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Short communication

Thin film TiO_2 electrodes derived by sol–gel process for photovoltaic applications

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Abstract

Nanocrystalline anatase TiO_2 thin films are prepared by a single spin-coating process from the sols with different ethanol content. The influence of the ethanol content and the heat treatment temperature on the structural and optical properties of the thin films is characterized by X-ray diffraction, atomic electron microscopy, and UV–vis spectroscopy. The results indicate that an anatase phase structure TiO_2 thin film with nanocrystallite size of about 20 nm and high transmittance can be obtained at the heat treatment temperature of 400 °C or above, that is to say, at the heat treatment temperature below 300 °C, the thin films grow in amorphous phase with a smooth surface; while the heat treatment temperature is increased up to 400 °C or above, the thin film develops a crystalline phase corresponding to the titanium oxide anatase phase.

Keywords: Nanocrystalline titanium oxide; Anatase; Thin films; Sol–gel technique; Electrode; Photovoltaic

1. Introduction

Nanocrystalline titanium oxide (TiO_2) is highly attractive as an electron transport layer materials in photovoltaic (PV) devices, because it has been used as a photocatalyst and is an n-type electrode in dye-sensitized photo-electrochemical solar cell. Therefore, hybrid polymer/TiO_2 PV devices have been under intense investigation and a number of research groups have reported progress in such hybrid devices in recent years [1–4]. Usually, TiO_2 thin films can be synthesized by a wide variety of techniques such as chemical vapor deposition [5], aerosol pyrolysis [6], electrodeposition [7], and sol–gel method [8–15]. However, the sol–gel method allows for the simple production of high purity films at low cost and the materials can be synthesized at low temperature without degrading the organic functional groups or the polymer. The solution nature of the sol–gel process leads to molecular level mixing and the production of nanostructured materials and films over a large surface area, these are helpful for improving the power conversion efficiency of the solar cell. In this paper, we report our study on the preparation, characterization, structural and optical properties of nanocrystalline n-type TiO_2 thin films derived by a sol–gel technique for photovoltaic applications.

2. Experimental study

Nanocrystalline TiO_2 thin films were prepared by using the sol–gel and spin-coating technique. Titanium isopropoxide [$Ti(OC_3H_7)_4$, TIP] was used as the TiO_2 precursor, absolute ethanol (99.9%) used as solvent, and nitric acid (HNO_3) used as a catalyst controlling the pH of the solution [10,11]. The matrix sol was prepared by two solutions. In the preparation of the solution I, TIP was first diluted with absolute ethanol under vigorous stirring for about 30 min. For solution II, absolute ethanol, deionized water, and nitric acid were mixed together and used as the acidic catalyst for hydrolysis of TIP. Two solutions (solutions I and II) were then mixed by adding the acidic solution (solution II) drop wise to the TIP–ethanol solution (solution I). The final mixture solution was stirred for about 20 h at room temperature. The final composition of the spin-coating solution in a molar ratio was TIP:H_2O:NHO_3 = 1:1:0.15 and ethanol = 10, 20, 30, and 50 M content, respectively. It should be noted that cleaning of the substrate is important for proper adhesion of the films. We used ITO glass (sheet resistance of 12 $\Omega\,sq^{-1}$) as substrates. They were ultrasonically cleaned in acetone and ethanol, respectively, rinsed with deionized

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water and dried with pure nitrogen. One layer of the sol–gel film was spun onto the substrate at 3000 rpm for 35 s. Then, the as-coated films were heated for 15 min in air at different temperatures.

The thickness of the TiO_2 thin films was measured by an Alpha-step 500 Surface Profiler. The morphology of the films was examined under an atomic force microscopy (AFM) by a Digital Instruments Nanoscope IIIa AFM using the tapping mode. X-ray diffraction (XRD) was employed to investigate the phase homogeneity of the TiO_2 thin films and this method was also used to estimate the size of the nanoparticles in the films. XRD was carried out for the films using a Rigaku Rint 2000 Series X-ray diffractometer equipped with a thin film attachment unit. The X-ray radiation source used was Cu Kα, obtained at 50 kV, 35 mA and the scanning speed was $2^\circ\ min^{-1}$ at a step of 0.04°. The UV–vis transmission spectra were obtained in the range of 200–1000 nm by a Perkin-Elmer Lambda 16 UV–vis spectrometer with a resolution of ±0.3 nm.

