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Effect of Annealed Temperatures on the Morphology of TiO_2 Films

Weeranut Kaewwiset*, Wandee Onreabroy and Pichet Limsuwan

ABSTRACT

Titanium dioxide (TiO_2) films were prepared by dip-coating method on the glass slide substrates at room temperature. The TiO_2 solution was synthesized from titanium tetraisopropoxide:$Ti(OC_3H_7)_4$ in isopropanol at molar ratio 1:4. This research focus on the surface and roughness of TiO_2 films which were characterized by atomic force microscopy (AFM). In the first experiment, TiO_2 films were deposited at 1, 5, 10 and 15 layers and annealed at 500 °C. Then, the films which were deposited for 15 layers were chosen to be annealed at different temperatures of 300, 350, 400, 450 and 500 °C. The results showed that, when the number of film layers increased, the grain sizes were clearly observed. The grain size depended on the annealing temperature. It was found that at the temperature of 300 to 500 °C, the grain sizes were 30-40 nm.

Key words: TiO_2, AFM, temperature

INTRODUCTION

Titanium dioxide (TiO_2) thin films were used in a variety of applications both in industrial and in our daily life such as detoxification of polluted water, air deodorization and protective anti-reflection coating (Xagas *et al*., 1999). TiO_2 has three phases: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Anatase and rutile are of engineering importance because their properties are unique (Qiu and Kalita, 2006). The anatase phase deposited at temperature below 800 °C, at higher temperature, it transformed to the more stable rutile phase (Sen *et al*., 2005).

Recently, there are many researchers working on TiO_2 dip coating or sol-gel method (Zaharescu and Crisan, 1998; Yu *et al*., 2002; Sreemany and San, 2006). TiO_2 crystalline size was controlled by annealing at various temperatures and the grain size was analyzed by using atomic force microscopy (AFM) (Hou *et al*., 2003; Verma *et al*., 2005).

This research focus on the analyzing of the grain size and roughness of TiO_2 thin films by annealing at different temperatures. TiO_2 sol-gel was prepared from Titanium tetraisopropoxide (TTIP) in isopropanol and pH of the solution was adjusted with nitric acid before the TiO_2 films was annealed at various temperatures. The AFM was used to scan and analyze the grain size of TiO_2 thin films at each temperature.

MATERIALS AND METHODS

The flow chart for the synthesis of TiO_2 is given in Figure 1. The solution was prepared from titanium tetraisopropoxide $Ti(OC_3H_7)_4$ (TTIP, 97% Aldrich) in isopropanol at molar ratio 1:4 under continuous stirring at room temperature, pH of the solution was adjusted to 2-3 by using

Department of Physics, Faculty of Science, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand.
* Corresponding author, e-mail: opticslaser@yahoo.com

nitric acid (Porkodi and Arokiamary, 2007). The solution was successively stirred about 2 hours until transparent sol was obtained. Sol was kept 24 hours before coating and aged for several months.

Glass slides which were used as substrates were cleaned with a mixture of sulfuric acid and hydrogen peroxide at a ratio of 3:1 by volume in an ultrasonic cleaner and followed by cleaning with de-ionized water. Finally, the glass was washed with acetone and dried at 100 °C for 30 minutes (Sreemany and Sen, 2004). TiO_2 thin films were deposited on glass slides by dip coating method at two different vertical withdrawal speeds of 1 and 2 cm/min. TiO_2 films were deposited 1, 5, 10 and 15 layers on substrates and during successive coatings, each layer was annealed at 120 °C for 30 min. When multiple dip coating was finished, the films were annealed again at various temperatures: 300, 350, 400, 450 and 500 for 2 hour at the heating rate 5 °C/min in an atmosphere.

In this research, the surface roughness and morphologies of the TiO_2 films obtained at different layers and heat treatment temperatures were evaluated by atomic force microscopy (AFM).

