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Journal of the European Ceramic Society 24 (2004) 335–339

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Hydrothermal processing of nanocrystalline anatase films from tetraethylammonium hydroxide peptized titania sols

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Abstract

Nanocrystalline anatase films were obtained by hydrothermally treating dip-coated TiO_2 gel films onto silicon substrates from tetraethylammonium hydroxide (TENOH) peptized titania aqueous sols diluted with different solvents (isoproponol, acetone and propanediol) at 240°C for 2 h. SEM, AFM and XRD analysis were used to characterize the microstructure and phase evolution of the films. The highest degree of homogeneity and good wettability towards the substrate could only be obtained with mixed solvents of acetone and isopropanol, yielding denser structure with homogeneously distributed fine grains among all the three solvents. A uniform distribution of fine grains of around 50 nm was obtained after hydrothermal treatment, while the film calcined at 500°C/2 h displayed larger grains of around 80 nm and were not so uniformly developed. All these results suggest that (a) TENOH peptized titania sol is a promising novel stock precursor for synthesizing TiO_2 films; (b) hydrothermal technique is quite efficient in preparing titania nanocrystalline films compared with calcination method.

Keywords: Hydrothermal methods; Peptization; Anatase; TiO_2; Films

1. Introduction

Nanocrystalline titania films have attracted sustained great scientific and technological interests because of their potential applications in the fields of photoelectronic optical devices, solar cells, gas sensors, photocatalysts and biomaterials.[1–3] The ulfrafine crystals in the films lead to unusual properties arising from the quantum confinement effects[4] and high surface area, which is essential for the chemical reactions involved in each specific application. In order to maintain higher surface area, it is necessary to use low temperature processing to prepare titania film. Wet-chemical synthesis routes, such as sol-gel processing, have been widely used to fabricate the crystalline titania film.[5,6] The main advantages of sol-gel technique for the preparation of materials are low temperature of processing, versatility, flexible rheology allowing easy shaping and embedding.[7] The most frequently used precursors for the titania film through sol-gel processing are the titania sols obtained by hydrolyzing acetic acid or acrylacetone stabilized titanium alkoxides.[7,8] Nevertheless, subsequent heat treatment should be carried out to remove the organic contents from the complexing species of titanium or the precursors to obtain crystalline phase. Alternative stock sols with lower organic contents and other synthesis ways to lower the crystallization temperature should be taken into account during the preparation of titania films. However, hydrothermal synthesis, in which the chemical reaction could take place under autogenerated pressure upon heating, is efficient to achieve crystalline phase at relatively lower temperature.[9–12] Recently, anatase nanoparticles were successfully prepared by hydrothermally treating tetraalklyammonium hydroxide-peptized titania sols.[11,12] Moreover, anatase phase was stabilized in the hydrothermally treated peptized sol. Anatase/rutile phase transformation took place at around 1050°C, which was almost 300°C higher than that for the unpeptized species. This stabilized anatase phase is essentially important in photocatalysis applications since anatase shows the highest catalysis activity among all the three polymorphs.

In the present work, we used TENOH-peptized titania sol as a new precursor for achieving the titania film. Nanocrystalline anatase films were obtained by hydrothermally treating the dip coated titania gel films at 240°C. The large surface area of the anatase films will

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0955-2219/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00224-3

be maintained after the crystallization is accomplished at relatively low temperature.

2. Experimental

Titanium butoxide (Aldrich, Spain) and tetraethylammonium hydroxide (TENOH, 20 wt.% aqueous solution, Merck, Germany) were used as precursor and peptizer, respectively. The peptized titania sol was prepared by adding TENOH to 0.5 M isopronol solution of titanium butoxide with a ratio of TENOH/Ti = 1 and H_2O/Ti = 20. In order to make the sols suitable for dip-coating, isoproponol, acetone and propanediol were separately used to dilute the peptized sols to half of their initial concentrations. A small quantity of water was added in order to avoid the immiscibility among the solvents. The polished silicon (100) wafers washed sequentially with deionized water, potassium hydroxide and deionized water again were used as the substrate for the films. The coating process was performed using a dipping and drawing procedure in dry atmosphere at room temperature. Films were drawn from the peptized sols at a drawing rate of 2 mm/s and immediately dried on a hot-plate at 200°C. After being coated with three layers, the as-obtained films were placed onto a support over the water surface in an autoclave vessel to avoid a possible strong rinsing on the films and hydrothermally treated at 240°C for 2 h (HT240). For comparison, the gel films were calcined in an oven at 500°C (CA500) for 2 h for investigating the phase and morphology evolution.

