



## TiO<sub>2</sub> THIN FILMS PREPARED BY SPIN COATING TECHNIQUE

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The titania nanocoatings on indium tin oxide (ITO) were successfully obtained by the sol-gel process in an aqueous solution using the titanium diethanolamine complex as the precursor. FT-IR, UV – VIS, Raman spectroscopy and X-ray diffraction techniques have been used to investigate the chemical and physical changes during the sol-gel process and the characteristics of the TiO<sub>2</sub> powder precursor. In this paper, we report on the preparation and characterization of TiO<sub>2</sub> films prepared using the hydrolytic sol-gel process and deposited on ITO glass substrates by spin coating technique.

### INTRODUCTION

TiO<sub>2</sub> thin films deposited on conducting glass are used in new type solar cells, liquid and solid dye-sensitized photo electro-chemical solar cells, as well as in solar cells extremely thin organic or inorganic absorbers. Recently, these films are intensively used in various interesting applications viz. photo-oxidation of water, photo-catalysis, and electro-chromic devices.<sup>1,2</sup>

A number of methods have been employed to prepare TiO<sub>2</sub> films, including e-beam evaporation, sputtering, chemical vapor deposition and sol-gel process. The sol-gel method is generally recognized as one of the most important techniques for fabrication of ceramic thin films because it possesses several advantages, such a low temperature processing, easy coating of large area, and being suitable for preparation of porous films and homogenous multi component oxide films. The sol-gel conventional method uses the hydrolytic route, which involves the initial hydrolysis of the alkoxide precursor followed by continual condensations between the hydrolyzed particles forming the gel.<sup>3</sup>

In this paper, we report the preparation of TiO<sub>2</sub> films by sol-gel spinning technique based on precursor solution employing diethanolamine as the stabilizing agent to prevent precipitation of titanium butoxide (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>) by ethanol.<sup>4,5</sup> The stabilizing action of diethanolamine is an outcome of its chelate forming ability with the alkoxides. Diethanolamine interacts with titanium alkoxide as a tridentate ligand.<sup>6</sup>

### EXPERIMENTAL

#### 1. TiO<sub>2</sub> films preparation

Precursor solutions for TiO<sub>2</sub> films were prepared by the following method: tetrabutylorthotitanate (17.02 mL) Ti(OBu)<sub>4</sub> and diethanolamine (4.8 mL) were dissolved in ethanol (67.28 mL). Introduction of ethanol prior to diethanolamine induces immediate precipitation due to highly reactive alkoxide, therefore diethanolamine, which has been added as a stabilizing agent for hydrolysis was initially stirred with ethanol followed by the addition of tetrabutylorthotitanate. After stirring vigorously for 2h at room temperature, a mixed solution of water (0.9 mL) and ethanol (10 mL) was added drop wise to the above solution with a burette under stirring. The resultant alkoxide solution was kept standing at room temperature for hydrolysis reaction for 2h, resulting in the TiO<sub>2</sub> sol. The chemical composition of the starting alkoxide

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solution was  $\text{Ti}(\text{OC}_4\text{H}_9)_4:\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}:\text{NH}(\text{C}_2\text{H}_4\text{OH})_2=1:26.5:1:1$  in molar ratio. Conducting ITO glass plates were used as the substrates for thin films. The films were formed on the substrates from a coating solution by spin-coating technique in an ambient atmosphere. The substrates coated with gel films were heat-treated at  $450^\circ\text{C}$  for 1h in air.

## 2. Analysis

The Raman spectra have been recorded at room temperature with a JASCO NRS 3300 spectrophotometer in a backscattering arrangement and equipped with a CCD detector ( $-69^\circ\text{C}$ ). The incident laser beam ( $1\ \mu\text{m}^2$  diameter at the sample surface) was focused through an Olympus microscope, and the Raman calibration was achieved by using the  $\text{Si}\ 521\ \text{cm}^{-1}$  peak. Excitation was performed with  $633\ \text{nm}$  laser at a power of  $1.4\ \text{mW}$  on the sample, with a spectral resolution of  $0.48\ \text{cm}^{-1}$  network using  $1200\ \text{L/mm}$ .

