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Materials Science and Engineering B 137 (2007) 31–39

MATERIALS SCIENCE & ENGINEERING B

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Study on the influence of heat treatment on the crystallographic phases of nanostructured TiO_2 films

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Received 16 November 2005; received in revised form 3 October 2006; accepted 6 October 2006

Abstract

Modified sol–gel method was applied for the synthesis of single-layer and multilayers TiO_2 films from titanium tetraisopropoxide (TTIP) as precursor, acetyl acetone (AcAc) as a complexing agent, and polyethylene glycol (PEG) as an additive. The films were deposited by spin- and dip-coating and characterized by SEM and XRD. Powdery samples were prepared from the same solutions after annealing at different temperatures and studied by IR spectroscopy.

XRD analysis revealed that phase composition of the obtained films depended on the used way of thermal treatment. If the multilayer spin-coated film was heated up to 773 K after the deposition of each layer then a mixture of anatase and brookite was obtained with crystallites size of 20 nm. On the other hand if the film was dried at 393 K after the deposition of each layer and heated up to 773 K only after the deposition of the last layer then the obtained sample contained pure anatase phase with crystallites size of 24.7 nm. A theoretical model was proposed to explain the observed results.

SEM images showed that spin-coated films were nanostructured and contained spherical nanometric grains and pores. It was shown that higher PEG concentration provided higher porosity of the films. Dip-coated films were composed of nanograins and geometric particles on entire crack free surface. The effect of several parameters on the films morphology such as PEG concentration, withdrawal speed, and method of heat treatment was investigated.

Keywords: Modified sol–gel method; Polymer; TiO_2 films; Brookite; Anatase

1. Introduction

Titanium dioxide is widely used for different applications mainly in painting industry and in photocatalysis for purification of water [1,2] or air [3]. Thin films of TiO_2 are used for manufacture of electrodes [4], gas sensors [5], antireflective coatings in solar cells [6], electrochromic films [7], self-cleaning glasses [8], etc. The films synthesis by sol–gel method is of particular interest because of the advantages ensured by this method [9]. During the past years, a possibility was found [10–12] to improve the properties of titania thin films obtained by this way by means of suitable modification of the precursor with polymers. The modification permits elegant synthesis of nanometric [13] and porous [14–21] titania films. Polyethylene glycol (PEG): $HO(–CH_2CH_2O–)_nH$ is especially suitable in this respect due to its complete decomposition at a relatively low temperature [10]. The thermal treatment of the modified gel films leads to their crystallization and oxide films formation.

Titanium tetraisopropoxide exhibits high hydrolysis and polycondensation rates and a trend to precipitate into condensed particles when combined with water. Sanchez and co-workers [22,23] reported that chemical modification of alkoxides with different agents is important in sol–gel processing. It leads to formation of a new molecular precursor that can exhibit a wide range of new properties. Chemical modification of transition metal alkoxide precursor by acethylacetone leads to slowing down of the above mentioned sol–gel process and thus stabilizes the sol. Furthermore in case of organic modification by polyols such as glycerol and polyethyleneglycol corresponding mixed alkoxide derivative can be achieved. The chemical modification has a strong effect on parameters, such as gelation time, particle morphology, porosity, etc.

Two different methods of heat treatment are usually used: (i) annealing of each layer at a temperature sufficient for

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doi:10.1016/j.mseb.2006.10.001

crystallization of the film [24,25] or (ii) drying of the titanium oxide film mostly at 373–423 K after each layer deposition in order to remove the solvent and subjecting to high-temperature heat treatment only after the deposition of the last layer [26,27]. However, to the best of our knowledge there are no publications comparing the results of these two kinds of heat treatment. In this paper, we study titania films obtained by modified sol–gel method and thermally treated by these two ways. We show the difference obtained and study the influence of the processing parameters on the crystalline phase of TiO_2.

Using sol–gel method we prepared nanostructured and/or porous titania coatings from chemically modified titanium tetraisopropoxide (TTIP) chelated with acetyl acetone (AcAc) and mixed with polyethylene glycol. The present study concerns the role of the method of thermal treatment in the formation of thin titania films with different crystalline phase composition. We investigate the effect of several parameters (the amount of PEG, method of heat treatment, withdrawal speed, etc.) on morphology and texture of titania thin films obtained by dip- and spin-coating.