The crystalline phase was determined by XRD (D/MAX-C, Rigaku). Thickness and morphology of the films were observed under Scanning Electron Microscope (Hitachi S-4100). The morphology of the sol was examined by a high-resolution transmission electron microscopy (HRTEM, Hitachi H9000-NA). More detailed observations of the surface morphology of the samples was carried out by AFM (AFM, Digital—Instrument, Nanoscope III). Differential thermal analysis and weight loss of the gel powder obtained from drying the sol at 100°C were measured by a thermometer (SETARAM. Labsys^{TM} TG-DTA16, France).

3. Results and discussion

Among all the three diluting agents, homogeneous gel films could be prepared from the acetone diluted peptized sols. This is probably due to the non-polarity character of acetone. Therefore, our preference was first towards using these acetone-diluted sols for coating the silicon substrates, assuming that they would be more compatible with the silicon substrate. In order to explore the full advantage of the non-polarity of solvent in the coating process, acetone was used as the unique solvent in diluting titanium butoxide, and then the peptized sols. However, it was surprising to realize that instead of any improvement of the wettability of the silicon substrates, a deteriorating effect was observed. This indicates that an extreme non-polar character of the solvent does not probably represent the best situation in terms of wettability. Therefore, the degree of polarity was tailored by mixing different solvents with some degree of polarity and non-polarity, which renders good wettability of the substrate by the sols. Similar positive effects from mixed solvent have been widely utilized in preparing powders and films.[13,14] The films involved in the following discussion were prepared from the mixed solvents of isopropanol and acetone.

Fig. 1 shows the DTA/TG results of the gel powder. Endothermic peaks in the range of l00–200°C can be attributed to desorption of water and other organics. No significant exothermic peak corresponding to the removal of the organics appeared, which is usually accompanied by a larger weight loss. It was also observed that weight loss stopped when the temperature reached 400°C. These strongly implied that in the peptized titania sols, a strong complexing linkage between

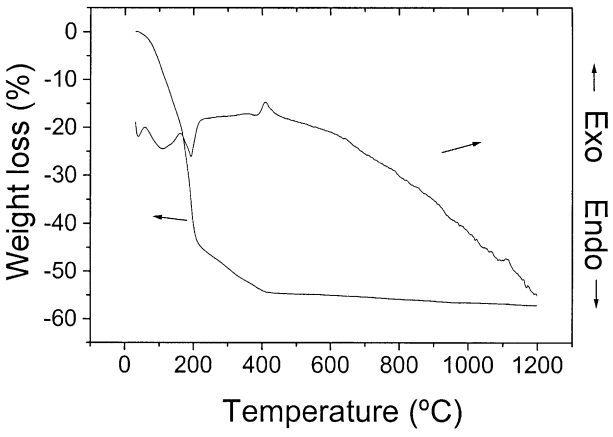


Fig. 1. DTA curves of the gel powder.

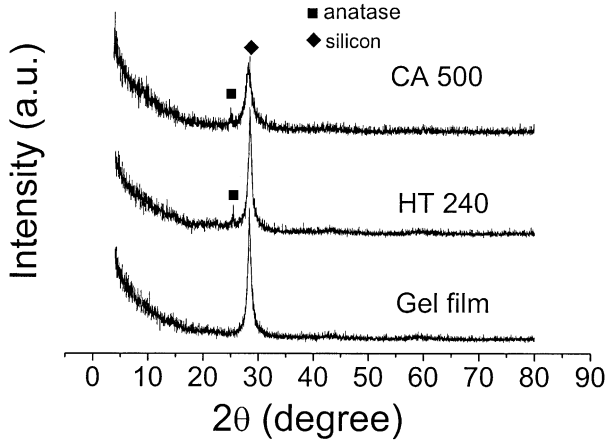


Fig. 2. XRD spectra of various films.