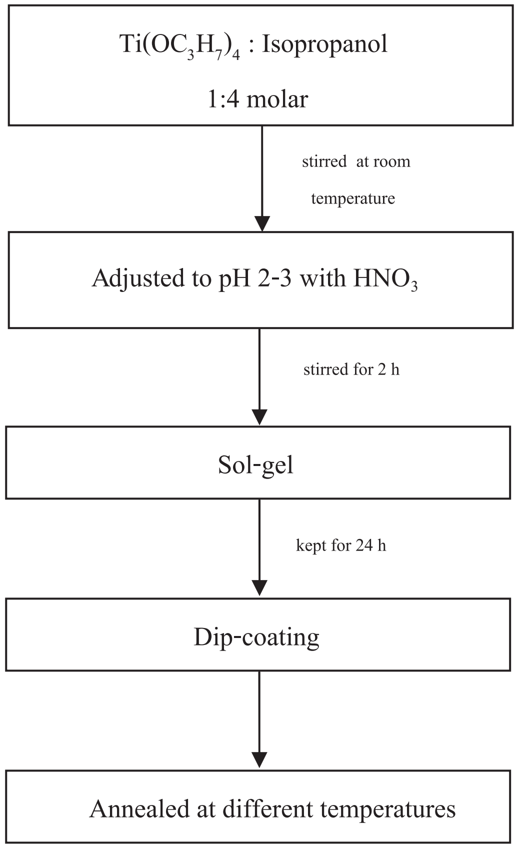

Figure 1 Flow chart of the sol-gel preparation of TiO_2 films.

RESULTS AND DISCUSSION

The surface morphologies of TiO_2 films deposited on glass slides substrates were observed by AFM and the influence of annealing temperature has been studied. The surface morphology pictures of TiO_2 films are shown in Figure 2 and 3. Figure 2 shows two and three dimensional AFM images of the TiO_2 films at different deposited layers at 500 °C. Figure 2 (a) and (b) represented the TiO_2 films deposited at 1 and 5 layers, respectively. It can be seen that both films show a rough surface, the difference on the surface could not be clearly observed. When the deposited layers were increased to 10 and 15 layers, Figure 2 (c) and (d), respectively, morphology and surface of the films were observed. When the films were deposited 15 layers the surface morphology were most clearly observed. These films were then chosen to be annealed at 300, 350, 400, 450 and 500 °C.

Figure 3 (a) shows the surface morphology of as-deposited TiO_2 films, column-like structure is found. The diameter of these column-like grains is about 27–37 nm. The surface of TiO_2 films is fine and compact. Figure 3 (b) and (c) are the surface morphology pictures of TiO_2 films annealed at 300 and 350 °C, respectively. Some column-like crystal grains of 500 nm in diameter appeared in this picture. Ya-Qi Hou *et al.* (2003) have studied the influence of annealed temperature of TiO_2 films and found that the anatase phase appeared at 300 °C. Our experiments agree with them, but most of the grains in these

