ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2013, *58*(2-3), 105-111

Dedicated to Professor Bogdan C. Simionescu on the occasion of his 65th anniversary

OPTICAL AND ELECTRICAL PROPERTIES OF TiO_2 THIN FILMS DEPOSITED BY SOL-GEL METHOD

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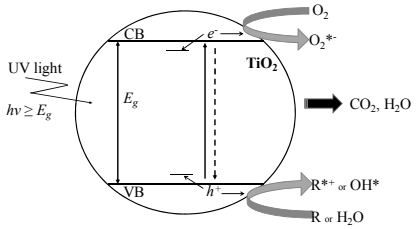
Received October 1, 2012

The effects of preparation temperature on the structural, optical and electrical properties of TiO_2 films prepared by sol-gel method have been analyzed by X-ray diffraction, scanning electron microscopy, optical and electrical measurements. The thin films exhibit a good transparency in the visible region with an average transmittance of about 90 %. The optical band gap and porosity decrease while the refractive index increase as the preparation temperature was higher. The electron transport mechanism in absence and under UV excitation is also discussed on the base of the electrical characterization.



INTRODUCTION

Transparent conducting films have attracted much attention due to their large scale application as electrodes for the development of liquid crystal displays, plasma display panels, organic electroluminescence, solar cells, etc. The properties requested by these films in the view of such applications are: high transmittance in the visible range, high electrical conductivity when the film is UV excited and high thermal stability. From this point of view TiO_2 is a fascinating material due to its wide-ranging chemical and physical properties like high chemical stability, high efficiency in organic and inorganic pollutants photo-decomposition,[1] high catalytic activity, biocompatibility and non-toxicity as well as to its low production cost. Thus TiO_2 is one of the most widely used materials in various applications such as: photocatalyst,[1] dye-sensitised solar cells,[2] chemical sensors,[3-5] in electrochromics[6] and electronic devices.[7] Moreover, intensive studies showed that TiO_2 layers have also a high *k*-dielectric constant, a property which is highly demanded for electroluminescent devices.[8]

The aim of our work is to measure the electrical properties of TiO_2 films excited with UV light in the absence of any adsorbed chemical species onto the film surface. Although the electrical properties of TiO_2 thin films exposed to UV irradiation were intensively studied in the last decade[4, 9-11] the behaviour of the free charge carriers produced by the UV excitation still remained unclear. This work is an attempt to overcome this problem by finding the relation between the structural, optical and electrical properties of the TiO_2 thin films prepared by sol-gel method, and the temperature of preparation.

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RESULTS AND DISCUSSION

Homogeneous thin films of TiO_2 with a thickness of about 100 nm were obtained by the sol-gel method and heat treated at various temperatures. Further, the films were characterized from the point of view of their morphological, optical and photo-electrical properties.

Structural Study

Fig. 1 shows the X-ray diffraction patterns of TiO_2 films treated at temperatures varying from 350 to 600°C.

The samples prepared at 350 °C showed a diffraction pattern with no features which proved that these films are amorphous or the crystallites are very small. On the other hand, the samples heated up to 500 °C revealed one diffraction peak at 25.3 ° which was assigned to the anatase phase (JCPDS card # 021-1272). The diffraction intensity for the preferred orientation at 25.3 ° along the (101) plane enhanced with increasing the temperature from 400 °C to 600 °C and thus the anatase crystalline phase became more pronounced. Moreover, for the films treated at 600 °C the XRD pattern revealed an additional peak at 37.8 ° belonging to the same anatase phase. No other phases of TiO_2, such as rutile or brookite were observed. The crystallite size was determined using Debye-Scherrer's semi-empirical formula.[12] As preparation temperature increased from 350 °C to 600°C, crystallite size doubled from 11.0 nm to 22.0 nm (Fig. 2).

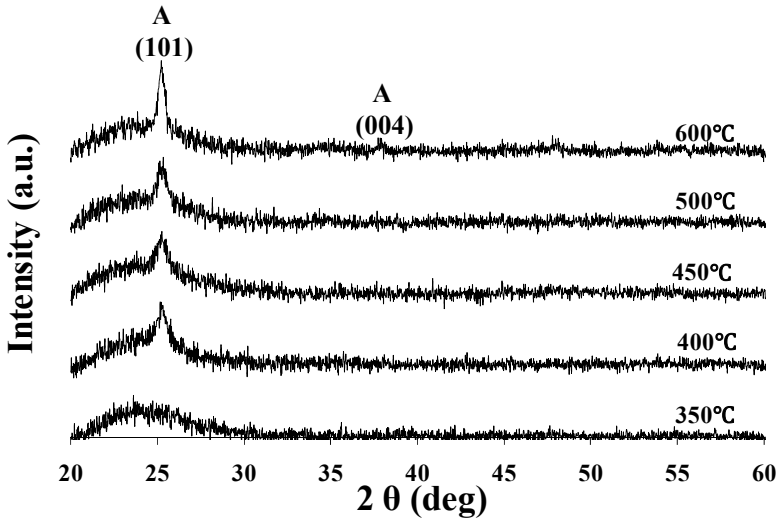

Fig. 1 – XRD patterns of TiO_2 films heat treated at various temperatures.

