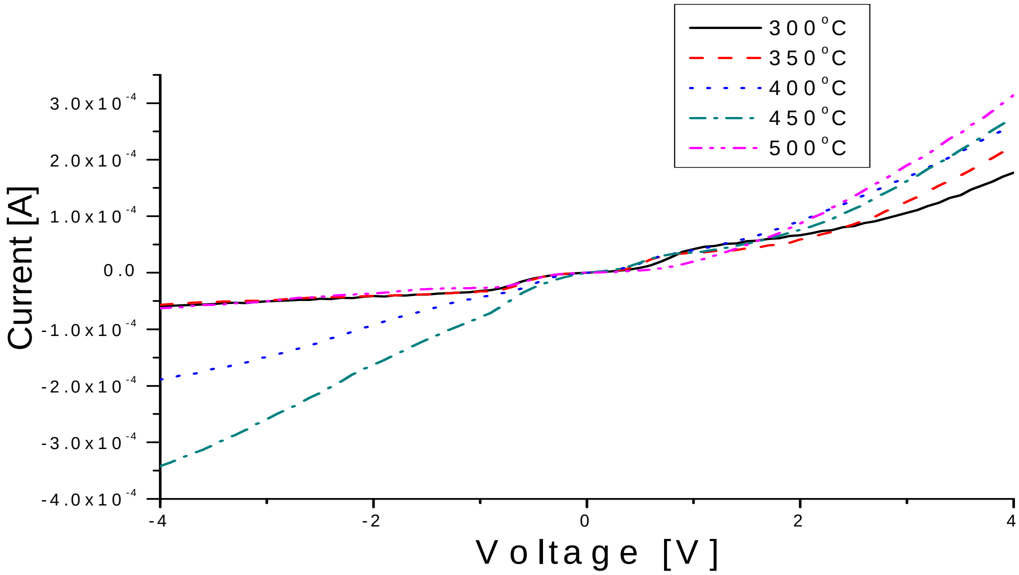

Figure 3. Shows I-V characteristics for TiO_2 thin films deposited onto silicon substrate.

3.2 Electrical Properties of TiO_2 Thin Film

Current-Voltage (I-V) measurements were performed using the TiO_2 thin film structures to determine their electrical properties. Figure 2 shows the schematic structure of the TiO_2 thin films which has gold (Au) on top of the thin film, which is used as a metal contact for I-V measurement.

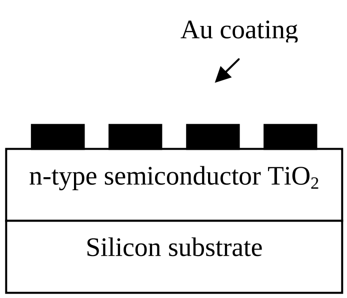

Figure 2. Diagram of Au coating process on silicon substrate.

3.3 I-V Characteristic TiO_2 thin film on silicon substrate

Figure 3 shows the I-V characteristic of TiO_2 thin films deposited on silicon substrate. I-V characteristics were measured at different annealing temperatures. The resistance decreased when the annealing temperatures were increase. This is due to the grain size. When grain size becomes larger, electron movement from particles to other particles improves. Therefore the resistivity of TiO_2 thin films decreased after the annealing process was done. The annealing process produces electronic contacts not only between the particles and the support but also between all the particles of the film. With I-V, we can also show that prepared TiO_2 thin film have n type conductivity. We can see that the I-V graph has a barrier and giving Schottky contact properties.

There are others method that can be used in characterizing TiO_2 thin films at different annealing temperatures, for example, BET surface area measurements and X-Ray Diffraction. In this study, we are only focusing on how annealing temperatures affect the surface morphology and the electrical properties. The investigations of the crystallinity of TiO_2 thin films at annealing temperatures require XRD characterization.

In the experiments, the annealing temperatures were carried out only until 500°C because based on the study of Z.W. Zhao et al. [12] and D.–J. Won et al. [13], at temperatures higher than 500°C, the TiO_2 thin film surface became rougher and decreased the contact surface of the thin film. With less contact surface, electron mobility decrease, and so, electrical properties also decrease. The research in preparation of TiO_2 thin film in the experiment is be used in Dye-sensitized Solar Cell (DSSC) applications. In the fabrication of DSSC, the thin film must have high porosity and a high contact surface. Referring to the study of K.-M. Lee at el. [14], DSSC performance depends strongly on TiO_2 film morphology. Nano particles are essential for increasing the surface are of the film in order to absorb sufficient dyes. Referring to Z.W. Zhao et al. [1] and D. –J. Won et al. [2], we believe that controlling the temperature below 500°C will be suitable for using the TiO_2 thin film in DSSC applications.

4. Conclusion

Titanium dioxide thin films have been successfully deposited onto silicon substrates by the spin coating technique and annealed at different temperatures. The surface morphology and electrical properties of the TiO_2 thin films were investigated by using SEM and I-V measurements. SEM measurements for TiO_2 thin films deposited on silicon showed that the porosity of the thin films increased at high annealing temperature. The grain size increased when the annealing temperature was increased. The resistivity of the TiO_2 thin films decreased when the annealing temperature increased.

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