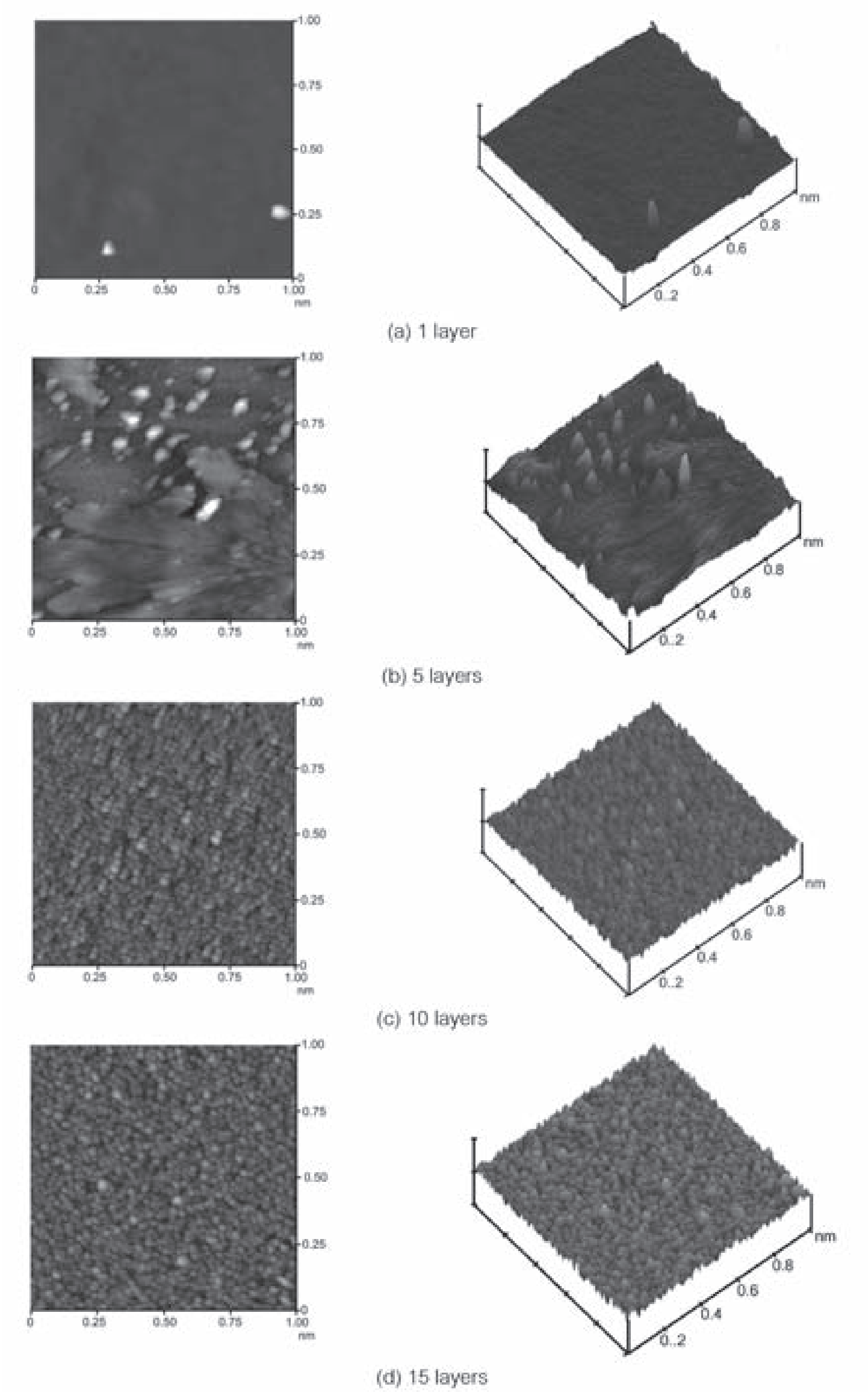

Figure 2 Two and three-dimensional AFM images of TiO_2 films with different deposited layers at 500 °C. (a) 1 layer, (b) 5 layers, (c) 10 layers and (d) 15 layers.

