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Preparation of TiO_2 Thin Films by Potentiostatic Method: The Effects of Electrode Potential and Electrodeposition Temperature†

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White films were electrodeposited by potentiostatic method on the indium tin oxide conductive glass substrate. After annealing at 450 ºC for 1 h, the films were characterized by XRD and SEM. According to the XRD patterns, the annealed films proved to be TiO_2 with anatase phase structure. The effects of the experimental parameters such as electrodeposition potential and temperature on formation of the deposited films were discussed. The optimal electrode potential and desirable electrodeposition temperature were 1 V and 30 ºC, respectively.

Key Words: TiO_2, Films, Electrodeposition, Potentiostatic method.

INTRODUCTION

As a semiconductor material with wide band gap, titanium dioxide (TiO_2) has important applications in renewable energy and environment fields such as photocatalytic water/air purification, hydrogen production from splitting water and high-efficiency/low-cost solar cells[1-8]. At present, there are many methods to prepare of TiO_2 thin film, such as sol-gel, sputtering, chemical vapour deposition, hydrothermal and electrodeposition method[9]. The electrodeposition method can be used to prepare TiO_2 thin films effectively. Electrodeposition process is a novel fabrication method[10]. Because of the controllability of potentiostatic method[11], there are quite a few process carried out in potentiostatic mode. In this work, well defined nanostructured white films with unique morphologies on indium tin oxide conductive glass substrates had been fabricated simply by using aqueous solution containing titanium trichloride and caustic soda instead of any toxic and expensive reagents *via* a low-temperature and environment-friendly soft chemical potentiostatic method. After annealing, the films proved to be TiO_2 with anatase phase structure. The preparation process factors, such as electrode potential, electroplating temperature will be discussed in this paper.

EXPERIMENTAL

All reagents were of analytical grade and used without further purification. The thin films were electrodeposited on commercial indium tin oxide glass (HYSTN80, Huayi Conductive Glass Co. Ltd., Anhui, PRC) substrates in potentiostatic mode.

All electrodeposition experiments were carried out by three-electrode cell, using Ti foil (3 cm × 3 cm), indium tin oxide glass substrate (1 cm × 1 cm) and saturated calomel electrode (SCE) as the counter electrode, working electrode and reference electrode, respectively. The cell was powered by a potentiostat (DJS-292, Shanghai REX Instrument Factory, Shanghai, PRC).

Before deposition, the substrate was cleaned by ultrasonic treatment in toluene, acetone and ethanol in turn, rinsed by distilled water and washed with deionized water, then dried in air. Afterward, it was immersed in plating electrolyte. The electrolyte contained 0.03 mol/L $TiCl_3$ and was raised to a predetermined pH value in the range 1.21-2.56 by adding 2 mol/L NaOH solution, under constant stirring. A pH meter (pHS-2C, Shanghai REX Instument Factory, Shanghai, PRC) was used as a pH detector.

Deposition potential was varied in the range 1 to 4 V (*vs.* SCE) and the time of deposition, t, from 30 to 240 min. The electrodeposition temperature was at 30-65 ºC. The distance between the working and counter electrode was maintained at 4 cm. Subsequently, the working electrode with film sample was taken from the cell and washed with deionized water, then dried in air at room temperature. The dry film samples were heated up in air at 100 ºC for 2 h. Finally, the samples were annealed at 450 ºC for 1 h.

The structure and overall crystallinity in the annealed films was characterized through θ-2θ scans operated on a X-ray diffractometer (Y-2000, Dandong radiative instrument group

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Co. Ltd. Liaoning, PRC) with CuK_α radiation. The annealed films' surface morphology was investigated through scanning electron microscopy on a field-emission SEM (Sirion200, FEI Company, USA) operated at 5 kV voltage value.

RESULTS AND DISCUSSION

The deposition potential is the key parameter to control the thin film electrodeposition during the processing, since it plays important role of deposition speed as well as adjusting working electrode's current value. A series of experiments with various value of potential has been investigated. The thin films were all uniform, crack-free and pore-free.

Fig. 1 shows different XRD patterns of the annealed thin film samples obtained with the same electrodeposition temperature, time and plating electrolyte pH value, *i.e.*, 30 ºC, 1 h and 2.5, respectively. Pattern (a), (b), (c), (d) are corresponding to the films obtained with electrode potential of (a) 4.000, (b) 3.000, (c) 2.000, (d) 1.000V *vs.* saturated calomel electrode, respectively. Pattern (e) is standard XRD pattern of TiO_2 with anatase structure. Peaks on the XRD pattern (a), (b), (c), (d) are accurately accorded with the standard pattern. It is obvious that the annealed films are all anatase structure.

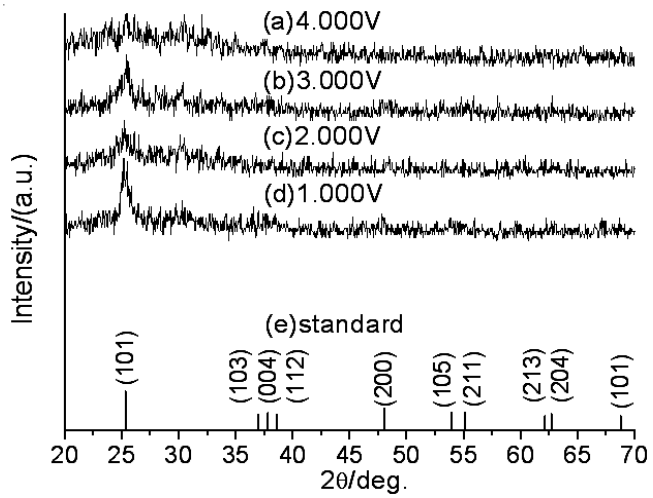

Fig. 1. XRD patterns of the films obtained with electrode potential of (a) 4.000, (b) 3.000, (c) 2.000, (d) 1.000V *vs.* SCE, (e) standard anatase TiO_2

On the XRD pattern (a), there are weak peaks which are not like the others at all, indicating the (a) film is amorphous. On the patterns (b), (c) and (d), the strongest peaks corresponding to (101) planes are very weak, indicating the films obtained are low degree of crystallinity.