3. Results and discussion

Thickness of the films can be varied by changing the ethanol molar content and heat treatment temperature. Fig. 1 shows the dependence of the film thickness on ethanol molar content. Here, these films were deposited on ITO glasses and heated at 500 °C for 15 min. Evidently, as the solution was further diluted by adding ethanol content (increase ethanol molar content), the film thickness drops. The results indicate that the films with a single layer thickness (spin-coating was done only once) range from 45 to 115 nm could be obtained within the studied ethanol molar content range. It should be mentioned that the film thickness value obtained under present condition is enough for an n-type electrode layer thickness in photovoltaic devices [9]. Thickness of the film obtained from the solution with 10 M ethanol content and heated at different temperatures was also characterized. As expected, the film thickness becomes thinner with an increase of the heat treatment temperature. For example, a single layer thickness of thin film reduces from 160 to 105 nm with increase the heat treatment from 400 to 600 °C.

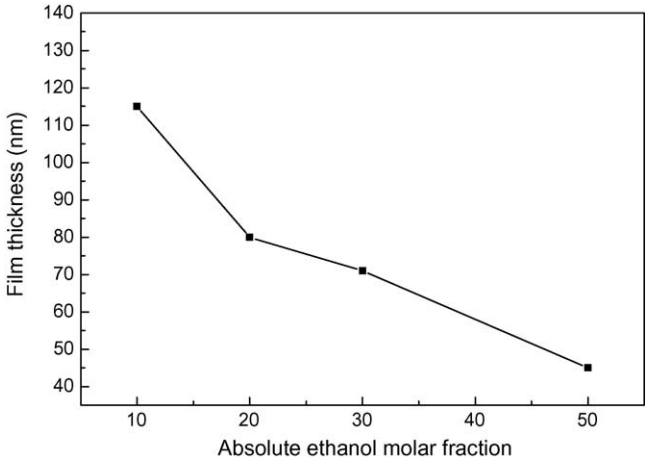

Fig. 1. Dependence of the thickness of TiO_2 films on ethanol molar content.

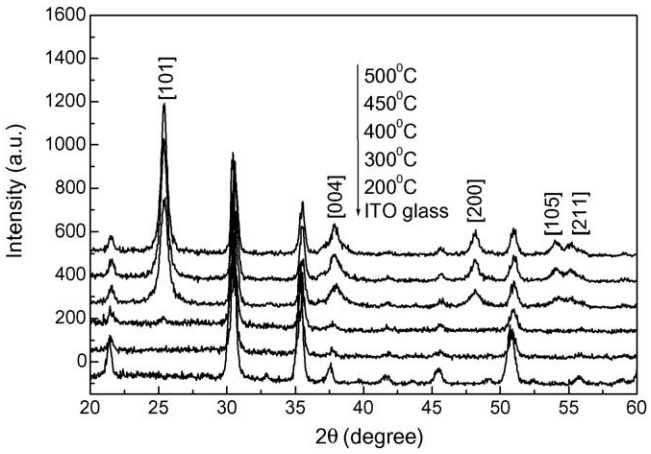

Fig. 2. XRD patterns of nanocrystalline anatase TiO_2 films heated at different temperatures.

