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Atomic force microscopy study of TiO_2 sol–gel films thermally treated under NH_3 atmosphere

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ABSTRACT

Multilayered TiO_2 films were obtained by sol–gel and dipping deposition on quartz substrate followed by thermal treatment under NH_3 atmosphere. In an attempt to understand the close relationship between microstructural characteristics and the synthesis parameters, a systematic research of the structure and the morphology of NH_3 modified TiO_2 sol–gel films by XRD and Atomic Force Microscopy is reported. The surface morphology has been evaluated in terms of grains size, fractal dimension and surface roughness. For each surface, it was found a self-similar behavior (with mean fractal dimension in the range of 2.67–3.00) related to an optimum morphology favorable to maintain a nano-size distribution of the grains. The root mean square (RMS) roughness of the samples was found to be in the range of 0.72–6.02 nm.

1. Introduction

Titanium containing compounds, TiN_x and TiO_xN_y like, are widely used as multifunctional materials (e.g. sensors, electronic devices, hard coatings, etc) [1–6]. The employment of TiO_xN_y as photocatalyst in the visible range is an important subject in scientific papers [7–10]. Literature studies have shown that an optimum concentration of nitrogen incorporated into the TiO_2 matrix preserves the anatase phase required by the photocatalytic activity and, in the same time reduce the optical band gap down to the visible range [7,8,11,12]. The versatility of preparation procedures has lead to a wide variety of structural, optical and electrical properties as well as a large variety of potential applications. Thus, the efficiency of TiO_2 has been substantially enhanced in photocatalitic reactions by dopping either with cations of the transitional metals (V, Cr, Mn, Fe) or with anions as N, C or F. The morphology of the titanium oxynitride films (TiO_xN_y), prepared by physical methods, has been intensively studied in the last years [2,10,13–16].

In this study, three-layered TiO_2 films have been deposited by the sol–gel method on quartz substrate, followed by thermal treatment in ammonia atmosphere in the range of 400–1000 °C. In order to understand the close relation between the microstructural characteristics and the sol–gel chemical route of preparation, a systematic study on the morphology of the multilayered TiO_2 films has been performed by Atomic force microscopy (AFM). Surface properties of the films such as surface topography, grains analysis, roughness and self similarity in terms of correlation lengths and fractal dimensions have been investigated.

2. Experimental details

2.1. Film preparation

TiO_2 thin films have been prepared by sol–gel method and deposited by dip-coating technique on quartz substrates. Tetrabutyl orthotitanate ($Ti[C_4H_9O]_4$–TBOTi) from Aldrich has been used as titanium precursor. A quantity of 35.22 ml TBOTi was dissolved in 166.20 ml ethyl alcohol (Panreac) in a closed beaker at room temperature under continuous stirring. The pH of the sol was adjusted to 1.5 by addition of 2 ml nitric acid (HNO_3). Deionized water (1.36 ml) was added and the solution was refluxed under dry atmosphere and stirring for 2 h at 60 °C. Quartz plates (50 mm × 10 mm × 1 mm) were dipped in the solution and were pulled out with a constant speed of 3.33×10^{-3} m/s. The films were thermally treated in air at 450 °C for 30 min with 5 °C/min heating rate. The dip-coating and the thermal treatment procedure was repeated three times. The as prepared three-layered TiO_2 films were designated as sample (1). These samples were consequently treated in a tube furnace under NH_3 flow in a range of

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Table 1
Samples name, preparation conditions and crystallinity.

Sample	Composition	TTT (°C)	Atmosphere during thermal treatment	Cryst. phase (XRD)
1	TiO_2	450	air	Anatase
2	N–TiO_2	400	NH_3	Anatase
3	N–TiO_2	500		Anatase
4	N–TiO_2	800		Titanium Oxynitride
5	N–TiO_2	1000		Osbornite

*TTT-means the temperature of the thermal treatment.

temperatures from 400 up to 1000 °C and samples from 2 to 5 were obtained (see Table 1).

2.2. Film characterization

The crystallographic structure of the TiO_2 films with three layers, thermally treated in ammonia atmosphere, was studied by X-ray Diffraction (XRD) method. For this purpose, a SIEMENS D500 diffractometer with a secondary graphite monochromator and CuKα radiation in Bragg–Bretano geometry was used. The films were scanned in the degree range between 10 and 80° with the velocity of 0.03°/10 s.

The surface morphology of the samples was investigated by AFM, dynamic (non-contact) mode, using an EasyScan 2 apparatus (Nanosurf AG, Switzerland) with a high resolution scanner (10 µm × 10 µm with vertical range of 2 µm and *z*-axis resolution of 0.027 nm). The scan rate was in the range of 1–2 Hz. The cantilever was with spring constants of about 34 N/m and the shape of the SiN tips was square pyramidal with radius of curvature of less than 10 nm and half angle 35° (sharp tips). SPIP™ software package (version 4.6.0.0) was used for image processing.