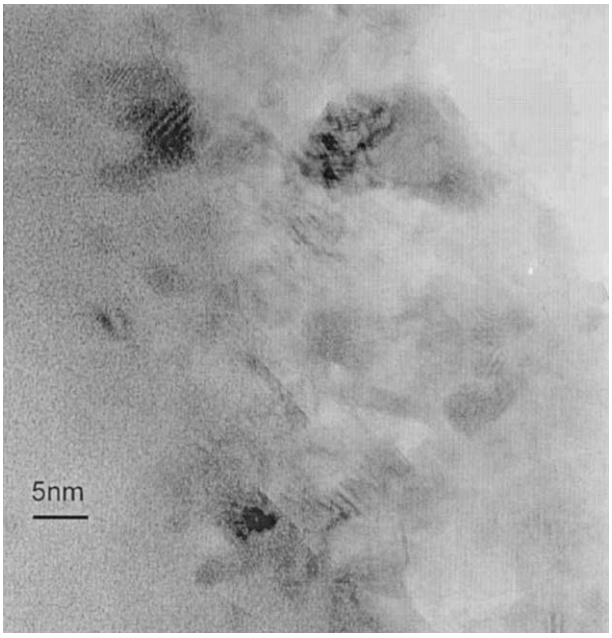
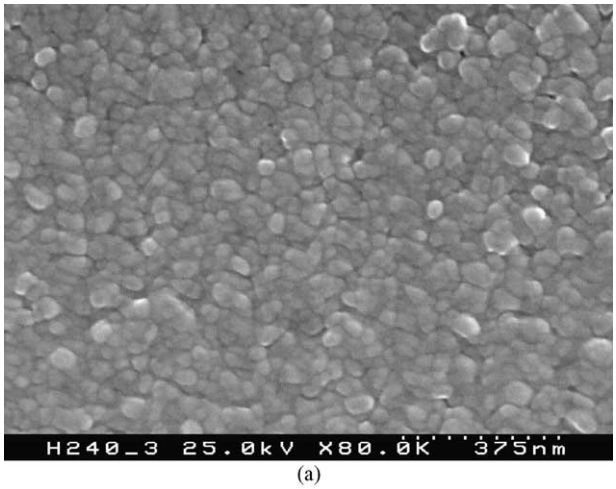
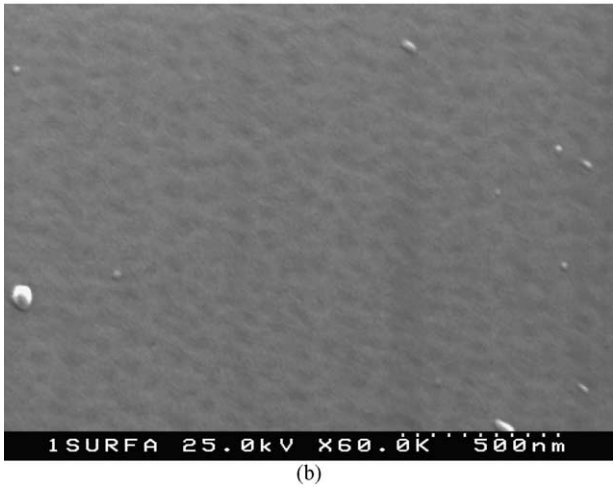


Fig. 3. HRTEM morphology of the TENOH-peptized titania sol.



(a)

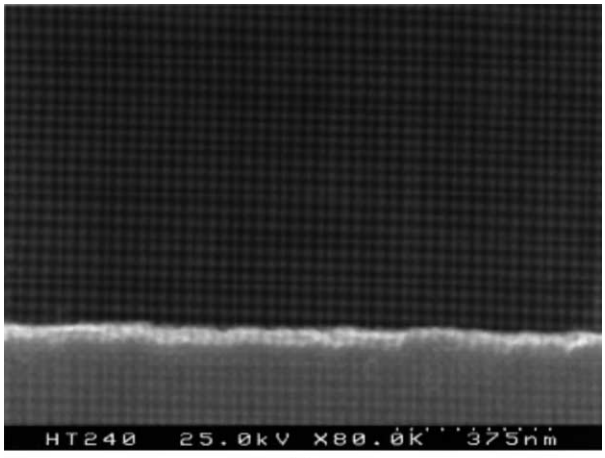


(b)