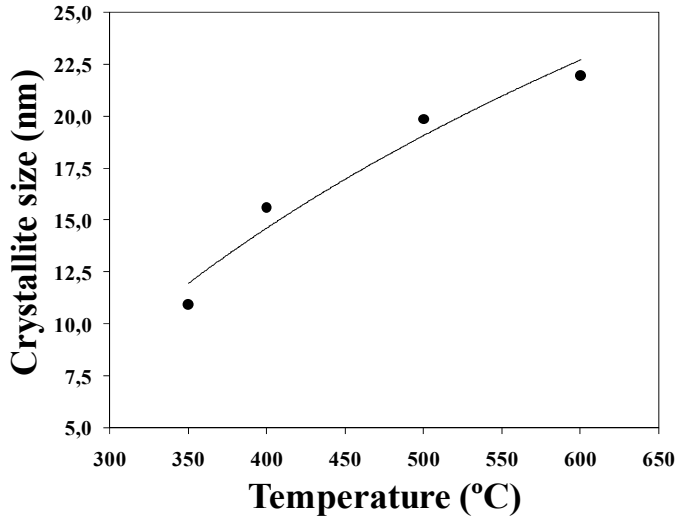

Fig. 2 – Dependence of the TiO_2 crystallites size with the preparation temperature.

Optical properties

The optical properties of TiO_2 sol-gel films were found to be influenced by the temperature treatment. The samples showed a good transparency in the visible region and a sharp fall in the UV region, corresponding to the band gap zone (Fig. 3).

The transmittance slightly varies from 88.5% to 89.4% for the samples prepared at 350 °C and 500 °C temperatures, respectively. According to the inter-band absorption theory, the optical band gap of TiO_2 films can be determined from the following relation.[13]

$$(\alpha h\vartheta)^m = A(h\vartheta - E_g) \quad (1)$$

where α is the absorption coefficient, A is a constant, $h\vartheta$ is the photon energy (eV), and m is the transition coefficient of optical absorption process. Theoretically, this coefficient takes the value of 1/2 and 3/2 when the transitions are indirect or 2 and 3 for the direct ones.[13] In the high absorption region, the optical absorption coefficient can be calculated using the relation: $\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right)$, where d is the film thickness and T is the transmittance of the film at each wavelength.

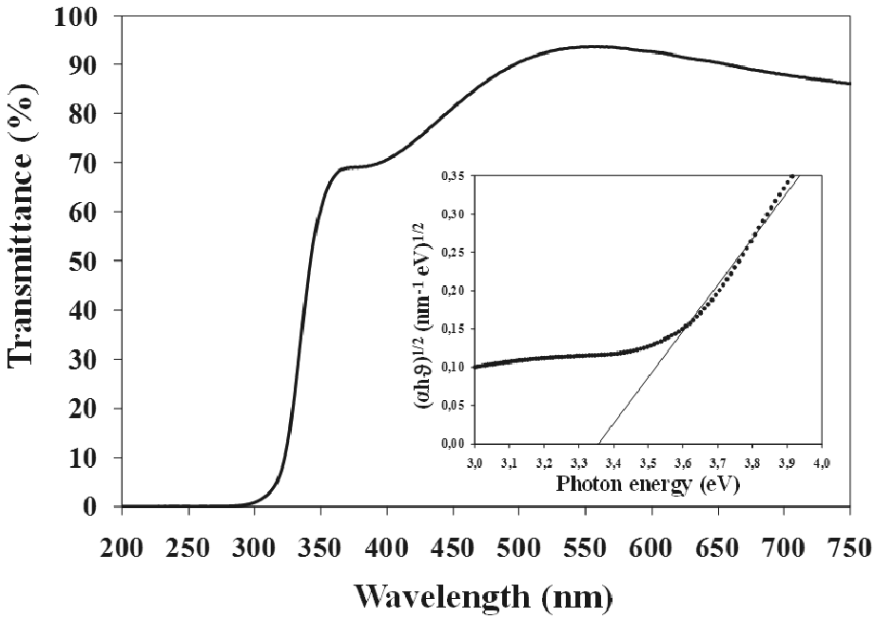

Fig. 3 – Transmission spectra of TiO_2 thin film prepared at 600 ºC.

