JOURNAL OF MATERIALS SCIENCE **36** (2001) 5923–5926

Preparation and characterization of TiO_2 thin films by the sol-gel process

TIANFA WEN, JIANPING GAO, JUYUN SHEN
The Third Department, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai, 200050, People's Republic of China
E-mail: tfwen@hotmail.com

ZHONGSHEN ZHOU
The Material Department, Northwest Institute of Light Industry, Xianyang, Shaanxi, 712081, People's Republic of China

Titanium dioxide (TiO_2) thin films have been prepared on microscope slide by the sol-gel process. The preparation of covering solution is investigated with the method of orthogonal experimental design, and the heat treatment temperature and time, which influenced on the films properties are discussed. And the TiO_2 thin films had been studied by the means of differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). © *2001 Kluwer Academic Publishers*

1. Introduction

Titanium dioxide (TiO_2) is an important inorganic functional material with good physical properties, which make it suitable for thin film applications. Because TiO_2 has high dielectric constant ε, TiO_2 films have often been used in microelectronic devices, e.g. in capacitors or as a gate dielectric in metal-dielectric-semiconductor devices [1, 2]. TiO_2 thin films are also often used as various optical coatings for its good transmittance in the visible region, high refractive index and chemical stability [3–6]. Recently TiO_2 has been widely investigated [7, 8] because of its high efficiency of hydrogen generation and also its high photostability in an aqueous solution, which opens prospects for the use of TiO_2 thin films as photocatalyst, bactericide, photoanodes, etc.

There are many methods to prepare TiO_2 films: chemical vapor deposition (CVD) [9], thermal [10] or oxidation of titanium [11], electron beam evaporation [12], ion sputtering [13] and the sol-gel method [3, 5].

The sol-gel technique has been used for making optical coatings about 50 years ago and in the last decade attracted more attention due to the intensive development of sol-gel technology. In comparison with other films technologies the sol-gel process has certain advantages: low process cost, low temperature of heat treatment, high evenness of the films and wide possibility to vary film properties by changing the composition of the solution, etc.

The orthogonal experimental design is an excellent method of experiment design, which has been widely used in scientific research. It has the quality "equilibrium and synthetic comparison," so it can obtain the conclusion of the research only for least experiment times.

This paper firstly deals with the preparation of the TiO_2 covering solution with the method of orthogonal experimental design, and the preparation of TiO_2 thin films on microscope slide substrates by the sol-gel process.

2. Experimental

TiO_2 thin films were prepared by the hydrolysis of titanium butoxide ($Ti(OC_4H_9)_4$), which is generally used for TiO_2 thin films or TiO_2 fine particles by the sol-gel method. Fig. 1 shows the chart of the process of making TiO_2 thin films.

In the whole process for making TiO_2 thin films, the preparation of the covering solution is one of the important stages of obtaining good TiO_2 thin films. The concentration of $Ti(OC_4H_9)_4$ in ethanol solution, the addition of H_2O and HCl, the temperature of solution greatly influenced on the hydrolysis of $Ti(OC_4H_9)_4$ to prepare the covering solution. According to the method of orthogonal experimental design, the experiment factors: the concentration of $Ti(OC_4H_9)_4$, the addition of H_2O and HCl, the temperature of solution were investigated.

After the covering solution was put on the substrate of microscope slide, the TiO_2 gel was soon formed. According to certain rules of thermal treatment, the TiO_2 gel on the substrate was annealed in the furnace, the TiO_2 thin films were obtained.

3. Results and discussion

3.1. Preparation of the covering solution with the method of orthogonal experimental design

According to the method of orthogonal experimental design, the factors: the concentration of $Ti(OC_4H_9)_4$,

TABLE I Results and analysis of the experiments

Experiment	Factor A	Factor B	Factor C	Factor D
1	1(8%)	1(0%)	1(3:1)	1(25°C)
2	1	2	2	2
3	1	3	3	3(55°C)
4	2(12%)	1	2(4:1)	3
5	2	2(2.5%)	3	1
6	2	3	1	2(40°C)
7	3(16%)	1	3(5:1)	2
8	3	2	1	3
9	3	3(5.0%)	2	1
Gelling Time				
Lever 1	112 h	0 h	49 h	158 h
Lever 2	96 h	159 h	170 h	110 h
Lever 3	109 h	158 h	98 h	51 h
Effect of Films				
Lever 1	Bad	Worse	Good	Better
Lever 2	Better	Good	Better	Bad
Lever 3	Good	Better	Good	Bad