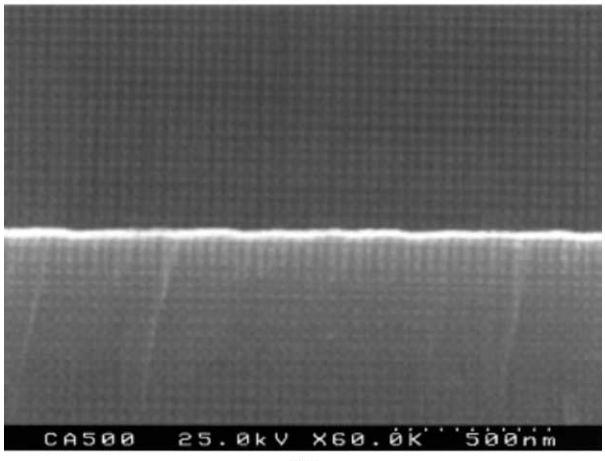
Fig. 4. SEM morphology of various films, (a) HT240, (b) CA500.

the titanium atoms and the organics was not expected, since the oxidation of the organic contents from the formed complexing species usually takes place at around 500°C with a remarkable weight loss. This is certainly not the case here. A peak corresponding to the crystallization of anatase was observed around the temperature of 450°C. However, anatase-rutile transformation takes place in the range from 1100 to 1200°C, in which an exothermic peak was observed. This indicates that anatase-rutile phase transformation in the TENOH peptized species was retarded to a higher temperature, compared with the non-peptized samples (890°C).[11]

Fig. 2 shows the XRD patterns of the untreated gel film, HT240 and CA500 films. Broad peaks corresponding to nanocrystalline anatase were found in the treated films. However, the gel film did not show any remarkable anatase peak. The formation of anatase at 240°C by hydrothermal treatment or at 500°C by heat treatment is attributed to the TENOH peptized sols, which not only facilitate the formation of anatase particles, but also promotes the crystallization of anatase in the films. In fact, anatase nuclei have already been



(a)



(b)

Fig. 5. SEM morphology of the fracture cross section of films, (a) HT240, (b) CA500.

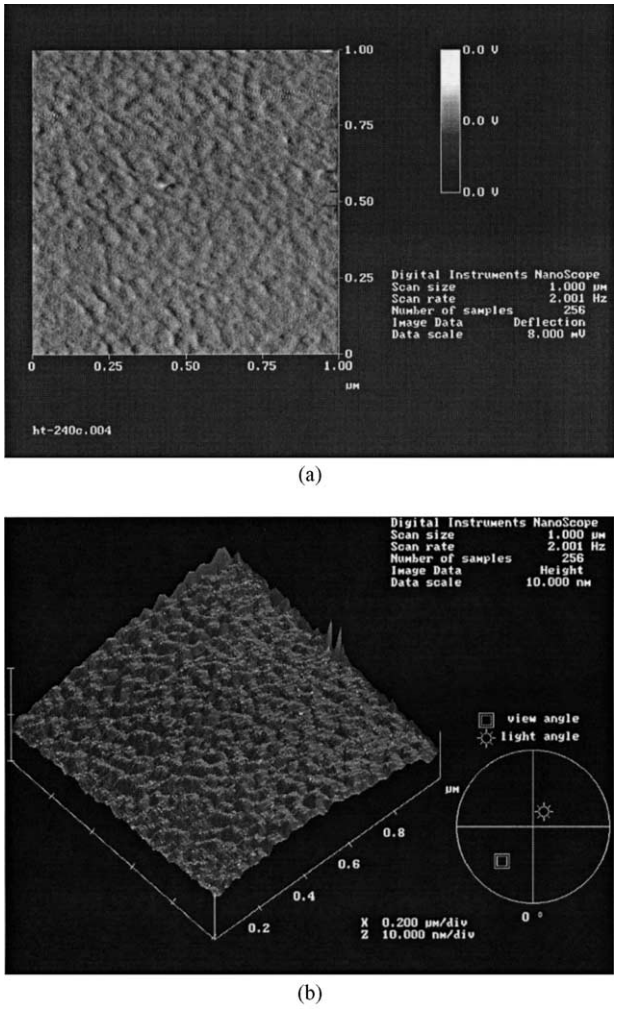


Fig. 6. AFM morphology of HT 240 film. (a) 2D, (b) 3D.

