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Elaboration and characterization of nanocrystalline TiO_2 thin films prepared by sol–gel dip-coating

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ABSTRACT

Nanocrystalline TiO_2 thin films were deposited on a ITO coated glass substrate by sol–gel dip coating technique, the layers undergo a heat treatment at temperatures varying from 300 to 450 °C. The structural, morphological and optical characterizations of the as deposited and annealed films were carried out using X-ray diffraction (XRD), Raman spectroscopy, Atomic Force Microscopy (AFM), visible, (Fourier-Transform) infrared and ultraviolet spectroscopy, Fluorescence and spectroscopic ellipsometry. The results indicate that an anatase phase structure TiO_2 thin film with nanocrystallite size of about 15 nm can be obtained at the heat treatment temperature of 350 °C or above, that is to say, at the heat treatment temperature below 300 °C, the thin films grow in amorphous phase; 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. We have accurately determined the layer thickness, refractive index and extinction coefficient of the TiO_2 thin films by the ellipsometric analysis. The optical gap decreases from 3.9 to 3.5 eV when the annealing temperature increases. Photocatalytic activity of the TiO_2 films was studied by monitoring the degradation of aqueous methylene blue under UV light irradiation and was observed that films annealed above 350 °C had good photocatalytic activity which is explained as due to the structural and morphological properties of the films.

1. Introduction

Titanium dioxide (TiO_2) is an important inorganic functional material with good physical properties, which make it suitable for thin film applications. Because TiO_2 has high dielectric constant ε, TiO_2 films have often been used in microelectronic devices, e.g. in capacitors or as a gate dielectric in metal-dielectric-semiconductor devices [1,2]. TiO_2 thin films are also often used as various optical coatings for its good transmittance in the visible region, high refractive index and chemical stability [3,4]. A variety of techniques have been used for the preparation of TiO_2 films including chemical vapor deposition [5], sputtering [6], and electron-beam evaporation (EBE) [7], and sol–gel [8]. The sol–gel technique has been used for making optical coatings about 50 years ago and in the last decade attracted more attention due to the intensive development of sol–gel technology.

Numerous literature reports on the fabrication of TiO_2 thin films by sol–gel dip coating technique using many types of titanium alkoxides as precursors. Legrand-Buscema et al. [9] used $Ti(O\text{-}nBu)_4$ as a precursor and acetic acid as a catalyst and acetylacetone is added as a chelating agent to decrease the reactivity and stabilize the sol. Ahn et al. [10] prepared the thin layers of TiO_2 by sol–gel process and their structural and optical properties were examined at various catalyst concentrations and calcination temperatures. Their thin films calcined at temperatures from 400 to 600 °C are anatase phase, and transform into the anatase to rutile phase at 800 °C, and further into the rutile phase at 1000 °C. The phase transformation temperature turns out to rely upon the concentration of catalyst HCl. The crystallite size of the films is increased with increasing catalyst concentration and calcination temperature. Mechiakh et al. [11] studied the influence of the temperature on the optical and structural properties of TiO_2 thin films, used tetrabutyl-orthotitanate as a precursor to prepare titanium solutions and thin films of TiO_2 in their sol–gel process. Their thin films crystallize, starting at temperatures from 400 to 800 °C are anatase phase, and transform into the anatase to rutile phase at 1000 °C, and further into the rutile phase at 1200 °C. In a previous study [12], we have found out the three-layered thin film crystallization, starts at 350 °C in anatase, and brookite phases. For a higher number (10) of layers and an annealing temperature of 400 °C we have found [13,14], that the crystalline structure changes from anatase–brookite to rutile, which normally does not appear below 800 °C as reported in literature [10].

In comparison with other film technologies the sol–gel process has certain advantages: low process cost, low temperature of heat treatment, high evenness of the films and wide possibility to vary

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film properties by changing the composition of the solution, etc. TiO_2 film can transform from amorphous phase into crystalline anatase and then into rutile phase during calcination [13,15]. The TiO_2 films with different structure varied in optical and photocatalytic properties.

The photocatalytic property of TiO_2 film can vary with the composition (stoichiometry, hydroxyl and impurity concentrations), the porosity, the surface roughness, the film thickness, the micro or nanostructure,..., although the influence of all these parameters is still a matter of debate [16–19].

Some researchers stated that the TiO_2 film consisting of anatase and rutile phases with an appropriate ratio has the best photocatalytic activity [20]. So, it is important to optimize the preparation process to obtain TiO_2 film with appropriate phase composition. And the key factors to influence the microstructure of TiO_2 film are substrate and anneal temperature [21–23]. In this work we have studied the recrystallization of TiO_2 films due to the post deposition annealing and correlated the annealing conditions with structure, morphology, and optical properties. The results of this study will update the data on sol–gel prepared TiO_2 films and its applications in photocatalysis. The deposited TiO_2 thin films were characterized using XRD, Raman, AFM, X-ray fluorescence, spectroscopic ellipsometry, IR and UV–vis spectrophotometer.

The aim is to show the feasibility of obtaining TiO_2 films with tailored structures going from amorphous to mainly anatase films, with soft fabrication conditions: the low temperature and moderate annealing treatment. These fabrication conditions help decrease the processing energy cost of films devoted to low-cost photocatalytic reactors for water depollution.