(A) the concentration of $Ti(OC_4H_9)_4$, (B) the addition of H_2O, (C) the addition of HCl, (D) The temperature of the solution,

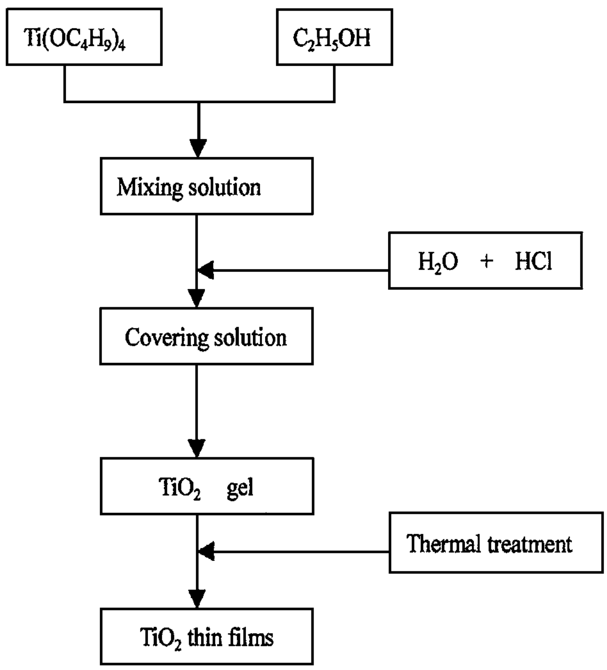


Figure 1 The process of fabrication of TiO_2 thin films.

the addition of H_2O and HCl, the temperature of solution were investigated to prepare the TiO_2 covering solution. Fig. 1 shows the experiment with various prescriptions and results.

According to the analysis of orthogonal experimental design, the relation between factors and gelling time, the effect of the films was seen in Figs 2, 3.

It is obviously noted that the concentration of $Ti(OC_4H_9)_4$, the addition of HCl, the temperature of solution are more greatly influenced on the preparation of the covering solution. According to the consideration the gelling time and the effect of the films, it may conclude that the suitable prescription of experiment is: the concentration of $Ti(OC_4H_9)_4$—12%, the addition of HCl—5.0%, the addition of H_2O—$[H_2O]/[Ti(OC_4H_9)_4] = 4:1$, the temperature of solution—25°C.

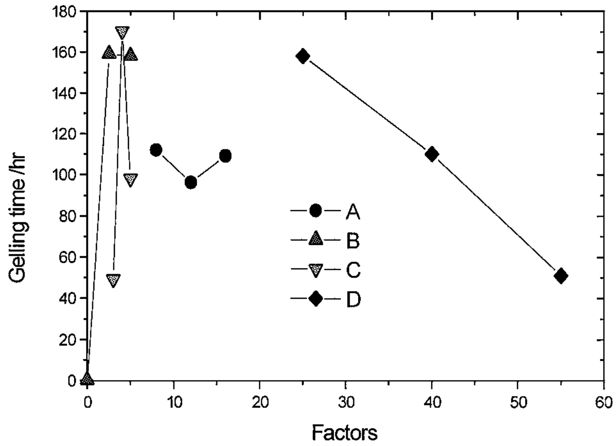


Figure 2 The correlation between gelling time of the covering solution and factors. (A) the concentration of $Ti(OC_4H_9)_4$, (B) the addition of H_2O, (C) the addition of HCl and (D) the temperature of the solution.

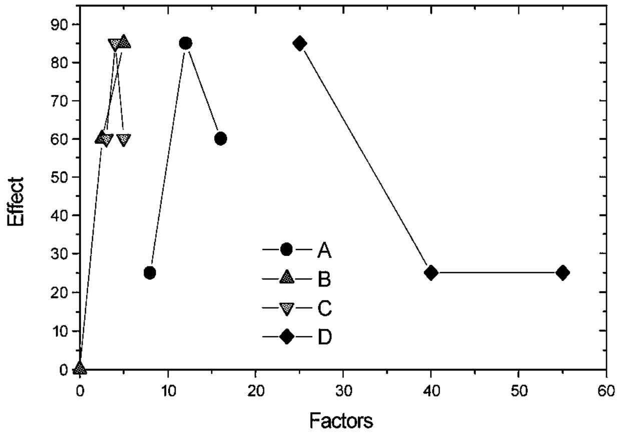


Figure 3 The correlation between effects of the TiO_2 thin films and factors. (A) the concentration of $Ti(OC_4H_9)_4$, (B) the addition of H_2O, (C) the addition of HCl and (D) the temperature of the solution. Worse—0, bad—25, good—60, better—85.

