Effect of annealing temperature on surface, structural and electrical properties of titanium dioxide thin films prepared by sol gel method

M. K. Ahmad[a], N. A. Rasheid[a], A. Zain Ahmed[c], S. Abdullah[b], and M. Rusop[a,b]
[a]*Solar Cell Laboratory, Faculty of Electrical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia*
[b]*NANO-SciTech Centre, Institute of Science, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysi*
[c]*Research Management Institute (RMI), Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia*

(Received 26 December 2007)

Nanocrystalline anatase and amorphous Titanium Dioxide (TiO_2) thin film have been prepared using sol-gel method and deposited by spin coater technique. The influence of annealing temperature on the structural, surface morphology and electrical properties of the thin film is characterized by Scanning Electron Microscopy (SEM) and I-V measurement. The result indicates that nanocrystalline anatase phase can be obtained at annealing temperature of 300ºC or above. Titanium dioxide thin films were deposited on silicon substrates. Annealing temperature at T=As deposited, 100°C, 300°C and 500°C have been observed. As deposited substrates is also observed. The result indicated electrical properties of titanium dioxide thin films were changed with annealing temperatures. As the annealing temperature rises, the resistivity will decreased. The SEM investigation showed that grain size of titanium oxide increased with higher annealing temperature. Furthermore, the SEM result indicated lattice matching between titanium dioxide and substrate is important to produce good quality titanium dioxide thin film after annealing process. The results suggest that surface porosity, electrical properties and surface morphology of titanium dioxide could be affected by changing annealing temperatures for electronic devices application.

I. INTRODUCTION

Many kind of application for metal oxide thin film now day has been discovered. Mainly come from electronics application, solar cell application, sensors, refractory, wear and corrosion-resistant coating. Titanium dioxide is promising oxide material that has useful in electrical and optical properties and also excellent transmittance of visible light [1-3]. This films synthesis by sol-gel method is particular interest because of the advantages ensured by this method [4]. The crystallization and oxide film formation effected by the thermal treatment of the modified sol-gel. Titanium tetraisopropoxide produced high hyrolysis and polycondensation rates and to precipitate into condensed particle when combined with water. Chemical modification of alkoxides with different agents is very important in sol-gel method. It can change formation of new molecular precursors that can produce a wide range of new properties.

The sol-gel technique has emerged as a new and promising processing route for nano-sized TiO_2 thin films fabrication because of its simplicity. For many technological applications, low processing temperature is highly desired because it enables the use of certain substrate materials and/or prevents harmful film-substrate interaction. In other hand, the sol-gel processing starting from metal alkoxide or some other metal-organic precursors still requires processing temperatures in excess of 400ºC for the crystallization and removal of organics. The strong reactivity of the alkoxide towards H_2O often results in an uncontrolled precipitation and limiting the use of the sol-gel technology. These problems have been overcome with the aid of chelating agents, such as acetic acid [5]. Amorphous and polycrystalline forms of $Ti0_2$ can be readily prepared using the sol-gel technique [6] which offers the possibility of relatively low cost, large-scale production of thin films. Many researches have been done to identify significant interactions between process parameters such as withdrawal rate, sol concentration and the number of coating layers and their effects on structural, optical and electrical properties of sol-gel derived TiO_2 thin films [7]. To optimize the properties of TiO_2 films, the films must be prepared with enhanced crystallinity. However, the as-deposited TiO_2 films are often mainly amorphous when the substrates are not heated during spin coating process, and this is the manner adopted industrially. So it is necessary in the preparation of TiO_2 films to anneal them after spinning to improve their crystallinity, thus achieving TiO_2 films optimum for applications in photo-catalysis, dye-sensitized solar cells, and photo-induced hydrophilicity [8-10]. On the other hand, the heat treatment can produce other effects on film structure, resulting in changes in some properties and chemical composition. Many annealing parameters, such as the atmosphere annealing time and temperature schedule, can affect the film structure. In this paper, we investigate as deposited thin film, 100ºC, 300ºC and 500ºC of annealing temperature.

II. MATERIAL AND METHODS

Silicon wafer was used as substrate. The silicon substrates were cleaned with acetone, methanol, distilled water and hydrogen fluoride, followed by drying in 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 heat at 50ºC and stirred for about 1 hour. Heating process is to increase 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 by using spin coating technique. Spin coating was set at one speed of 3000 rpm, 30 sec and nitrogen (N_2) gas at 60 psi. TiO_2 solution was dropped 10 times onto the substrates and TiO_2 thin films were dried in the oven at 100°C for 10 minutes. 10 times drop and 1 time dry process was considered as 1 cycle and this processes were repeated for 5 times. After that, the films were annealed at 100°C, 300°C and 500°C for 1 hour in the furnace without using any gases.The surface morphology of TiO_2 thin films were observed by using Scanning Electron Microscope in same magnification. The electrical properties were measured by using current-voltage (I-V) measurement. The surface morphology and electrical measurement were carried out for the films prepared at different temperatures, from as deposited thin film, 100ºC, 300ºC and 500ºC.