Fourier Transform Infrared (FTIR) spectra of the solution (liquid film technique) and the powder (KBr pellet technique) in the absorbance mode have been recorded in the wavenumber range of  $500\text{--}4000\ \text{cm}^{-1}$  with a resolution of  $4\ \text{cm}^{-1}$ .

UV-VIS absorption spectra of the  $\text{TiO}_2$  thin films deposited on ITO glass were taken on a JASCO V-550 spectrometer, in the wavenumber range of  $200\text{--}900\ \text{nm}$  with a resolution of  $1\ \text{cm}^{-1}$ .

X-ray diffraction (XRD) measurements were performed using a BRUKER D8 Advance X-ray diffractometer, working at  $45\ \text{kV}$  and  $45\ \text{mA}$ . The  $\text{Cu}_{\text{K}\alpha}$  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 Warren-Averbach X-ray profile Fourier analysis of the (101) and (200) anatase peak profiles were processed by the XRLINE<sup>7</sup> computer program in order to determine the effective crystallite mean size ( $D_{\text{eff}}$ ).

## RESULTS AND DISCUSSION

### 1. Precursor characterization

The X-ray diffraction patterns of the titania precursor calcined at different temperature (Fig. 1a) and the Raman spectra of a nanocrystalline power, obtained in the same condition (Fig. 2) reveal the fact that the  $450^\circ\text{C}$  is the lowest annealing temperature at which anatase phase appears. Anatase phase remains the dominant form of  $\text{TiO}_2$  present until about  $600^\circ\text{C}$ , when rutile phase takes over.

Fig. 1b shows the effective crystallite size distribution for the powder obtain by the heat treatment of the precursor solution at  $450^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $550^\circ\text{C}$ , respectively  $575^\circ\text{C}$ . For particles crystallized to the anatase phase, the nanocrystallite effective size, increases from  $170.8\ \text{\AA}$  to  $251.8\ \text{\AA}$ .

Anatase is tetragonal, belongs to space group  $D_{4h}^{19}$  ( $I4/amd$ ) and has two  $\text{TiO}_2$  units per primitive cell. It has six Raman active modes, corresponding to symmetries  $A_{1g}+2B_{1g}+3E_g$ .<sup>8-10</sup> Rutile is also tetragonal and belongs to the space group  $D_{4h}^{14}$  with two  $\text{TiO}_2$  molecules per unit cell. There are four Raman active modes with symmetry of  $A_{1g} + B_{1g} + B_{2g} + E_g$ .<sup>11,12</sup> In Table 1 Raman modes of anatase and rutile reported in the literature<sup>8</sup> are presented.