3. Results and discussions

3.1. Structure and topography

The XRD analysis (Fig. 1) has revealed that the as prepared TiO_2 films (sample 1), as well as the samples treated in NH_3 at 400 and 500 °C (samples 2 and 3) consist of nanocrystalline TiO_2 in the anatase phase with (101) preferential orientation. The treatment at 800 °C resulted in development of a titanium oxynitride phase (TiO_xN_y) while at 1000 °C the arising of a titanium nitride in the form of $TiN_{0.9}$ (osbornite) could be noticed.

Fig. 2 shows the 3D topography of the TiO_2 films as obtained from AFM measurements at a scale of 4 µm. Except for the as prepared sample, whose surface seems to be defects rich (because of the globular-shaped deposits), the surface of the ammonia treated films exhibits particular nanostructural features, i.e. a high density of grains with nanometric dimensions.

Regarding the roughness of these surfaces, and corroborated with the XRD results, it seems to be a tendency of superficial roughness lowering (smoothing), down to the sub-nanometric level through developing the anatase crystalline phase. By further increasing the temperature of the thermal treatment up to 800 °C, the beginning of the titanium oxynitride phase formation brings no significant changes in topography and roughness. Though, a change in granulation shape and roughness could be easily observed at 1000 °C, a temperature favorable for titanium nitride developing.

In comparison, for TiO_xN_y films, prepared by reactive pulsed magnetron sputtering, Braic et al. [2] reported RMS values of about 8.5 nm, which is found to increase with the oxygen content in the film. A further increase of RMS by thermal annealing in air (of about 15%) was found in their work. In another work, Orlov [15] revealed that the surface morphology of the polycrystalline titania thin film have shown mainly featureless flat regions with a *z*-roughness in the order of 1 nm (with a minority component of the surface consisted of nanocrystallites with *z*-roughness of ≥3 nm).

3.2. Grain analysis

The photocatalytic activity in the visible range of N doped TiO_2 films was reported in 2001 by Asahy et al. [8]. For photocatalytic applications, the anatase phase was found to play a major role because it preserves more superficial active sites. In its turn, the photocatalytic activity depends on the crystallinity of TiO_2, so that the increased crystallinity enhances the photocatalytic activity. Therefore, nanostructured materials with small crystallite size, high surface area and open porosity are appropriate for these applications.

Thus, the grains superficial structure of the TiO_2 films thermally treated under ammonia flux was further analysed. In fact, the reason of the thermal treatment in NH_3 atmosphere is to decrease the optical band gap of the TiO_2 down to the visible range. This change has to be accompanied by the preservation of the nanostructured anatase phase which is the most active phase of TiO_2 in photocatalysis.

For a better view, the grain analysis was performed at a scale of 1 µm. In Fig. 3, two representative images for the morphology of the N–TiO_2 films have been selected. Thus, image 3a (sample 3) shows in details the geometry and surface arrangement of the grains which are supposed to be in the TiO_2 anatase phase – the most favourable for catalytic applications. It can be seen that these grains, with near similar shapes, are uniformly and compact dispersed on the surface of the film. In comparison, the grains of the film thermally treated at 1000 °C, Fig. 3b (sample 5), exhibit different shapes and surface arrangement. These grains seem to have a longish geometry and a less compact arrangement as compared with sample (3). For all samples, the surface grains have been statistically analysed with the SPIP package. In this sense, Fig. 3c depicts the contour image of each grain identified based on the so-called watershed method without gradient [SPIP manual – available on www.imagemet.com] for image in Fig. 3b. In Fig. 3d, the mean grain dimensions (length, width and perimeter) have been plotted for all samples as a function of temperature annealing. By comparing with the curve of RMS roughness from Fig. 2f, it can be observed the same tendency: a compact, smooth arrangement of the grains at middle temperatures, specific for the anatase phase, while at high temperatures the surface grains become larger and less compact arranged. Of course, because of the surface deposits, the grains of the as-prepared film are the largest in this series of samples.

Mohamed at al. [13] reported AFM images for TiO_xN_y films with different O_2/N_2 ratios, with a topography showing a large number of

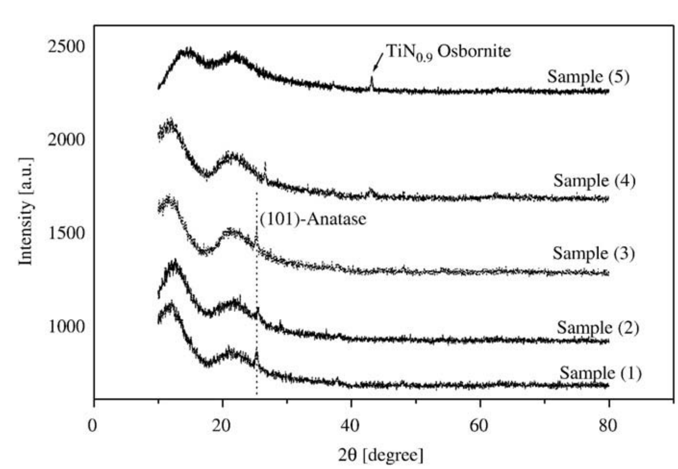

Fig. 1. X-ray diffraction patterns of the studied samples.