Effect of Annealed Temperatures on the Morphology of TiO$_2$ Films

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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$_3$H$_7$)$_4$ 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 $^\circ$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 $^\circ$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 $^\circ$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 $^\circ$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$_3$H$_7$)$_4$ (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...
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). TiO₂ thin films were deposited on glass slides by dip coating method at two different vertical withdrawal speeds of 1 and 2 cm/min. TiO₂ 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 °C for 2 hour at the heating rate 5 °C/min in an atmosphere.

In this research, the surface roughness and morphologies of the TiO₂ films obtained at different layers and heat treatment temperatures were evaluated by atomic force microscopy (AFM).

**RESULTS AND DISCUSSION**

The surface morphologies of TiO₂ films deposited on glass slides substrates were observed by AFM and the influence of annealing temperature has been studied. The surface morphology pictures of TiO₂ films are shown in Figure 2 and 3. Figure 2 shows two and three dimensional AFM images of the TiO₂ films at different deposited layers at 500 °C. Figure 2 (a) and (b) represented the TiO₂ 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 TiO₂ films, column-like structure is found. The diameter of these column-like grains is about 27–37 nm. The surface of TiO₂ films is fine and compact. Figure 3 (b) and (c) are the surface morphology pictures of TiO₂ 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 TiO₂ 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$_3$H$_7$)$_4$. 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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**LITERATURE CITED**