Fig. 2 shows the XRD patterns of the films with 50 M ethanol content and heated at different temperatures. It can be seem that for the heat treatment temperature below 400 °C, no any signal from the film is observed, indicating that the film heated below 400 °C is still amorphous phase and there is no any crystalline phase to be observed in the film. As the heat treatment temperature is increased up to 400 °C or above, a clear signal of the diffraction peaks starts to appear, the intensity of these diffraction peaks increases with an increase of the heat treatment temperature. It should be stressed here that all peaks observed can be assigned to specific lattice planes of the anatase phase of TiO_2, which corresponds to JCPDS Patterns No. 21-1272. These XRD results demonstrate that nanocrystalline anatase TiO_2 sol–gel thin films can be obtained when a heat treatment temperature is at 400 °C or above. The crystallite size of the (1 0 1) plane from the films shown in Fig. 2 was determined from the Scherrer formula [16] and the values derived thereby are 141, 154, and 161 Å, which corresponds to the heat treatment temperatures of 400, 500, and 600 °C, respectively. These results demonstrate the presence of the nanocrystalline TiO_2 particles in the films.

A confirmation of the crystallization process studied by XRD was carried out by AFM observation and the experimental results are shown in Fig. 3. These results indicate that a film heated below 400 °C develops a smooth surface and a true amorphous phase is developed, which is in total agreement with the result obtained by XRD. A granular morphology starts to appear when the heat treatment temperature is increased to 400 °C (Fig. 3(a)), which indicates the presence of crystalline grains and corresponds to the XRD results that the film shows a crystalline phase structure at the heart treatment temperature of 400 °C. For higher heat treatment temperature, the crystalline grains grow in a more irregular way, a more clear morphology, and relative uniform grain size can be observed in Fig. 3(b). As can be observed directly from the image shown in Fig. 3(b), it can be deduced that an about 20 nm grain size can be obtained, which is almost the same with the value obtained by XRD from the Scherrer equation. However, with the heat treatment temperature further increase up to 600 °C (Fig. 3(c)), the crystalline grains grow up obviously and the distribution of the grain size is not uniform as