2. Experimental procedure

2.1. Synthesis

Experimental procedure used for preparation of the sols was similar to that reported in [10,11], but the authors of refs. [10,11] prepared the sol with diethanolamine ($(CH_2CH_2OH)_2NH$) as a complexing agent and the solvent was ethanol.

The stabilizing agent used in our system was AcAc [13]. The sol–gel solutions were prepared as follows: TTIP: $Ti(OC_3H_7{}^i)_4$ (98% purity, Acros) and AcAc: $CH_3(CO)CH_2(CO)CH_3$ were dissolved in 2-propanol (*i*-PrOH, "Loba Chemie Apolda", A.R.). The obtained solution was transparent and of orange color, which is typical for chelate complex formed. The reaction of the complex formation is exothermic. After vigorous stirring at room temperature, a mixed solution of distilled water and *i*-propanol was added dropwise to the above solution under stirring. Finally, various amount of PEG was added to obtain sols for deposition. The average molecular weight of polyethylene glycol (Fluka) was 400 g/mol. A suitable amount of the solvent was chosen in order to obtain better titania layers. A series of samples and sols (pH being in the range of 3.5–4.5) were prepared by varying titanium concentration, wt.% of PEG, number of deposited layers, method of deposition and conditions of thermal treatment.

By the described above procedure, we prepared different sols A–C by varying parameters as described below (see Table 1). In sols A and B, the molar ratio of the components was TTIP:*i*-PrOH:H_2O:AcAc = 1:30:1:1 while in sol C it was 1:50:1:1. Correspondingly, titanium concentration in sols A and B was 0.35 mol/L while in C—0.25 mol/L. The added amount of PEG was 10 wt.% for sol A and 1 wt.% for sols B and C. The viscosity of the prepared sols was about 5–10 cP. The obtained sols were transparent and stable in hermetically closed cell for at least 1 year.

The films were deposited by spin- and dip-coating on soda-lime glass plates. The sizes of the substrates used for the deposition by spin-coating were 26 mm × 26 mm and 10 mm × 10 mm, while for dip-coating, 76 mm × 26 mm. The thickness of the substrates was about 1 mm. Table 1 summarises the most interesting samples obtained as described above and discussed in this paper.

2.2. Spin-coated samples

Before spin-coating the optically transparent microscope glass slides were thoroughly cleaned firstly with chromerge solution (H_2SO_4/Cr_2O_3), then with a mixture of hydrochloric and nitric acid, and finally with ethanol and acetone successively [28]. The sols were deposited dropwise on the substrates, which were rotated with velocity of 1500 rpm reported by Peshev and Slavova [29].

Two four-layer samples (S1 and S2) have been prepared from sol C. Organic/inorganic composite titania films were obtained. Slow heating at the rate of 2–5 °C/min was used to avoid cracks formation (so-called stepwise heat treatment) [13,24]. Sample S1 was subjected to stepwise thermal treatment up to 773 K and then annealed at this temperature for 2 h after the deposition of each layer [24,25]. Each layer of sample S2 was subjected to

Table 1
Chemical composition of sols used for deposition and preparation conditions of series of samples

Samples	Sol ref.	Molar ratio, TTIP:*i*-PrOH:H_2O:AcAc	PEG/TTIP (wt.%)	$[Ti]_f$ (mol/L)	NDL[a]	MD[b]	Velocity	TT: T0 = 393 K; (30′); T1 = 623 K (2H); T2 = 773 K (2H)
S1	C	1:50:1:1	1	0.25	4	Spinning	1500 rpm	T2
S2					4			T0 + T2
S3	A	1:30:1:1	10	0.35	1	Spinning	1500 rpm	T2
S4					1			T0 + T2
S5					2			T2
S6	B	1:30:1:1	1	0.35	1	Spinning	1500 rpm	T2
S7	C	1:50:1:1	1	0.25	1	Dipping	10 cm/min	T1
S8							10 cm/min	T1 + T2
S9							1 cm/min	T1
S10							2 cm/min	T2

[a] NDL, number of the deposited layers.
[b] MD, method of deposition.