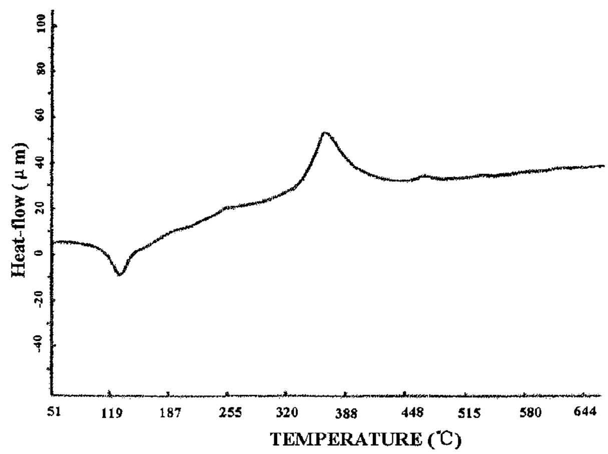


Figure 4 The DTA of TiO_2 gel powder.

3.2. Differential thermal analysis (DTA) of TiO_2 gel

Fig. 4 shows the DTA of TiO_2 gel powder. The rate of heating is 10°C/min.

On the curve of DTA, there is a endothermic peak at about 128°C, which owes to the volatilization of some organic materials. And there is a exothermic peak at about 380°C, it means that some anatase were formed

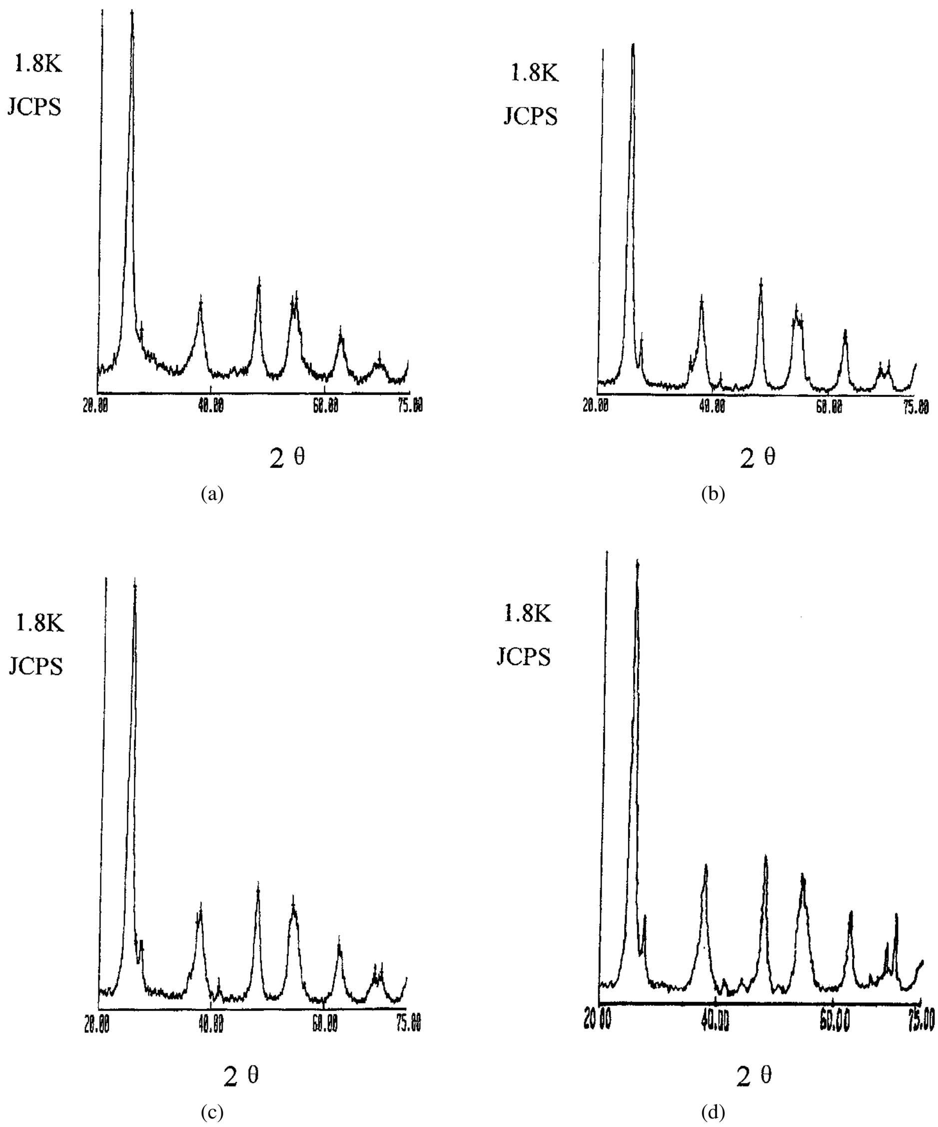


Figure 5 XRD of TiO_2 thin films. (a) Annealed at 350°C for 0.5 h; (b) Annealed at 450°C for 0.5 h; (c) Annealed at 450°C for 3.5 h; (d) Annealed at 550°C for 3.5 h.