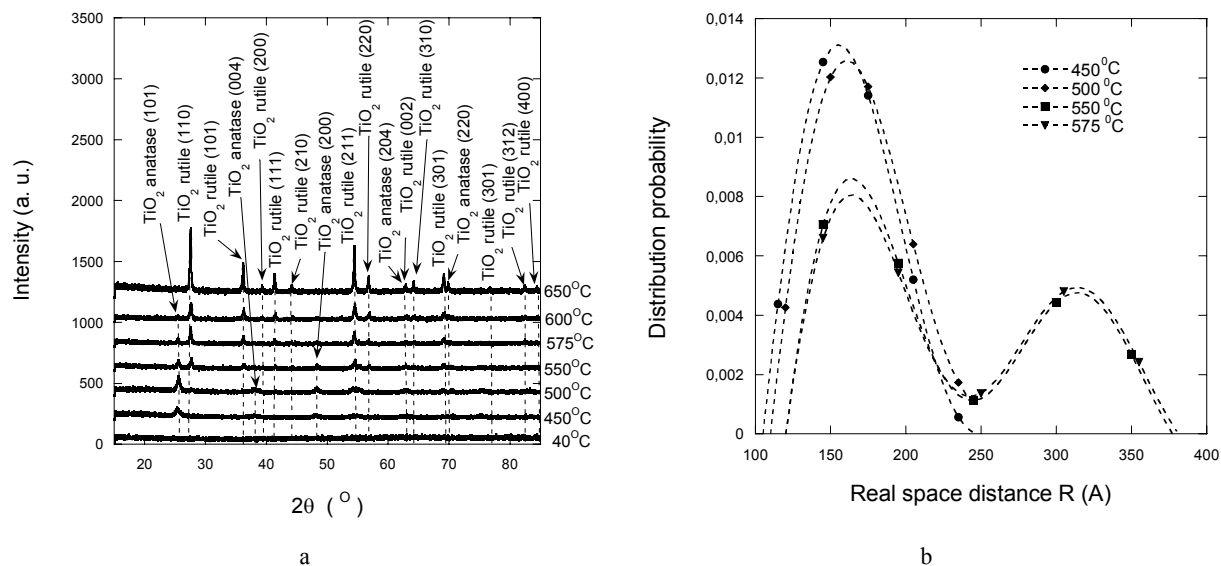


Fig. 1 – a. The X-ray diffraction pattern of the titania precursor calcined at:  $40^\circ\text{C}$ ,  $450^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $550^\circ\text{C}$ ,  $575^\circ\text{C}$ ,  $600^\circ\text{C}$  and  $650^\circ\text{C}$ . b. Effective crystallite size distribution along the [101] crystallographic direction for the  $\text{TiO}_2$  anatase structure.

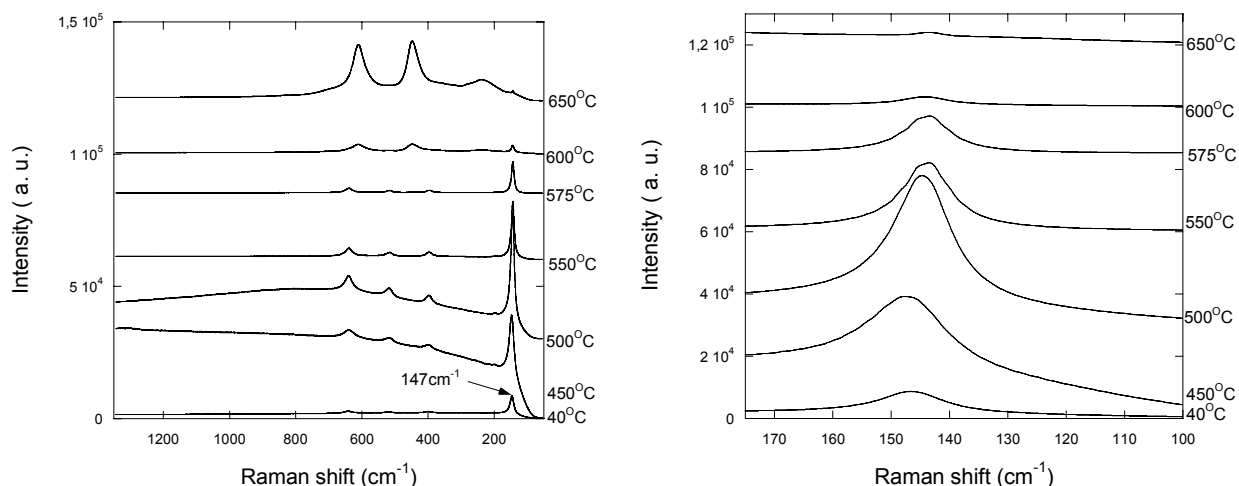
Fig. 2 – Raman spectra of nanocrystalline TiO<sub>2</sub> powders.

