



Effect of solution composition on anatase to rutile transformation of sprayed TiO₂ thin films



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ABSTRACT

Acetylacetone is used as a chelating agent for titanium(IV) isopropoxide to inhibit hydrolysis and stabilize the precursor solution. The effect of the molar ratio between titanium(IV) isopropoxide and acetylacetone of 1:1, 1:2, 1:3 and 1:4 in the precursor solution on the morphological, structural and optical properties of TiO₂ thin film was investigated. These properties were studied using Fourier transformed infrared spectroscopy, scanning electron microscopy, Raman spectroscopy, X-ray diffraction and UV–vis spectroscopy as a function of the molar ratios for the as-deposited thin films and films annealed at temperatures of 700, 800 and 950 °C. Mixed anatase and rutile phases were detected after annealing at 800 °C for 1:1 and 1:2 molar ratios and at 700 °C for 1:3 and 1:4 molar ratios. The optical band gap decreased from 3.45 to 3.02 eV with an increase in the annealing temperature in agreement with corresponding structural changes.

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1. Introduction

Deposition of TiO₂ thin films from titanium alkoxides requires the use of chelating agents to prevent fast hydrolysis and stabilize the precursor solution. Stabilization can be achieved by ways in which hydrolysis/condensation sites are blocked by non-hydrolyzable moieties or by chelating ligands that are resistant to hydrolysis compared to alkoxyl groups [1]. The composition of the precursor solution can be controlled to obtain thin films with the desired structural, morphological, optical and electronic properties. Different chelating agents have been reported in literature including acetylacetone (AcacH), acetic acid, methylacetoacetate, ethylacetoacetate, diethanolamine (DEA) and polyethylene glycol (PEG) [1–5].

Djaoued et al. have reported on the effect of different complexing agents on the properties of TiO₂ thin films prepared by dip coating and showed that phase transformation from anatase to rutile is delayed up to 900 °C with AcacH but starts at around 750 °C with DEA and PEG agents [2]. A study on the impact of AcacH and Ti-source molar ratio between 1 and 8 on the properties of (Pb,Ba)TiO₃ showed that the titanium precursor solution is fully stabilized when the molar ratio is ≥ 3 [6]. The rate of hydrolysis–condensation reaction is inversely proportional to the amount of ligand/complexing agent and relates to the particle size of the TiO₂ sol [5]. Ethanol is commonly used as the solvent but studies have shown that the dilution of monomeric titanium(IV)

isopropoxide (TTIP) stabilized in AcacH leads to substitution of isopropoxy groups by ethoxy groups resulting in the formation of oligomeric species [7]. The solvent can as well affect the structure of the species in the solution and their relative reactivity hence controlling the properties of the TiO₂ thin films. It is important therefore to investigate the effect of TTIP:AcacH molar ratio on the properties of TiO₂ thin films.

In this paper we report morphological, structural and optical properties of TiO₂ thin films deposited by chemical spray pyrolysis (CSP) from TTIP precursor with different amounts of AcacH chelating agent in ethanol solvent. CSP has the advantage of being scalable to large areas, flexibility in the choice of precursor materials and their combinations, potential for low cost electronic applications and possibility of coating different types of substrates. The effect of TTIP:AcacH on the phase transformation of TiO₂ thin films from anatase to rutile is also presented.

2. Experimental details

TiO₂ thin films were deposited onto c-Si and glass substrates from titanium(IV) isopropoxide (TTIP) precursor with AcacH as the chelating agent (both solutions from Merck Schudart OHG) in ethanol solvent by pneumatic CSP [8]. TTIP:AcacH molar ratios of 1:1, 1:2, 1:3 and 1:4 were obtained by mixing 2.1 ml of TTIP with 0.7, 1.4, 2.1 and 2.8 ml of AcacH, respectively, and filling up the container with ethanol while stirring up to 30 ml of solution. TTIP concentration in the spray solution was 0.24 mol l⁻¹. Compressed air with a flow rate of 8 l/min was used as the carrier gas while the spraying rate was adjusted to about

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1.5 ml/min by dividing the amount of solution sprayed by the spraying time. The number of spray cycles was set to ten, each consisting of a spray for 60 s and a pause of 60 s. The deposition temperature (T_s) set to 450 °C was taken as the temperature of the tin bath on which the substrates were placed during deposition. Each c-Si/TiO₂ sample from each molar ratio was cut into four smaller sizes and annealed at 700, 800 and 950 °C for 30 min at each temperature using Nabertherm L5/11/06D furnace. One piece from each molar ratio was not annealed to serve as a reference.