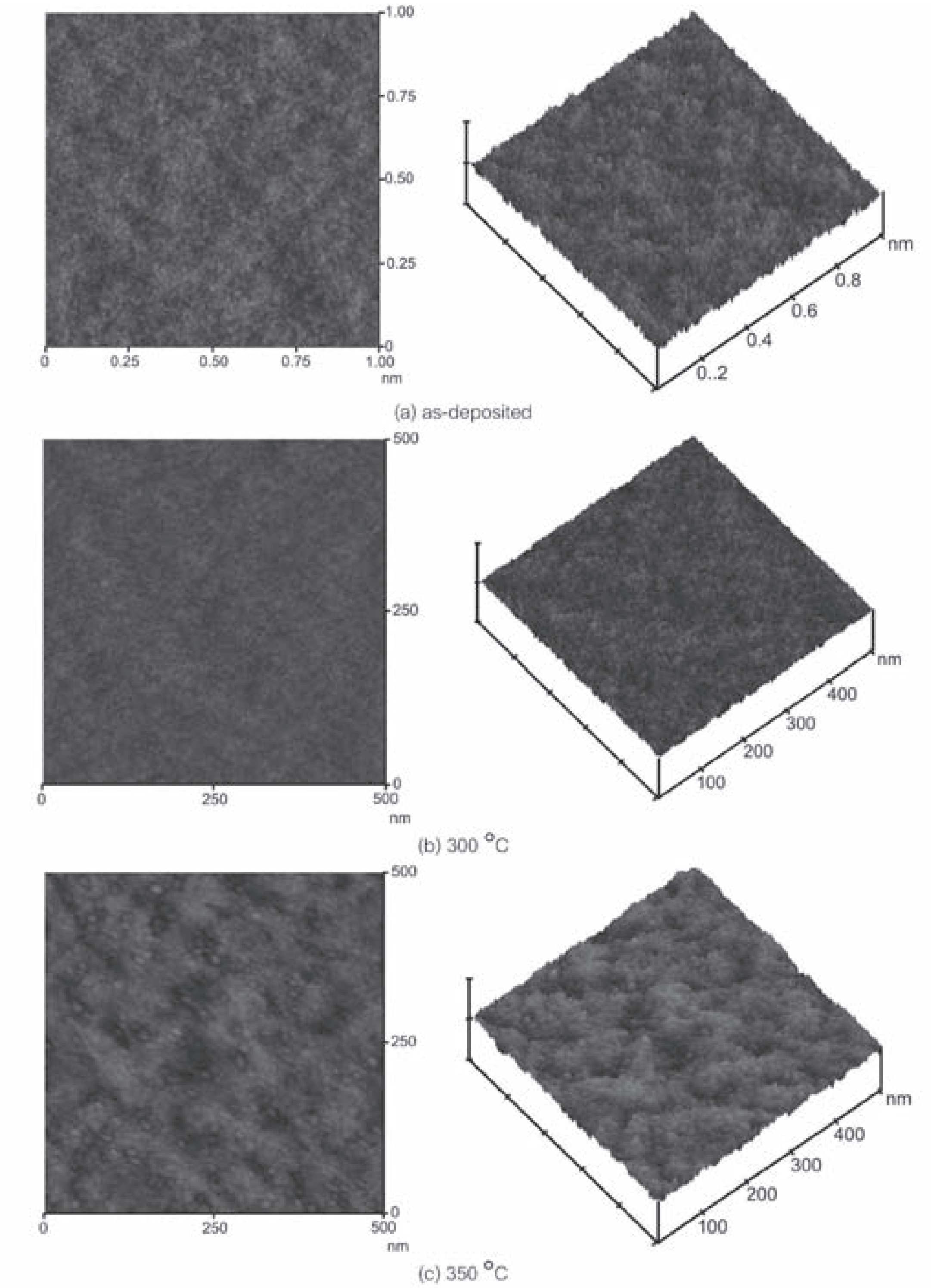

Figure 3 Two and three-dimensional AFM images of TiO_2 films annealed at different temperatures. (a) as-deposited, (b) 300 °C, (c) 350 °C, (d) 400 °C, (e) 450 °C and (f) 500 °C.