from the amorphous TiO_2. Above 380°C, there is no obvious endothermic or exothermic peak on the curve, it shows that anatase transform to rutile gradually.

For the films easily cracked at the temperature of the endothermic peak or exothermic peak with high rate of heating, the rules of heat treatment may be determined as follow:

Room temperature ~ 120°C	rate: 10°C/min
120°C–140°C	rate: 5°C/min
140°C–370°C	rate: 10°C/min
370°C–390°C	rate: 5°C/min
390°C–450°C	rate: 10°C/min
450°C	annealed for 0.5 h

After the above heat treatment, the free-crack TiO_2 thin films were prepared.

3.3. X-ray diffraction (XRD) of the TiO_2 thin films

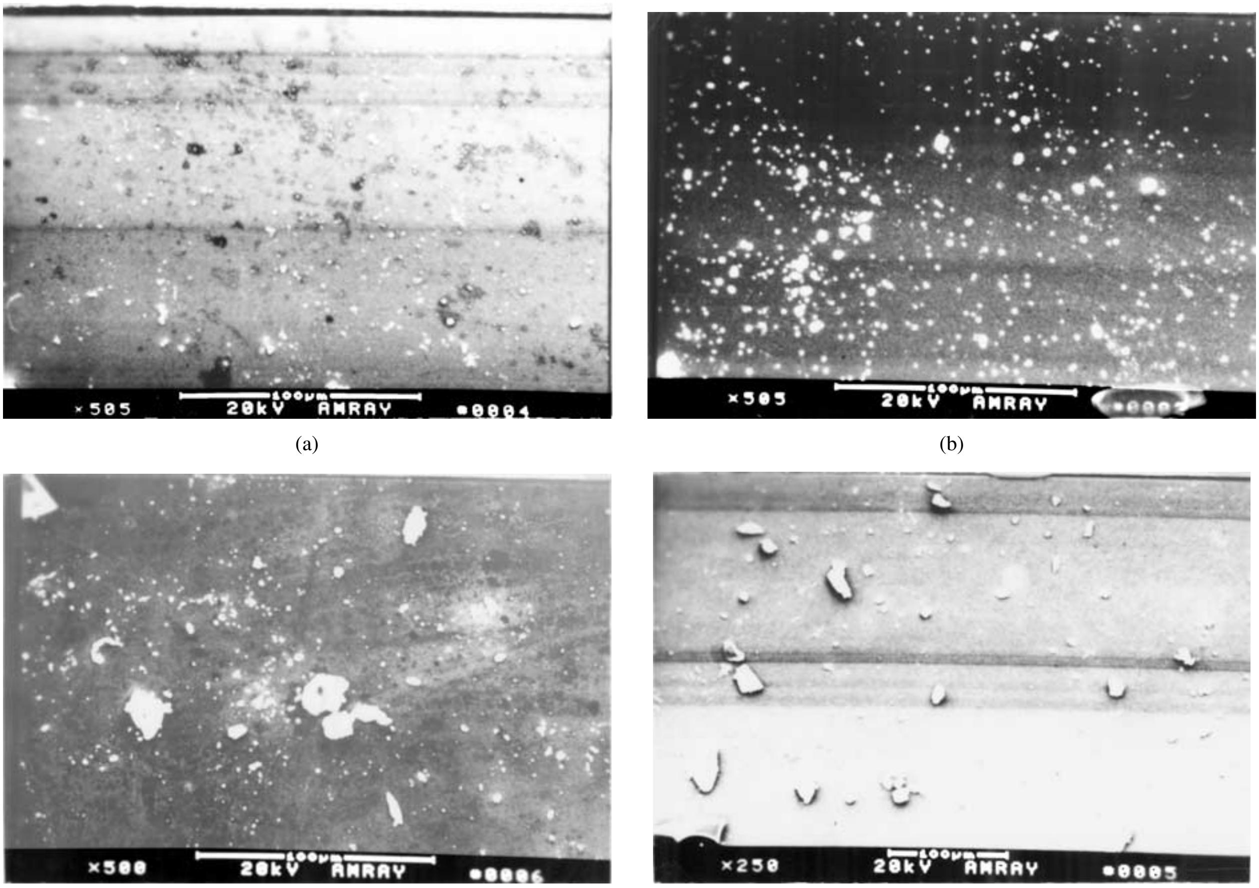
X-ray diffraction-patterns of TiO_2 thin films are presented in Fig. 5 a–d.