Table 1

Raman active phonons for TiO<sub>2</sub> anatase and rutile

Anatase		Rutile	
Mode	Frequency (cm <sup>-1</sup> )	Mode	Frequency (cm <sup>-1</sup> )
E <sub>g</sub>	144	B <sub>1g</sub>	143
E <sub>g</sub>	197	E <sub>g</sub>	447
B <sub>1g</sub>	399	A <sub>1g</sub>	612
A <sub>1g</sub>	514	B <sub>2g</sub>	826
B <sub>1g</sub>	514		
E <sub>g</sub>	639		

The powder obtained at 40°C shows a broad spectrum with same indication of the Raman modes. In the spectrum of the precursor solution heated at 450°C, the emission band at 147cm<sup>-1</sup>, typically for the anatase form, its intensity increases at higher temperatures till 650°C, when only the emission band 447cm<sup>-1</sup>, typical for the rutile is present.

It can be seen that the strongest peak at 147cm<sup>-1</sup> shows some shift towards higher wavenumbers compared with the 144cm<sup>-1</sup> from the reference data. The blue shift can be a result of the quantum size effects and organic compounds chelated with the Ti atom.<sup>13</sup>

The FTIR spectra for the precursor and precursor solution prepared by the alkoxide process are shown in Fig. 3. The C-O stretching in diethanolamine appears at 1088cm<sup>-1</sup>. The shift in the position of the band ascribed to the C-O stretching is shifted to a lower wavenumber, *i. e.* from 1088 to 1049 cm<sup>-1</sup> showing a weakening of the

C-O bond due to its chelation with the TiO<sub>6</sub> octahedra.<sup>6</sup>

This indicates that diethanolamine stabilizes the alkoxide based sol due to its interaction as a tridentate ligand with the titanium alkoxide. The C – N stretching vibration has a red-shift from 1124 cm<sup>-1</sup> to 1073 cm<sup>-1</sup>, showing the DEA has formed a complex with Ti(OBu)<sub>4</sub>.<sup>14</sup> The absorption at 1126 cm<sup>-1</sup> (Ti-O-C) are quasi-exclusively due to Ti-butoxy species.<sup>15</sup> The organic fragment disappears at 450°C. For the powder heat treated at: 450°C, 500°C, 550°C, 575°C, 600°C and 650°C, only the peak of Ti-O-Ti network is present (Fig. 4).

## 2. Film characterization

The UV absorption property of TiO<sub>2</sub> films is an important factor for the photo catalysis. The absorption of the TiO<sub>2</sub> thin films after the heat treatment (Fig. 5) presents a red shift as compared that of TiO<sub>2</sub> thin film.