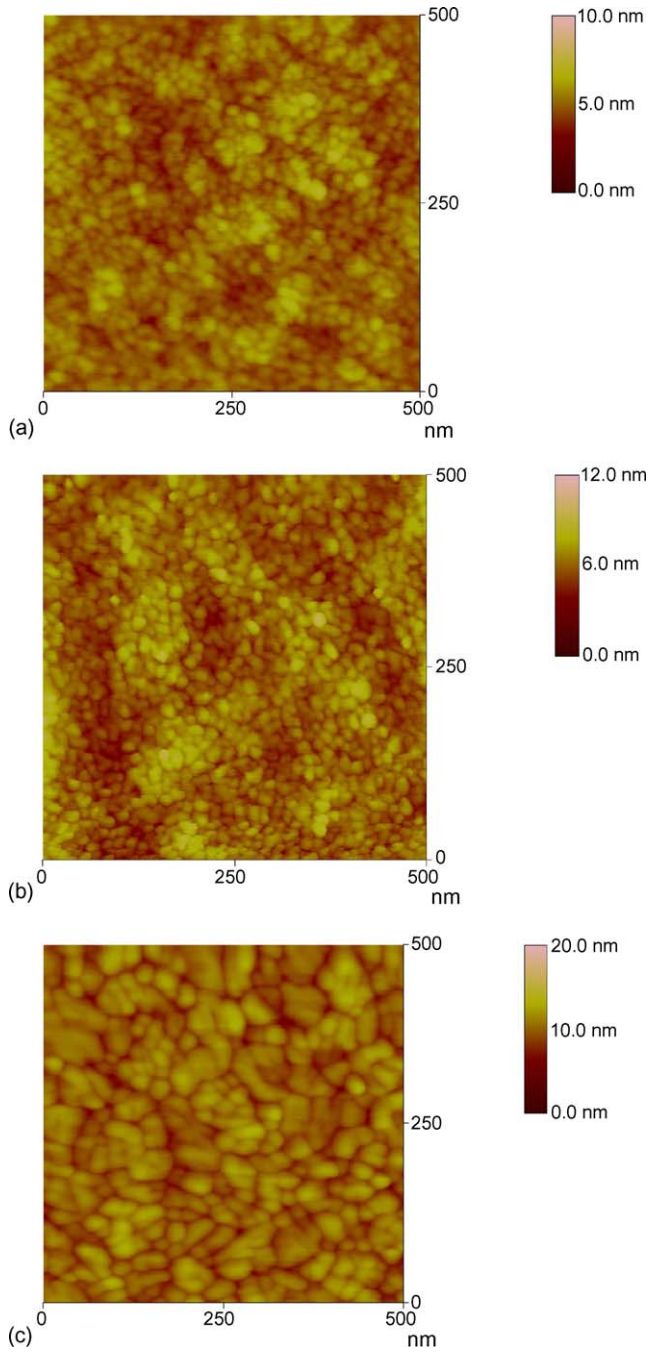

Fig. 3. AFM images of TiO_2 films heated at different temperatures: (a) 400 °C, (b) 500 °C and (c) 600 °C.

compared with that of the film as shown in Fig. 3(b). Observing carefully from Fig. 3(c) that some grains agglomerate to form a bigger grain and its size is up to about 100 nm. Obviously, the value of the grain size is bigger than that obtained by XRD from the Scherrer equation, indicating that those relative big grains observed in Fig. 3(c) are not single crystals. Furthermore, the root mean square (RMS) surface roughness of the films shown in Fig. 3 was also observed by AFM over a 5 μm × 5 μm area. It is noted that the RMS surface roughness is relative small when the heat treatment temperature is below 300 °C, it is probably related to the film is still a amorphous phase, which indicates a dense, smooth, and uniform morphology with a relative low surface roughness can be obtained. However, with an increase of the heat treatment temperature, a crystalline phase starts to appear and leads to an appearance of the grains. Therefore, the surface roughness thus increases and the film becomes relatively coarse. Actually, when the heat treatment temperature is further increased up to 600 °C and the grain of the film grows up, the film has relatively big surface roughness value of about 1.2 nm.

Fig. 4 shows the optical transmittance spectra of the films with different ethanol molar content and heated at different heat treatment temperatures, respectively. Note that these films were coated once and deposited on ITO glass. It can be seen from Fig. 4(a) (films heated at 500 °C) that all films have high transmittance and the absorption edge is at about 300 nm. In addition, the transmittance of the films becomes lower as the ethanol molar content increases; due to the films actually become thicker (Fig. 1). The interference fringes at the short wavelength range between 300 and 700 nm can be clearly observed from all the films due to relative thin. This behavior is further demonstrated from the films heated at different temperatures in Fig. 4(b), which interference fringes become more obvious for those films heated at higher temperature (500 and 600 °C). However, for those films heated at 200 and 300 °C, there is no obvious interference fringes observed. It can be also seen from Fig. 4(b) that the transmittance of the films becomes lower as the heat treatment temperature increases, due to the scattering from the grains