It is observed that the peaks are very sharp, and it shows that when the temperature of the heat treatment and the time of preservation increase, the amount of rutile changed from anatase also increase.

3.4. Scanning electron microscopy (SEM) of the TiO_2 thin films

SEM studies were conducted to investigate microstructure and crystallization. Fig. 6 shows SEM-micrographs of Sample a–d.

After thermal treatment at 350°C and for 0.5 h, there were a few crystals with small size in the films, but the surface was not very even; the crystals with still small size of Sample b were more than that of Sample a, and they were well-dispersed, the surface of the films was uniform with free-crack. As the temperature and the time increased, the size of crystals enlarged and crystals dispersed very disorderly in Fig. 6c, and the cracks were seen in the TiO_2 films of Sample d. And the thickness of the TiO_2 films of Sample a–d was about 82–96 nm derived from Dektak^{3}st surfacefiler (Veeco Instruments Inc., USA).



(a) (b) (c) (d)

Figure 6 SEM of TiO_2 thin films. (a) Annealed at 350°C for 0.5 h; (b) Annealed at 450°C for 0.5 h; (c) Annealed at 450°C for 3.5 h; (d) Annealed at 550°C for 3.5 h.

4. Summary

1. By the sol-gel process TiO_2 thin films with good uniformity, free-crack, were successfully prepared on the substrate of microscope slide.

2. The preparation of the TiO_2 covering solution was an important stage of making TiO_2 thin films. With the method of orthogonal experimental design, the experiment factors: the concentration of $Ti(OC_4H_9)_4$, the addition of H_2O and HCl, the temperature of solution were investigated. And the optimum experiment prescription of the covering solution was acquired.

3. It was concluded that with the increment of the temperature and the time, analyzed by the means of DTA, XRD, SEM, the sizes and quantity of the crystals in the films were also increased. After thermal treatment at 550°C and for 3.5 h, the surface had cracked and the crystals dispersed disorderly in the TiO_2 films.

Acknowledgement

The first author shows his sincere thanks to the support from Hi-teck Research and Development Program in China, and also to Doctor Jiuming Zhang for reading manuscript, and be grateful for Ms. Bian's encouragement.

References

1. T. FUYUKI and H. MATSUNAMI, *Jpn. J. Appl. Phys.* **25** (1986) 1288.
2. P. A. BERTRAND and P. D. FLEISCHAUER, *Thin Solid Films* **103** (1983) 167.
3. H. SCHRODER, in "Physics of Thin Films," Vol. 5: G. Hass and R. E. Thun (Academic, New York 1969) p. 87.
4. H. K. PULKER, "Thin Film Science and Technology," Vol. 6: Coatings on Glass (Elsevier, Amsterdam, 1984).
5. B. E. YOLDAS and T. W. O'KEEFE, *Appl. Opt.* **18** (1979) 3133.
6. B. E. YOLDAS, *ibid.* **21** (1982) 2960.
7. D. DUOHONG, E. BORGARELLO and M. GRATZEL, *J. Am. Chem. Soc.* **103** (1981) 4685.
8. S. NISHIMETO, B. OHTANI, A. SAKAMOTO and T. KAGIYA, *Nippon Kagaku Kaishi* **246** (1984) 52.
9. JIONG-PING LU, JENGDAW WANG AND RISHI RAJ, *Thin Solid Films* **204** (1991) L13.
10. N. NABAVI, S. DOEUFF, C. SANCHEZ and J. LIVAGE, *Mater. Sci. Eng. B* **3** (1989) 203.
11. B. MORRIS HENRY, U.S. Patent, 4,200,474, 1978.
12. M. LOTTIAUX, C. BOULESTEIX, G. NIHOUL, *et al.*, *Thin Solid Films* **170** (1989) 107.
13. M. H. SUHAIL, G. MOHAN RAO and S. MOHAN, *J. Appl. Phys.* **71**(3) (1992) 1421.

Received 4 April 2000
and accepted 23 July 2001