It can be observed that variation of electrode potential in the deposition system has notably effect on determination of micro-morphology of the deposited TiO_2 thin films. Because the higher electrode potential results in more irreversible electrodeposition process, the film prepared with electrode potential of 4.000V (*vs.* SCE) is amorphous totally. Comparing XRD patterns samples in Fig. 1, it can also be observed that the films prepared with electrode potential of 1.000V (*vs.* SCE) has the most strong (101) reflection peak than the others and the higher electrode potential is, the weaker (101) peak become. Commonly, the strong reflection peaks imply the good degree of crystallinity[12]. According to the (101) peaks' intensity, the sample (d) has the best degree of crystallinity and the best electrodeposition electrode potential is 1.000V (*vs.* SCE).

Morphology characterization and discussion: Fig. 2 shows the top-view SEM images of the annealed TiO_2 films obtained with the same electrodeposition potential, plating electrolyte pH value and time, *i.e.*, 1.000 V (*vs.* SCE), 2.5 and 1 h, respectively. Image (a), (b) are corresponding to the films obtained with electrodeposition temperature of (a) 30, (b) 45 ºC, respectively. Two images indicate that thin films have a porous cellular structure with a large internal surface area. The crystalline grains in two images are small and two thin films are of low degree of crystallinity. It can be seen that two films are all constituted of crystalline grains like amorphous grapes without simple and regular shape; nevertheless, comparing SEM images of (a) and (b) samples in Fig. 2, there are more big pores in the image (b) than (a) and the morphology of (a) is more uniform than (b). The difference between the two images can reveal that factor of electrodeposition temperature near room temperature had notably effect on morphology of the deposited TiO_2 thin films. Considering the morphology and the convenience of plating process, electroplating temperature of 30 ºC is more desirable than 45 ºC.

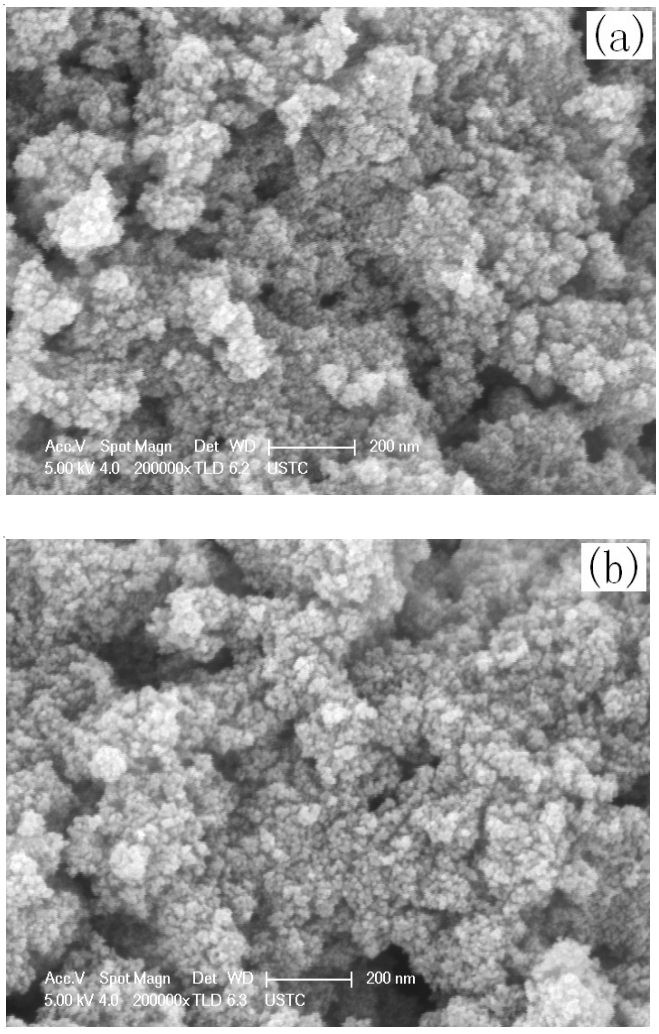

Fig. 2. SEM images of the films obtained with electrodeposition temperature of (a) 30, (b) 45 ºC

Conclusion

In summary, a low-temperature and environment-friendly soft chemical electrodeposition technique had been successfully applied to fabricate TiO_2 thin films. Because of controllability, the potentiostatic mode was applied to deposition process. The results show that TiO_2 thin films can electrodeposited as electrode potential arranging from 1.000-4.000 V (*vs.* SCE) at 30-45 ºC for 1 h with the pH 2.5 electrolyte which contained 0.03 mol/L $TiCl_3$. Electrode potential was the key parameter to the film deposition. The factor of electrodeposition temperature had notably effect on the morphology of the thin films. The optimal electrode potential and desirable electrodeposition temperature were 1 V (*vs.* SCE) and 30 ºC, respectively.

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