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Short Communication

Rare earth-doped TiO_2 nanocrystalline thin films: Preparation and thermal stability

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Abstract

A colloidal sol–gel route was used for the synthesis of nanoparticulate TiO_2 and Ln^{3+}-doped TiO_2 sols (Ln = Eu or Er; contents of 1, 2, or 3 mol.%), from which the corresponding functional nanocrystalline thin films were subsequently obtained by the dip-coating method. It was found that the as-synthesized sols are not entirely suitable for the preparation of homogeneous thin films due to the water's high surface tension, a problem that is however solved by diluting the sols in ethanol. Appropriate dilution conditions were then determined, and the effect of this dilution on the sol viscosity identified. Finally, the phase composition in the as-deposited condition and the thermal stability of the dip-coated thin films were investigated by X-ray thermodiffractometry up to 1000 °C. It was found that the as-deposited thin films are homogenous and formed by the desired anatase nanoparticles, which eventually start to transform into rutile particles at high temperature. However, no precipitation of titanates occurs in the temperature range investigated. Also, it was observed that increasing the Ln^{3+} content improves the thermal stability of these anatase nanocrystalline thin films, an effect that is, if any, slightly more marked for Eu^{3+} than for Er^{3+}.

Keywords: Ceramic thin films; TiO_2; Phase transformation

1. Introduction

There is great interest in the preparation of ceramic thin films for their utilization in many functional applications, including photo-induced applications. TiO_2, a well-known semiconductor oxide, is one of those ceramics with an attractive set of properties for the fabrication of thin films used in photocatalytic,[1] photoluminescent,[2] electrochemical[3] and photoelectric[4] devices, to name a few potential applications. Anatase, especially if doped with trivalent lanthanides and having a particle size in the nanoscale, is the preferred polymorph of the TiO_2 variants (*i.e.*, anatase, rutile, brookite, and β-TiO_2) for photo-induced applications, which justifies the research efforts put on its synthesis[5–8] and on the study of its thermal stability.[8,9]

Polycrystalline ceramic thin films, including TiO_2-based thin films, can in principle be deposited using various methods. Dip-coating is one of the most widely-used methods for depositing oxide ceramics onto large surfaces, where the substrate is first immersed into and subsequently extracted from a precursor liquid solution or suspension thus creating the thin film. This method also offers certain advantages in terms of simplicity, versatility, cost, processing temperatures, quantities produced, etc. Normally, the ceramic precursor solutions/suspensions have been prepared by the polymeric sol–gel route,[10–14] which uses organic solvents (*i.e.*, alcohols). Today, however, there is a growing demand for preparing these solutions/suspensions using an aqueous media, and therefore the colloidal sol–gel route, which uses water instead of alcohol and is thus clearly more environmentally friendly and cost-effective, is being the subject of increasing attention.[6,15]

With these premises, the present study was undertaken with two objectives in mind. The first is to prepare TiO_2 nanocrystalline thin films of anatase phase, both undoped and doped with

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different concentrations of Ln^{3+} (Ln = Eu or Er; contents of 1, 2, or 3 mol.%) ions, by the dip-coating method from nanoparticulate sols synthesized by a colloidal sol–gel route. The second is to assess the thermal stability of these anatase thin films, as a function of temperature up to 1000 °C. The details of the experiments and the major findings are described below.

2. Experimental

The TiO_2 sols were prepared by adding titanium(IV) isopropoxide (97%, Sigma-Aldrich, Germany) to a stirring mixture of deionized water (18.2 MΩ cm^{-1}, ultrapure Milli-*Q*, France) and nitric acid (65%, PANREAC, Spain) in water:alkoxide and H^+:Ti^{4+} molar ratios of 50:1 and of 1:5, respectively; HNO_3 was used as a catalyst and dispersing agent. For the preparation of the Ln^{3+}-doped TiO_2 sols (Ln = Er or Eu), the corresponding lanthanide(III) acetate hydrate ($Ln(OOCCH_3)_3 \cdot xH_2O$, Sigma-Aldrich, Germany) was dissolved in the H_2O–HNO_3 mixture to a molar ratio Ln^{3+}:TiO_2 of 1:99, 2:98, and 3:97 (hereafter referred to simply as 1, 2, or 3 mol.% Ln^{3+}) prior to the addition of the titanium(IV) isopropoxide. The synthesis temperature was maintained constant during the entire process at 35 °C.