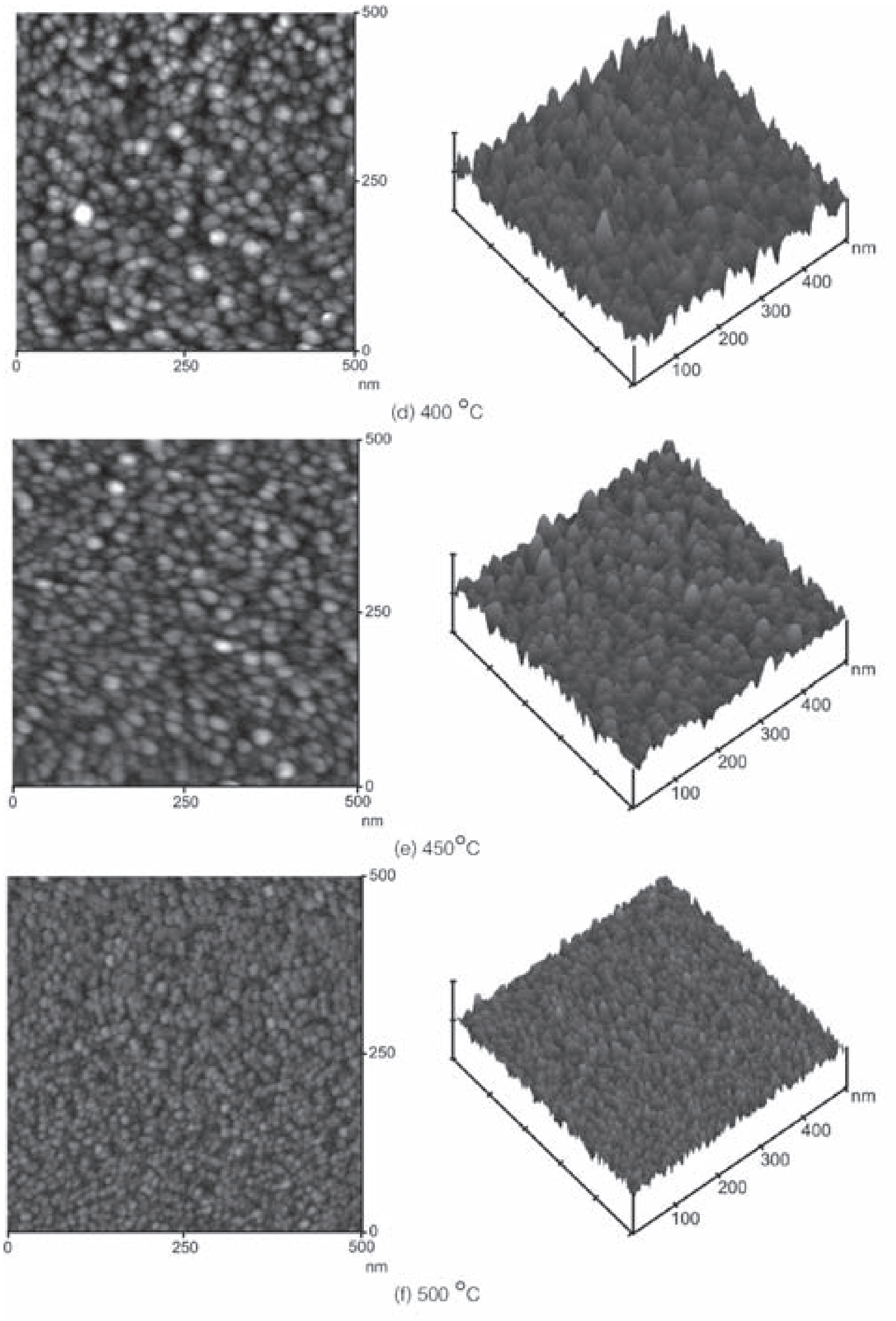

Figure 3 (continued).

films should be still amorphous. Figure 3 (d), (e) and (f) show surface morphologies of TiO_2 films annealed at 400, 450 and 500 °C, respectively the grain size of the annealed films were estimated at about 27.69, 32.69 and 36.54 nm, respectively. The larger anatase crystal grains were observed and the differences between the large and small grains were obviously observed.

In order to support the AFM observation, rms roughness measurement of TiO_2 films have been carried out. The rms values increase slowly from 0.266, 0.516, 1.192, 1.355 to 1.647 nm when the annealing temperature increases from 300, 350, 400, 450 to 500 °C, respectively. When the temperature was increased the roughness and grain size were also increased.

CONCLUSION

Atomic force microscopy (AFM) was used to study the influence of the thermal treatment on the structural and properties of sol-gel TiO_2 films produced from $Ti(OC_3H_7)_4$. The TiO_2 films were deposited at room temperature by dip-coating method. The TiO_2 films can be clearly observed when the films were deposited for fifteen layers and annealed at 500 °C. After the films were annealed at 300 to 500 °C for 2 hr, some crystal grains with anatase structure appeared. The roughness and grain size were increased with increasing annealed temperature.

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