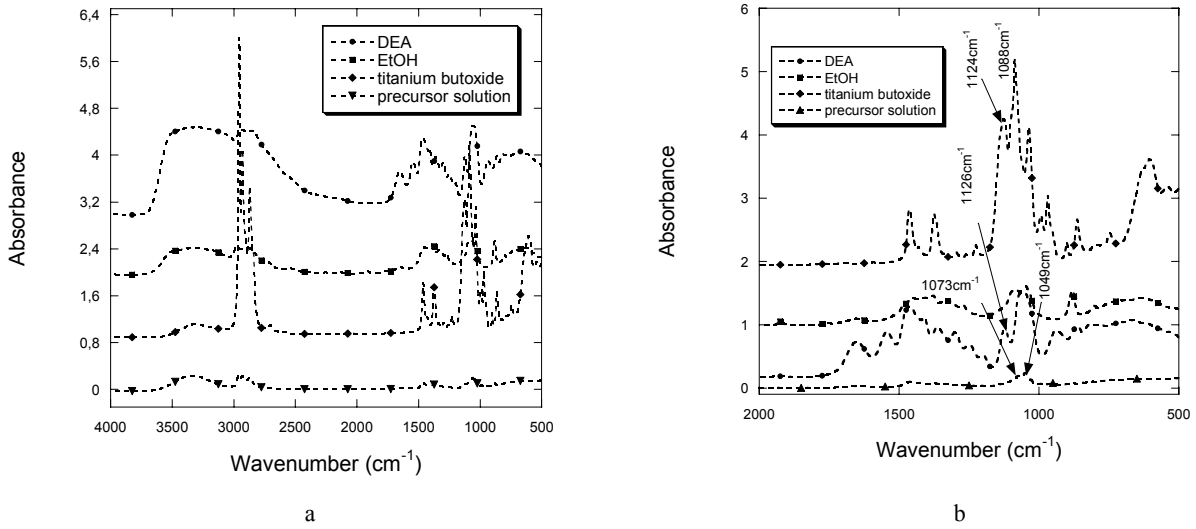


Fig. 3 – The FTIR spectra for TiO<sub>2</sub> precursor and precursor solution.

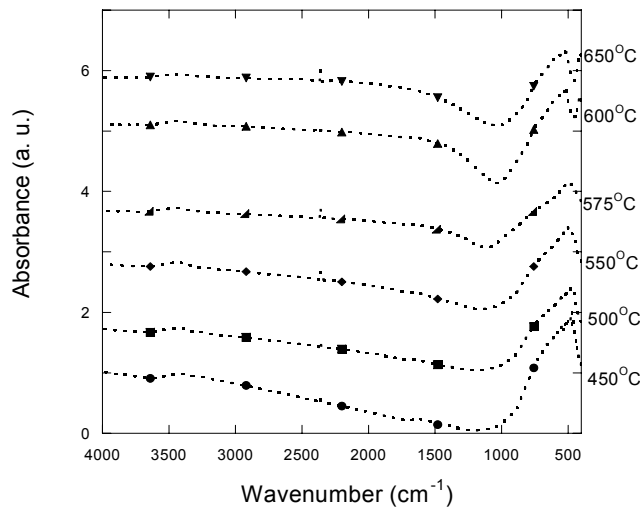


Fig. 4 – FT-IR spectra of TiO<sub>2</sub> powders prepared at different temperatures.

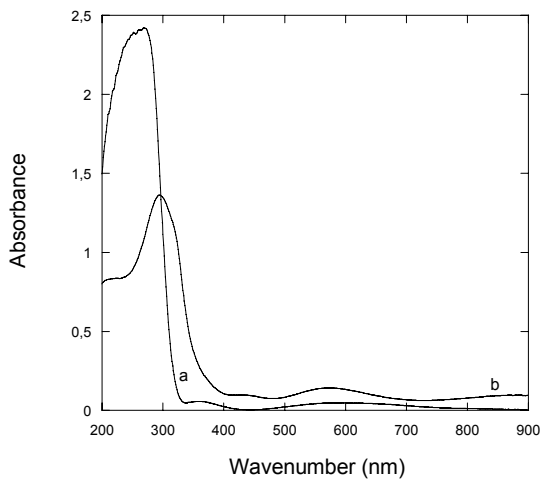


Fig. 5 – UV – VIS measurements of TiO<sub>2</sub> thin films before (a) and after (b) the heat treatment.

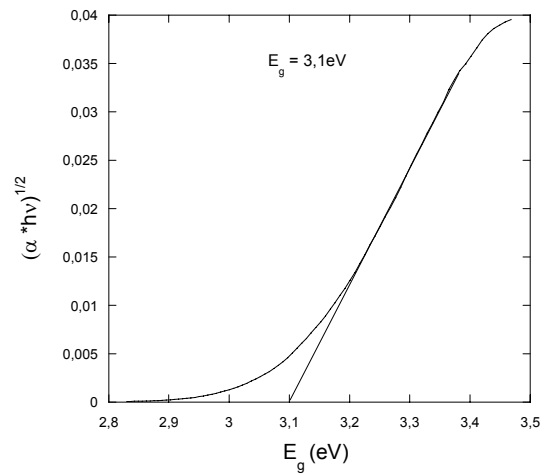


Fig. 6 –  $(\alpha \cdot h\nu)^{1/2}$  as a function of  $h\nu$  for the TiO<sub>2</sub> film after the heat treatment.