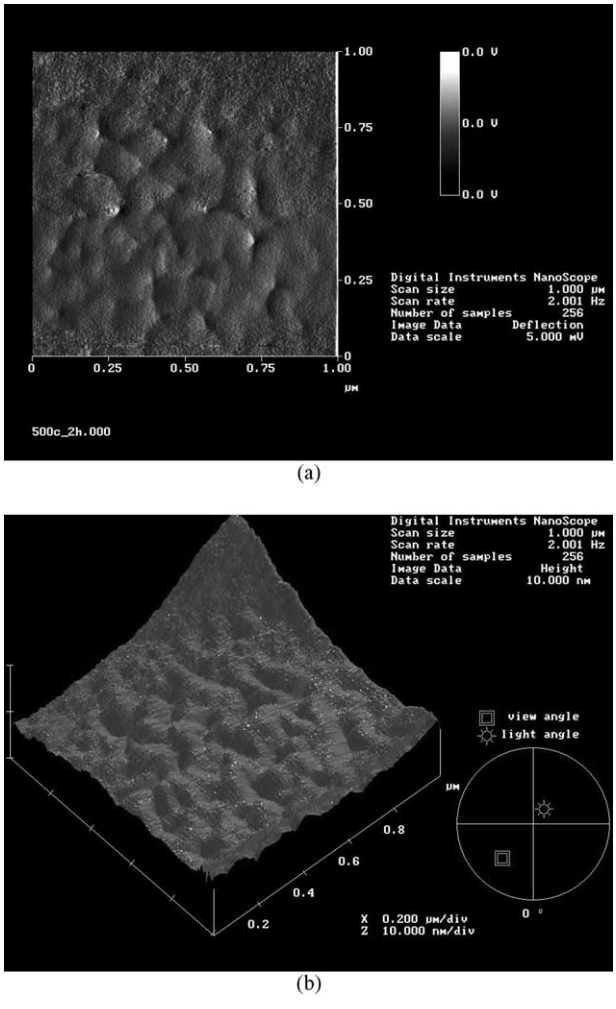


Fig. 7. AFM morphology of CA 500 film. (a) 2D, (b) 3D.

formed in the peptized sols as shown in the HRTEM micrograph (Fig. 3). Obviously, the primary particles with several nanometers are crystalline. The formation of anatase at low temperature might be attributed to the unique character of the precursors, in which tiny crystalline nuclei already appeared after peptization.

Fig. 4 shows the SEM morphology of various films. Dense structure with homogeneously distributed fine grains (around 50 nm) is observed in the hydrothermally treated films (HT240). However, the surface of the CA500 film was too flat, making it difficult to get an image in the same mode as clear as for the sample HT240. A clear image of the surface could only be obtained by tilting the sample stage by 45°C (as shown in Fig. 4b), the morphology also reflected a denser structure. The fractured cross section images of the films were presented in Fig. 5. It could be observed that the thicknesses of the films were around 50, and 40 nm for HT240 and CA500, respectively.

Close observation on the films was carried out by Atomic Force Microscopy (AFM). 2D and 3D images of the samples revealed that HT240 sample showed a more uniform distribution of fine grain of around 50 nm (Fig. 6 a and b), which is consistent with SEM observation, while DC500 sample displayed bigger grains of around 80 nm and were not so uniformly developed (Fig. 7 a and b).

4. Conclusions

The results presented and discussed along the present work show that hydrothermal treatment is an efficient technique for preparing nanocrystalline anatase films. Acetone alone formed high homogeneous diluted titania sols, but the best combination of high homogeneity and good wettability of the silicon substrates could be achieved by using mixed solvents. The as deposited coatings already exhibited nanocrystalline anatase nuclei, which gave rise to the formation of dense and homogeneous nanocrystalline anatase films by hydrothermally treating TENOH peptized titania sols at 240°C.

Acknowledgements

The first and second authors would gratefully acknowledge the FCT, Portugal, for the grants under the contracts SFRH/3553/2000 and SFRH/6648/2001.

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