TiO$_2$ thin films prepared by sol - gel method

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Abstract. There is a growing awareness that titania (TiO$_2$) and TiO$_2$-based oxide systems are the most promising candidates for the development of photoelectrodes for photoelectrochemical cell (PEC) for solar-hydrogen production [1]. The PEC is equipped with a single photoelectrode (photoanode) and cathode, both of which are immersed in an aqueous electrolyte. In this work we present a sol-gel method to prepare TiO$_2$ thin films on ITO using tetraisopropoxides of titanium, acetylacetone, 1-butanol and Tween 80 as surfactant. The films were deposited on ITO coated glass slides by spray pyrolysis. UV-VIS spectra and fluorescent measurements were made for the solutions and films. X-ray diffraction was used for structural investigations and the morphology of the film was studied by Scanning Electron Microscopy.

1. Introduction

TiO$_2$ has found wide and important applications in many fields of chemical engineering and materials engineering including either traditional catalysis, or photocatalysis, dye-sensitized solar cells, lithium-insertion-based devices, integrated circuits, gas sensors and in the paint industry [2]. Most of these applications are a consequence of its n-type semiconducting property and realized with micro or nano structured TiO$_2$ powders or thin films.

A number of methods have been employed to prepare TiO$_2$ films, including e-beam evaporation, sputtering, chemical vapor deposition and sol-gel process. The sol-gel conventional method uses the hydrolytic route, which involves the initial hydrolysis of the alkoxide precursor followed by continual condensations between the hydrolysed particles forming the gel.

This process is carried out at room temperature, and the desired morphological properties of the particles are obtained by controlling the conditions under which the synthesis is carried out. Moreover, sol-gel processing route is particularly attractive for the scaling-up of oxide thin films fabrication, since the liquid precursor can easily be applied on a substrate by dipping, spinning or spraying [3] and heat treated at lower temperatures.

The spray-coating technique potentially offers the advantage of conformal film deposition on non-planar structures (e.g. steps, stacks or trenches) on semiconductor chips [4].

In this paper, we report the preparation of TiO$_2$ films using the hydrolytic sol-gel process to obtain the oxide and the spray-coating technique to deposit the films on ITO glass substrates.
2. Experimental

2.1. Preparation of coating solution
Firstly, 1-butanol sol was made, which include 0.496M commercial ultrapure titanium isopropoxide (TTIP, Fluka), 0.28M acetylacetone (99%, Alfa Aesar), 0.92M H$_2$O and 1-butanol (absolute). Subsequently, Tween 80 and 1-butanol solvent were added to the 1-butanol sol. During the sol preparation, the alkoxide solution was vigorously stirred at room temperature, so as to keep a homogeneous mixture of the chemical compositions.

2.2. Deposition and thermal treatment of precursors films
The film consists on five layers of TiO$_2$ was obtained by spray pyrolysis. The as obtained films were heat-treated at 600ºC, 1 h.

2.3. Analysis
UV–VIS absorption spectra of the TiO$_2$ coating solutions and thin films deposited on ITO glass were taken on a JASCO V-550 spectrometer. X-ray diffraction (XRD) measurements were performed using a BRUKER D8 Advance X-ray diffractometer, working at 45 kV and 45 mA. The Cu K$_\alpha$ radiation, Ni filtered, was collimated with Soller slits. A germanium monochromator was used. The data of the X-ray diffraction patterns were collected in a step-scanning mode with steps of $\Delta 2\theta = 0.01^\circ$. Pure silicon powder (standard sample) was used to correct the data for instrumental broadening. The microstructural informations obtained by single X-ray profile Fourier analysis of the TiO$_2$ anatase nanoparticles were the effective crystallite mean size ($D_{\text{eff}}$) and the root mean square (rms) of the microstrains, averaged along the [hk l] direction, $<\varepsilon^2>^{1/2}_{hk l}$ [5]. The Warren-Averbach X-ray profile Fourier analysis of the (101) and (200) anatase peak profiles were processed by the XRLINE [6] computer program. The unit cell parameters were calculated by Rietveld refinement using the PowderCell software [7]. PowderCell program enables a quantitative phase (volume fractions) analysis method by comparison of the different scattering powers of the component materials.

The morphology of the films was investigated by Scanning Electron Microscopy using a JSM 5600 LV field emission – high resolution scanning electron microscope equipment with an Oxford INCA Crystal electron backscattering diffraction (EBSD) systems.

3. Results and Discussion

3.1. Precursor characterization
The X-ray diffraction pattern of the dried (100ºC) hydrolyzed precursors, shown in figure 1, evidences its amorphous nature with a slight crystallization tendency. The powder prepared by sol-gel method was quasi-amorphous to X-ray as long as it was calcined below 500ºC. On heating to 500ºC, for 1h the reflections corresponding to titania anatase are detected (figure 1).

Figure 2 shows the effective crystallite size distribution for the powder obtain by the heat treatment of the precursor solution at 500ºC, respectively 600ºC.

3.2. Films characterization
The UV absorption property of TiO$_2$ films is a important factor for the photocatalyst. The UV spectra of TiO$_2$ films before and after calcinations were shown in figure 3. It has been reported that the band-gap electronic transition of anatase TiO$_2$ is indirect [8]. After heat treatment the intensities of absorption peaks of TiO$_2$ film increased and the peak position slightly shifted to a higher wavenumber, because formation of TiO$_2$. 
With regard to the relationship between the absorption coefficient $\alpha$ and the incident photon energy $h\nu$ near the band edge, one can write out a good approximation [8] as 

$$(\alpha \times h\nu)^{1/2} = A (h\nu - E_g)^{1/2},$$

where the photon energy is $h\nu$, $h$ being the Planck constant, and $E_g$ is the indirect optical band-gap. From the function curve $(\alpha \times h\nu)^{1/2}$ vs $h\nu$, shown in figure 4, the band gap energy of indirect transition is calculated to be about 3.45 eV, which is larger than of 3.2 eV reported for the bulk TiO$_2$ anatase, indicating a quantum size effect [8].

The diffraction pattern of the TiO$_2$/ITO thin film (figure 5) exhibit the diffraction peaks owning to anatase phase however, thiny amount of the rutile phase (7.4% volume fraction) at 2$\theta$ of 27.43° was also detected. The value of the anatase particles size are $D_{eff} = 5.4$ nm, indicating low crystallinity of the anatase phase.
The films were free from the pinholes and cracks as generally observed in sprayed films due to its high deposition temperature (figure 6). Formation of was study SEM using quantitative analyses such as EDX (figure 7). This analysis confirms the TiO₂ thin films formation also.

4. Conclusions
TiO₂ thin films were prepared by a sol-gel spray coating process using titanium alkoxide. XRD analysis of our titanium precursor powder shows that starting from 500°C annealing temperature the TiO₂ anatase is the main crystalline phase. The band gap energy of indirect transition of the TiO₂ thin films is calculated to be about 3.45 eV, indicating a quantum size effect. Our nano structured TiO₂ thin films which has a little red-shifted compared with the band-gap energy of the TiO₂ indirect electronic transition may be a more efficient candidates in the development of photoelectrodes for photoelectrochemical cell (PEC) used in solar-hydrogen production.

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