The chemistry of the precursor solutions was probed by Fourier transform infrared (FTIR) spectroscopy using Perkin Elmer GX-1 spectrometer over wavenumber range of 370–4000 cm⁻¹. A Zeiss Ultra-55 field effect scanning electron microscope (FESEM) was used to study the morphology and to determine the thickness of the TiO₂ thin films. The acceleration voltage for the SEM measurements was 4.0 kV. Vibrational spectroscopy was performed on TiO₂ thin films by Raman spectroscopy using Horiba Jobin Yvon Labram HR 800 micro-Raman spectrometer in the spectral range of 50–800 cm⁻¹. The wavelength of the laser used to probe the samples was 532 nm. The XRD diffractograms were obtained from Rigaku Ultima IV diffractometer fitted with Cu K α radiation source of wavelength 0.15406 nm and operating at 40 kV, 40 mA, using the silicon strip detector D/teX Ultra. The measurements were performed over a 2 theta scan range of 10–60° with 0.02° step width at the rate of 5°/min. The mean crystallite size was calculated using the Scherrer formula. The total transmittance and reflectance data were measured with Jasco V-670 spectrophotometer equipped with an integrating sphere in the spectral range between 300 and 2000 nm.

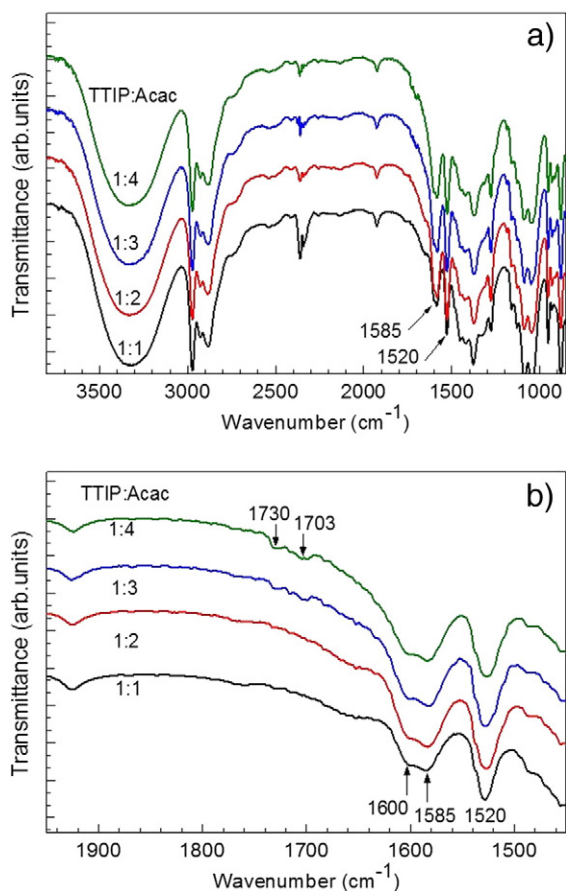


Fig. 1. (a) FTIR transmittance spectra of the precursor solutions with different TTIP:AcacH molar ratios of 1:1, 1:2, 1:3 and 1:4 and (b) the change in IR absorption at 1703 and 1730 cm⁻¹ due to excess AcacH after chelation with TTIP precursor.