The aqueous sols were used in their as-prepared condition, and were also diluted in absolute ethanol (99.5%, Panreac, Spain) using different dilution conditions (*i.e.*, ethanol contents in the range 8–60 vol.%). The viscosity of the as-prepared and diluted sols was measured using a rotational rheometer (RS50, Haake, Thermo, Germany) with a double-cone/plate sensor configuration (DC60/2°, Haake, Thermo) operated in controlled shear rate mode with the following measurement cycle: linear increase of the shear rate from 0 to 1000 s^{-1} in 300 s, plateau at 1000 s^{-1} for 60 s, and decrease to zero shear rate in 300 s. The average particle size in selected sols was also measured, using dynamic light scattering (DLS; Zetasizer Nano ZS, Malvern, UK).

Thin films were deposited from the sols at room-temperature onto well-cleaned, single-crystal (plane (1 0 0)) Si substrates (~2 × 1 cm^2) by the dip-coating method, using a withdrawal rate of 0.5 mm s^{-1}. Atomic force microscopy (AFM; Nanotec Electronica, Spain) was used to observe the surface topography of selected thin films, with the sole objective of confirming their homogeneity and nanocrystalline nature. Finally, the phase composition in the as-deposited condition and the thermal stability of the thin films were investigated by X-ray thermodiffractometry (XRTD), using to that end a high-resolution diffractometer (D8 Advance, Bruker AXS, Karlsruhe, Germany) of pure Cu-$K\alpha_1$ incident radiation (λ = 1.5406 Å) that is equipped with a linear ultra-fast detector and with a micro-furnace high-temperature chamber.[9] The XRTD patterns were acquired *in situ* in the temperature range 30–1000 °C with a temperature step of 3 °C, heating ramp of 3 °C s^{-1}, and delay time of 2 s, and the acquisition was done with the detector operating in snapshot mode (fixed 2θ mode) for 60 s with its window being opened at 11° 2θ to register simultaneously the angular range 21–32° 2θ. The crystalline phases were identified with the aid of the PDF2 database.

3. Results and discussion

The first step was the preparation of TiO_2-based thin films using directly the sols in their as-synthesized condition. However, as can be seen in Fig. 1 for the undoped TiO_2 sols, the resulting thin films were, unfortunately, quite inhomogeneous. This is because the water's high surface tension (~72 mN m^{-2} at 25 °C)[16] induces the formation of many drops during the slow drying stage at room temperature (water's boiling temperature is ~100 °C). Based on this and earlier results[7] we decided to dilute the sols in ethanol, which has a lower surface tension (~22 mN m^{-2} at 25 °C) and boiling temperature (~78 °C)[16] than water, and investigate the effect of the ethanol concentration on the quality of the resulting thin films. Photographs

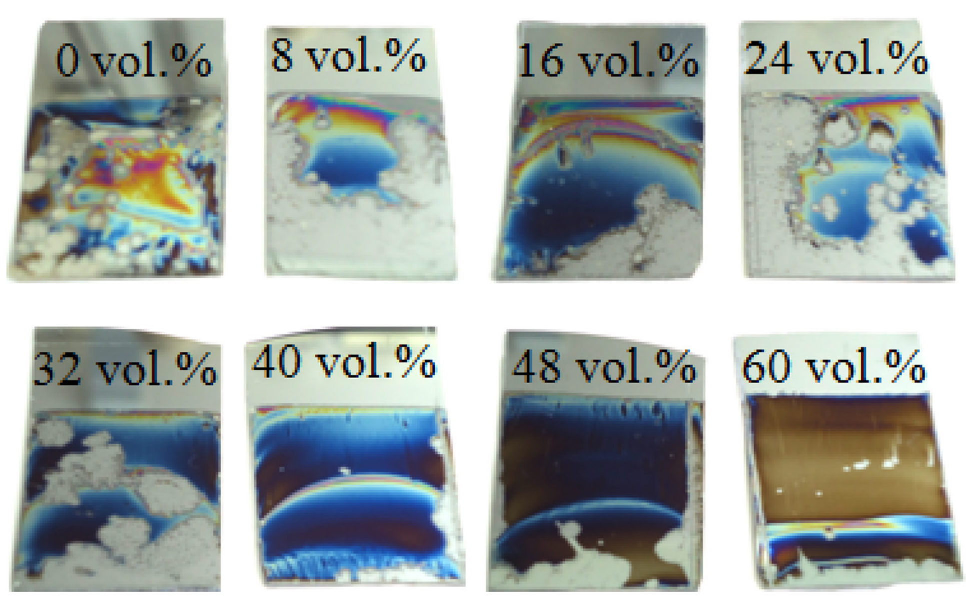

Fig. 1. Photographs of the undoped TiO_2 thin films obtained by the dip-coating method from the as-synthesized and diluted sols. The number in each photograph indicates the dilution condition (*i.e.*, ethanol concentration in vol.%). The substrate dimensions are 2 cm length × 1 cm width.