2. Materials and methods

2.1. Preparation of the coating solutions

TiO_2 sol used for the deposition of the films by dip-coating method was obtained by the partial hydrolysis and condensation of tetrabutyl-orthotitanate $(OC_4H_9)_4Ti$ with H_2O. In this process butanol and acetic acid were used as solvent and catalyst, respectively. In sol–gel technique in order to obtain stable sol solution the proportion of $(OC_4H_9)_4Ti$, C_4H_9OH, $C_2H_4O_2$, and H_2O must be controlled. In this work, we used 1 mol tetrabutyl-orthotitanate, 1 mol H_2O, 4 mol butanol, and 3 mol acetic acid. During the preparation of the sol a mixture of water and butanol was added drop by drop into a flask containing tetrabutyl-orthotitanate, acetic acid, and butanol. The solution was stirred at room temperature for about 1 h. A gel film was formed on the ITO coated glass substrate (the use of ITO substrate has great advantages in solar cell applications) by dipping it into the solution and pulling it up at a constant rate of 0.6 cm s^{-1} by a dipping machine (Fig. 1). This process is optimal for producing highly uniform coatings, by simple control of the thickness through control of the speed of withdrawal from the coating solution. The gel films on the ITO coated glass substrate contain residual butanol and very probably water from the condensation reaction. The dip coated ITO coated glass substrate was therefore left to dry at ambient temperature (humidity equal 38%) followed by heating at 100 °C in an oven for a minimum of 15 min.

2.2. Preparation of TiO_2 coatings

A dip-coating apparatus made in our laboratory was used for the depositions. The substrate was lowered into the coating solution and then withdrawn at a regulated speed of 0.6 cm s^{-1}. After each coating, the films were first dried at 100 °C for 15 min. The films are obtained after 4 dippings and were then heat-treated at different temperatures ranging between 300 and 450 °C with increasing temperature rate of 5 °C min^{-1} for 2 h in furnace. The thickness of the thin films obtained varies between 140 nm (300 °C) and 108.4 nm (450 °C) depending on the temperature of annealing.

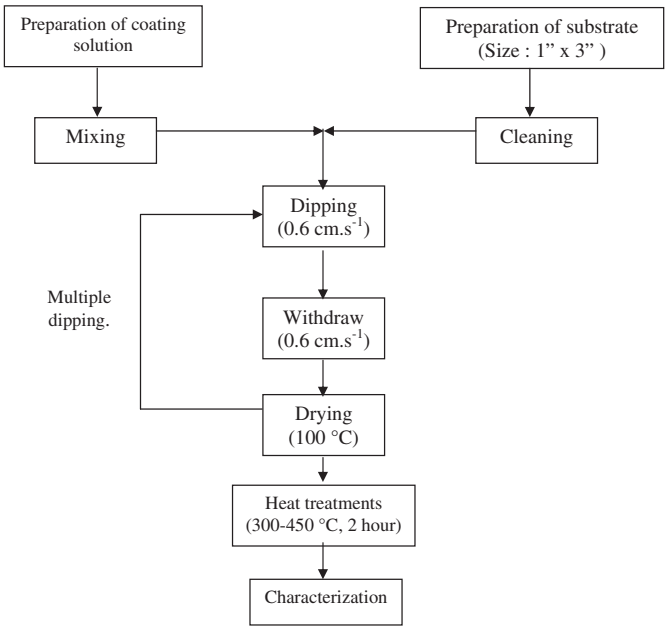

Fig. 1. Flow chart for preparing titanium dioxide thin films.

2.3. Material characterization

Thin film grazing X-ray diffraction was used for crystal phase identification. XRD patterns were obtained with a Siemens D5005 diffractometer using CuKa radiation at 40 kV and 20 mA. The Raman spectra were recorded at room temperature with a Jobin-Yvon Labram HR combined Raman-IR microanalytical spectrometer equipped with a motorized xy stage and autofocus. The spectra were generated with 17 mW, 632.8 nm He–Ne laser excitation and were dispersed with the 1800 gr/mm grating across the 0.8 m length of the spectrograph. The laser power was 9 mW on the sample surface. The spectral resolution of this apparatus is estimated to be less than 0.5 cm^{-1} for a slit width of 150 μm and a confocal hole of 300 μm. Morphology study was performed using tapping mode of a Topometrix TMX 2000 Explorer AFM. Optical properties of the films deposited on ITO coated glass substrates were examined by a UV–vis spectrophotometer (UV3101PC). The FT-IR spectra were obtained with a Fourier transform infrared spectrometer (genesis II DTGS). The

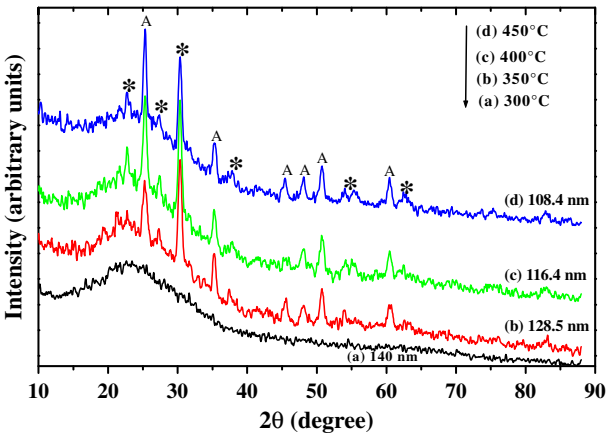

Fig. 2. The evolution of diffraction patterns of the thin films of oxide obtained after 4 dippings and various annealings at 300 (a), 350 (b), 400 (c) and 450 °C (d). The labeling of the peaks is as follows: A = anatase, * = substrate.