III. RESULTS AND DISCUSSION

The surface morphology of the films has been observed using scanning electron microscopy (SEM-JEOL). SEM images shown in Fig. 1 have evidenced crack free films with small grain boundaries being observed in the as deposited annealed film. The films annealed at 100ºC, 300ºC and 500ºC, exhibit a unique feature of simultaneous presence of irregularly shaped polycrystalline grains and dark regions. These dark regions in the films represent the presence of high porosity. The highest degree of porosity has been exhibited by the 500ºC annealed films. Formation of well-defined grains with the increasing annealing temperature is also evident from Fig. 1, which shows segregation of the polycrystalline grains into fine grains at 500ºC, i.e. annealing at higher temperatures results in finer clusters. With an increase in annealing temperature, the clusters reduce in size and also their shape changes from irregular to elliptical. The SEM study has clearly illustrated that the distribution of clusters in the 100ºC, 300ºC and 500ºC annealed films is different with the as deposited film that showing clustering of the nanosized grains and the latter exhibiting fine-grained microstructure. As mention in K. Madhusudan Reddya *et al*., Anatase phase in TiO_2 thin film exist at 250ºC until 800ºC and gain its significant only after nanostructured material condition in formed [11]. From the images that gained from this experiment, the TiO_2 thin film clusters size reduce as the annealing temperature increased. With this, high porosity of thin film and high electrical properties can be obtained. The crystalline clusters will give high quality in electrical properties due to electron in the thin film can easily move to one another.

Current-Voltage (I-V) measurements were performed using the TiO_2 thin films structure to determine their electrical properties. Fig.2 shows the schematic diagram of electrode TiO_2 thin films used for I-V measurement which deposited on silicon substrates. The electrode was deposited using Aurum (Au) material.

Fig. 3 shows the I-V characteristic of TiO_2 thin film deposited on silicon substrate. I-V characteristics were measured with different annealing temperature. I-V characteristic was determined that resistance will decrease when the annealing temperature is increase. This is due to the grain size. When grain size becomes larger, large grain size will improved electron migration. Therefore resistivity of TiO_2 thin films also can increase considerably after thermal treatment. Thermal treatment produces electronic contacts not only between the particles and the support but also between all the particles of the film.

IV. CONCLUSION

Titanium dioxide thin films have been successfully deposited by using sol-gel method of spin coating technique and annealed at different temperatures. The surface morphology and electrical properties of TiO_2 thin films were investigated by using SEM and I-V measurement. According to SEM studies, the films are homogeneous, porous, and uniform. The same study also demonstrates that the cluster size reduces as a function of annealing temperature. SEM measurements for TiO_2 thin films deposited on silicon showed that **t**he porosity of thin film increase at high annealing temperature. The grain size increase when the annealing temperature is increased. The resistivity of the TiO_2 thin films increased with increased of annealing temperature and for various annealing temperature.