3. Results and discussions

3.1. Chemistry of precursor solution

The FTIR spectra for the precursor solutions with different TTIP:AcacH molar ratios are shown in Fig. 1. The broad absorption band that centered at 3300 cm⁻¹ belongs to the stretching vibrations of O–H bonds and the peaks at 2995–2880 cm⁻¹ range are assigned to C–H bond vibrations from isopropoxide groups [9]. The peaks in 1600–1525 cm⁻¹ range show C–C and C–O bonds of acetylacetonate (Acac) groups bonded to Ti indicating chelation of TTIP by AcacH. The absorption peak at 1585 cm⁻¹ from the solution of 1:1 molar ratio was relatively less intense compared to the peaks from solutions of 1:2, 1:3 and 1:4 molar ratios which may indicate a comparatively lower degree of chelation. Complete chelation has been reported for solutions with 1:2 molar ratio and the presence of excess AcacH for TTIP:AcacH molar ratio of $\geq 1:3$ [6].

AcacH shows two tautomeric forms; the *enol* form that dominates most organic forms and the *keto* form which dominates in water [9]. A double absorption band between 1590 and 1520 cm⁻¹ comes from a split of the *enol* tautomeric AcacH C=O bond expected at 1620 cm⁻¹ which indicates the chelation occurring between TTIP and AcacH. A doublet peak at 1703 and 1730 cm⁻¹ are assigned to the bonding vibration of the *keto* tautomeric C=O group [10,11] as shown in Fig. 1(b). These absorption peaks at 1703 and 1730 cm⁻¹ for the ratios 1:3 and 1:4 indicate the presence of excess AcacH after chelation [10]. They are attributed to C=O carbonyl group not involved in Ti chelation. Boland et al. reported that if the ratio of AcacH to TTIP is less than 2, the titanium precursor is not fully stabilized [6]. The multiple peaks at 800 cm⁻¹ and below belong to the Ti–O–Ti and Ti–O stretching bonds.

3.2. Surface morphology

Fig. 2 shows SEM micrographs of TiO₂ thin films sprayed from precursors with TTIP:AcacH molar ratios of 1:1, 1:2, 1:3 and 1:4 as indicated. TiO₂ thin films from TTIP:AcacH molar ratios of 1:2 and 1:3 were uniform, homogeneous and dense while the films from precursor ratios 1:1 and 1:4 were inhomogeneous and formed islands. The islands did not change even after annealing. The films showed small nanosized grains (20–30 nm) of elliptical shape similar to what has been observed also for ultrasonically sprayed TiO₂ thin films [12]. The effective layer thickness for all the thin films as determined from their cross sections by SEM ranged between 175 and 190 nm.

The sizes of the crystals increased with an increase in annealing temperature as can be seen in Fig. 3 for TiO₂ thin films deposited from TTIP:AcacH of 1:3. After annealing at 700 °C, the smaller grain sizes were about 50 nm and a larger one of about 200 nm (Fig. 3(a)). The grain sizes increased to between 100–300 nm and 100–350 nm after annealing at 800 and 950 °C (Fig. 3(b) and (c)), respectively. The film thicknesses decreased to between 100 and 140 nm after annealing due to densification of the film after all organics evaporated.

3.3. Structural properties: Raman and XRD

Raman spectra for the TiO₂ thin films deposited at 450 °C from TTIP:AcacH molar ratios of 1:2 and 1:3 are shown in Fig. 4(a) and (b), respectively. The spectrum from the c-Si substrate is also included as reference with its main peaks appearing at 302 and 520 cm⁻¹. All as-deposited samples showed anatase main peaks at 143 and 638 cm⁻¹, which are due to O–Ti–O symmetric stretching vibrations [12,13]. After annealing at 700 °C, the intensity of this main anatase peak for the sample deposited from 1:2 molar ratio increased strongly as shown in Fig. 4(a). The full width at half maximum (FWHM) of the anatase peak decreased from 12.8 cm⁻¹ to 9.5 cm⁻¹. The increase in the peak intensity and reduction in FWHM corroborates the increase in the crystallite size of the anatase phase [14]. After annealing at 800 °C, the anatase peaks

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