The relation between the absorption coefficient  $\alpha$  and the incident photon energy  $h\nu$  can be written as  $(\alpha \times h\nu)^{1/2} = A (h\nu - E_g)^{1/2}$ , for allowed indirect transition, where the photon energy is  $h\nu$ ,  $h$  being the Planck constant, and  $E_g$  is the indirect optical band-gap.<sup>16</sup>

The band gap energy was evaluated by extrapolating the linear part of the curve to the energy axis intercept. The allowed indirect optical absorption of the TiO<sub>2</sub> anatase band gap at about 3.1eV was then found.

The film thickness ( $\sim 280 \pm 20$  nm) was evaluated from the UV – VIS measurements using

the relationship between the absorbance oscillation order, refractive index, thickness and wavelength.<sup>17</sup>

$$d = \frac{m \lambda}{4n_m} \quad (1)$$

where:  $d$  is the film thickness,  $n$  – refractive index for each of the even orders,  $m$  – peak – order and  $\lambda$  the radiation wavelength.

The diffraction pattern of the TiO<sub>2</sub>/ITO thin film (Fig. 7) exhibits the diffraction peaks characteristic to anatase phase. The value of the anatase particles size are  $D_{eff} = 32.8$  nm, indicating low crystallinity of the anatase phase (Fig. 8).

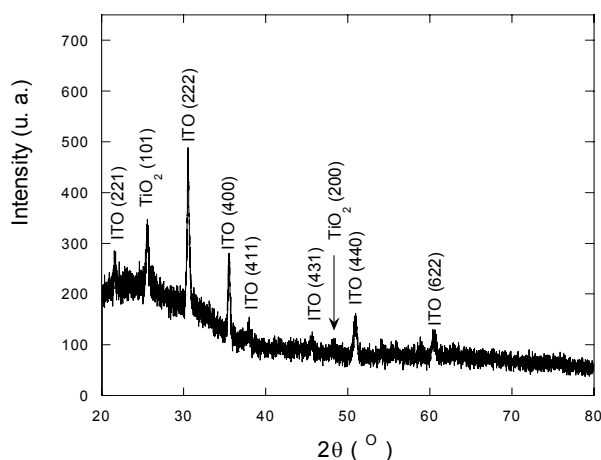


Fig. 7 – The XRD pattern of TiO<sub>2</sub>/ITO thin film.

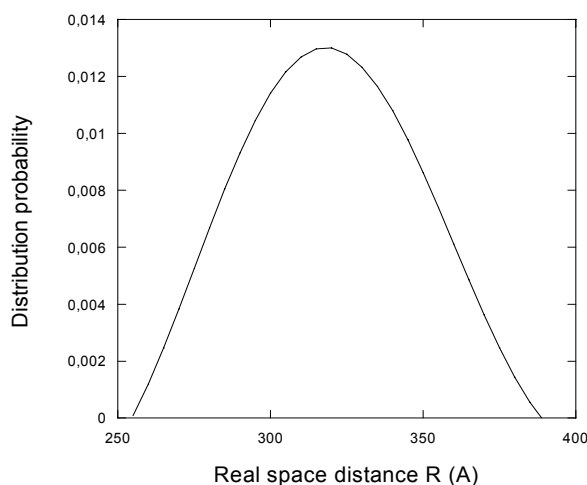


Fig. 8 – Effective crystallite size distribution for the TiO<sub>2</sub> anatase structure.

## CONCLUSIONS

XRD analysis of our titanium precursor powder shows that starting from 450°C annealing temperature the TiO<sub>2</sub> anatase is the main crystalline phase. Anatase remains the dominant phase form of TiO<sub>2</sub> until about 600°C, when rutile takes over. These results are confirmed by the Raman and FT-IR measurements.

The diffraction pattern of the TiO<sub>2</sub>/ITO thin film shows a low crystallinity of the anatase phase. Further investigations are necessary to improve both the shelf life of the coating solutions and the deposition process of the TiO<sub>2</sub> oxide films.

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