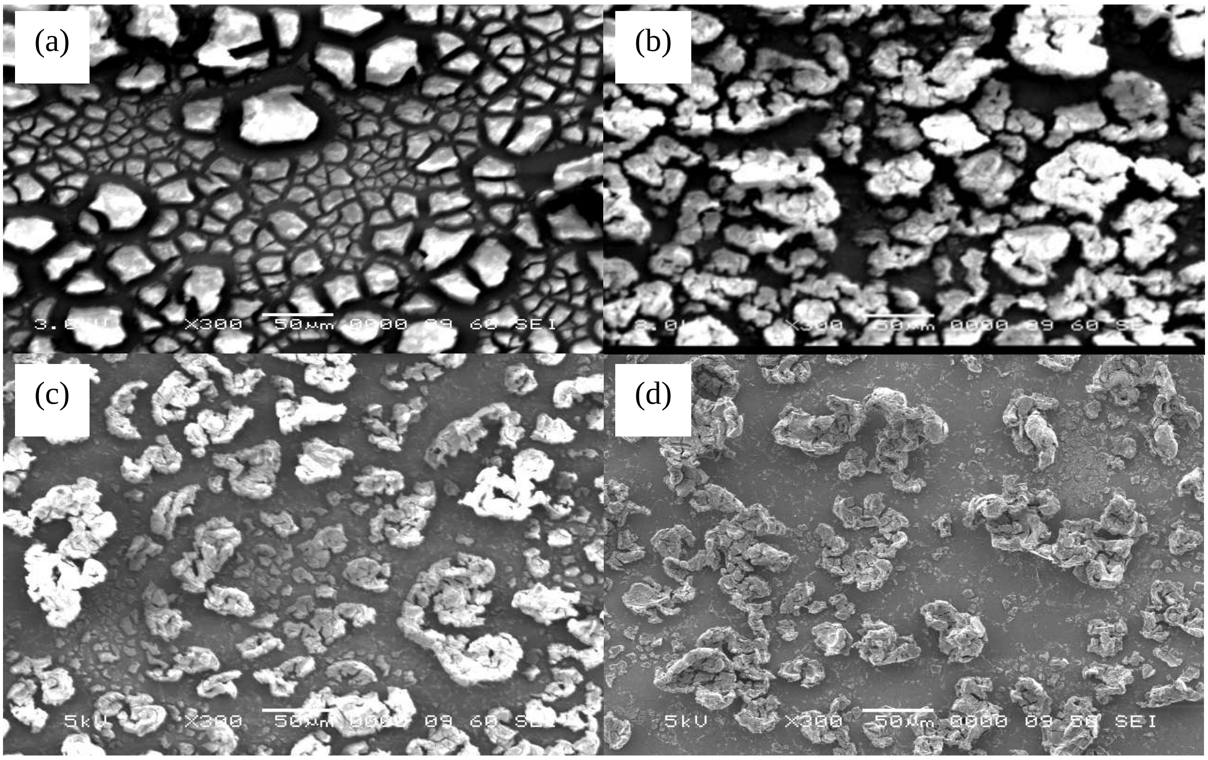

FIG. 1. SEM image of TiO_2 thin film at as deposited and anneal at 100ºC, 300ºC and 500ºC using spin coater method at speed of 3000 rpm on silicon substrate respectively.

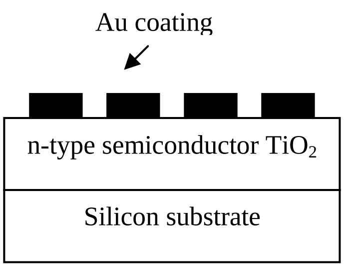

FIG. 2. Diagram of Au coating process on silicon substrate.

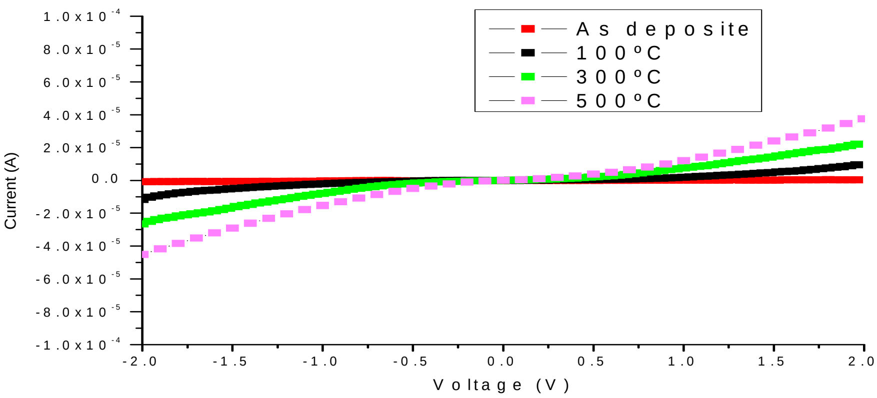

FIG. 3. I-V characteristic for TiO_2 thin film deposited onto silicon substrate.

ACKNOWLEDGEMENT

This work was financially supported by Institute of Science and Research Management Institute (RMI), Universiti Technologi MARA (UiTM), Malaysia. The authors gratefully thank to all member of NANO-SciTech Centre, UiTM for technically support and Universiti Tun Hussin Onn Malaysia (UTHM) in this research technical support.

REFERENCES

[1] Q. Fan, B. McQuillin, A.K. Ray, M.L. Turner and A.B. Seddon, J. Phys., D, Appl. Phys., **33**, 2683 (2000).

[8] C. Guillard, H. Lachheb and A. Houas, J. Photochem. Photobiol. A: Chem., **158**, 27-36 (2003).

[10] J. N. Hart, R. Cervini and Y. B. Cheng, Sol. Energ. Mater. Sol. Cells, **84**, 135-143 (2004).

[3] D. H. Kim, J. S. Yang, K. W. Lee, S. D. Bu, D. W. Kim and T. W. Noh, J. Appl. Phys., **93**, 6125 (2003).

[11] R. K. Madhusudan, V. M. Sunkara and A. R. Ramachandra, Materials Chemistry and Physics, **78**, 239-245 (2002).

[9] M. Nakamura, T. Aoki and Y. Hatanaka, J. Mater. Res., **16**, 621-626 (2001).

[5] C. Sanchez, J. Livage, M. Henry and F. Babonneau, J. Non-Cryst. Solids, **100**, 65-76 (1998).

[2] T. Sasaki, Y. Ebina, M. Watanabe and G. Decher, Chem. Commun., 2163 (2000).

[7] U. Selvaraj, A. V. Prasadarao, S. Komarneni and Roy, J. Am. Ceram. Soc., **75**, 1167-1170 (1992).

[6] S.M. Tracey, S.N.B. Hodgson, A.K. Ray and Ghassemlooy, J. Muter. Process. Technol., **7**, 86-94 (1998).

[4] D. Uhlman and G. Teowe, J. Sol Gel Sci. Technol., **13**, 153-162 (1998).