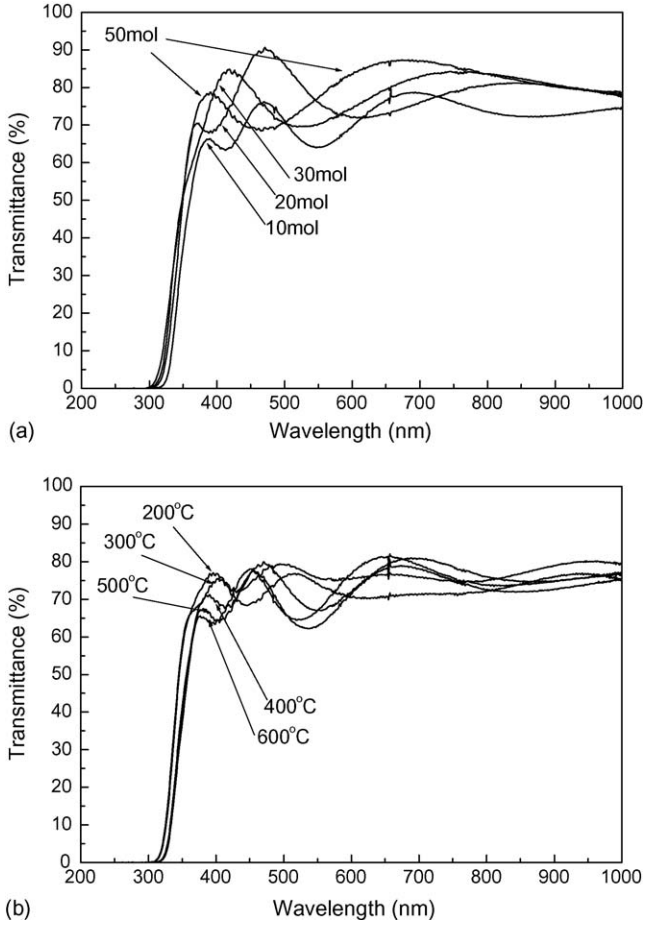

Fig. 4. Optical transmittance spectra of TiO_2 films: (a) with different ethanol content and (b) at different temperatures.

appeared in the films due to an increase of the heat treatment temperature.

4. Conclusions

Nanocrystalline anatase TiO_2 thin films with a good crystalline quality and a crystallite size of about 20 nm were investigated by the sol–gel spin-coating technique. The influence of the ethanol molar content and heat treatment temperature on the structural and optical properties of the films was also studied by AFM, XRD, and UV–vis spectra. From the analysis of the crystalline properties, granular morphology and surface roughness of the as-deposited films, it is noted that the crystalline properties of the films is dependent on the heat treatment temperature. The results indicates that a heat treatment temperature of 500 °C and a solution with 50 M ethanol content are necessary to achieve a good quality crystalline anatase TiO_2 thin films for photovoltaic applications.

References

[1] P.A. van Hal, M.M. Wienk, J.M. Kroon, W.J.H. Verhees, L.H. Slooff, W.J.H. van Gennip, P. Jonkheijm, R.A.J. Janssen, Adv. Mater. 15 (2004) 118.
[2] L.H. Slooff, M.M. Wrienk, J.M. Kroon, Thin Solid Films 451–452 (2004) 634.
[3] J.D. Kwon, P.H. Kim, J.H. Keum, J.S. Kim, Solar Energy Mater. Solar Cells 83 (2004) 311.
[4] S. Yanagida, G.K.R. Senadeera, K. Nakamura, T. Kitamura, Y. Wada, J. Photochem. Photobiol. A: Chem. 166 (2004) 75.
[5] G.K. Boschloo, A. Goossens, J. Schoonman, J. Electronchem. Soc. 144 (1997) 1311.
[6] L. Kavan, M. Grätzel, Electrochem. Acta 40 (1995) 643.
[7] Y. Lei, L.D. Zhang, J.C. Fan, Chem. Phys. Lett. 338 (2001) 231.
[8] C.J. Barbé, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, M. Grätzel, J. Am. Ceram. Soc. 80 (1997) 3157.
[9] J. Xu, X. Zhao, J. Du, W. Chen, J. Sol–Gel Sci. Technol. 17 (2000) 163.
[10] M. Takahashi, K. Tsukigi, T. Uchino, T. Yoko, Thin Solid Films 388 (2001) 231.
[11] Q. Fan, B. McQuillin, D.D.C. Bradley, S. Whitelegg, A.B. Seddon, Chem. Phys. Lett. 347 (2001) 325.
[12] H. Liu, W.S. Yang, Y. Ma, Y.A. Cao, J.N. Yao, J. Zhang, T.D. Hu, Langmuir 19 (2003) 3001.
[13] S. Sen, S. Mahanty, S. Roy, O. Heintz, S. Bourgeois, D. Chaumont, Thin Solid Films 474 (2005) 245.
[14] K. Pomoni, A. Vomvas, Chr. Trapalis, Thin Solid Films 479 (2005) 160.
[15] B. Guo, Z.L. Liu, L. Hong, H.X. Jiang, J.Y. Lee, Thin Solid Films 479 (2005) 310.
[16] H.P. Klug, L.E. Alexander, X-Ray Diffraction Procedures, Willey, New York, 1974.