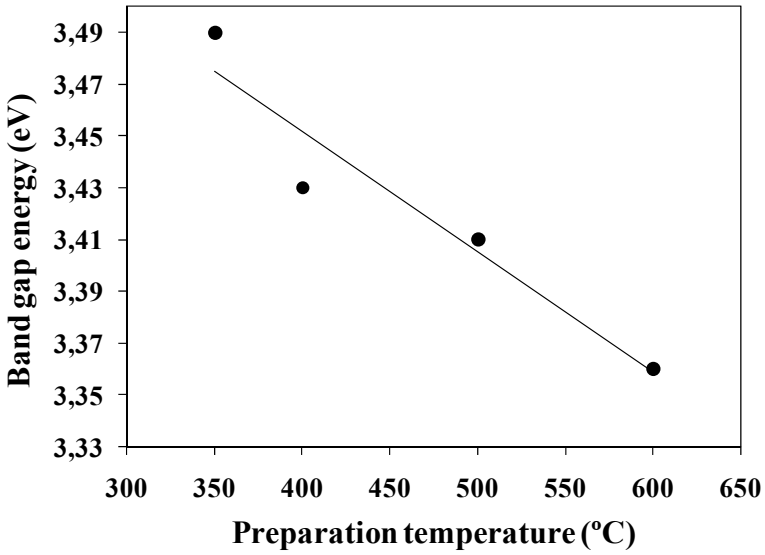

Fig. 4 – Variation of optical band-gap energy with the preparation temperature.

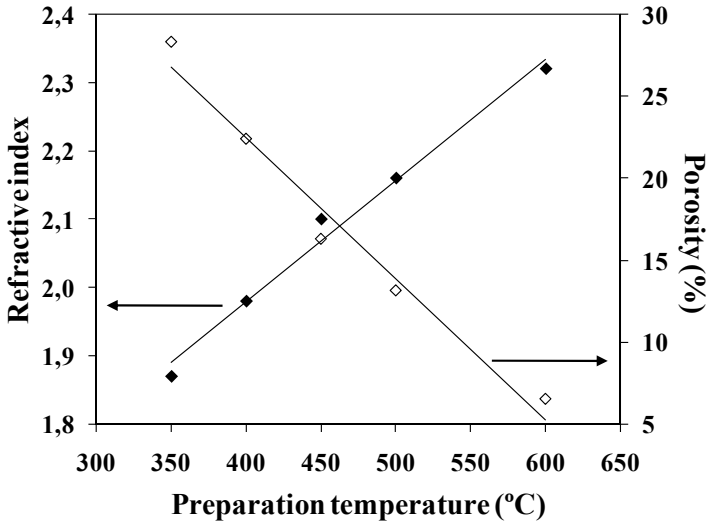

Fig. 5 – Refractive index (left-side) and porosity (right-side) versus preparation temperature.

The optical band gap was found by plotting Tauc's equation for m = 1/2 and extrapolation of the straight line part of the curve to $(\alpha h\vartheta)^{1/2} = 0$, the inset of Fig. 3. The optical band gap energy of the films thermally treated at 350 ºC was 3.49 eV and decreased to 3.36 eV for the sample prepared at 600 ºC (Fig. 4). The reason could be a better crystallization process and therefore, a large size of the grains and crystallites.[14, 15]

The refractive index was calculated using Swanepoel's method [16] and the porosity (P) was determined using the Lorenz-Lorentz relation:[17]

$$P(\%) = 1 - \frac{n^2 - 1}{n^2 + 2} \cdot \frac{n_b^2 + 2}{n_b^2 - 1} \qquad (2)$$

where n_b is the refractive index of the pore-free anatase TiO_2 (n_b = 2.49 [18]) and n is the refractive index of the thin films. At high preparation temperatures the pore size diminished by grains' compaction, the material becomes more densely packed and as a consequence, the refractive index increases and the porosity decreases. The results are shown in Fig. 5.

Electrical Properties

In this section the DC electrical properties of TiO_2 sol-gel films are presented. The electrical measurements were carried out using a two-probe set-up station connected to a Keithley 6517A LCR meter. The I - V characteristics were driven for a voltage range within 0 to +3.0 V (steps of 0.05 V) and recorded in air at room temperature both in the absence ("dark") and under the UV exposure ("photo").

The dark current was perturbed severely by the noise level of the LCR meter (not shown) which led us to conclude that the electrical measurements in the absence of UV excitation were limited due to the apparatus performances (~ 10 nA). The intensity of the dark current could be lower than that limit and thus, cannot be estimated correctly. However, previous published works indicate values of about 1 pA.[19, 20]

The electron transport mechanism in TiO_2 materials was studied by several researchers during the last decade.[21-26] It is well-known that the electrical conductivity of a metal oxide in air can be assigned to intrinsic defects and more precisely, to oxygen vacancies due to the stoichiometry deviation. On the other hand, the physics of polycrystalline materials is based mostly on the grain boundary effect. According to this, a large number of defects around boundaries strongly affect the carriers charge driven process.[27] These defects act as traps for the free charge carriers and finally reduce the electrical conduction. In our case, the small value of the dark conductivity can be caused by the lower density of the free charge carriers within the material, by the high barrier height at grain boundaries, or by a combination of both.

The photo-electrical properties of the TiO_2 sol-gel films under UV light irradiation were measured for samples prepared at different temperatures (Fig. 6). The I-V curves are linear over the whole range of voltages which means that between TiO_2 films and electrodes there was an ohmic-like contact. The photocurrent strongly increased more than four orders of magnitude from 3.2 x 10^{-9} to 2.3 x 10^{-5} A, reached a maximum for the sample prepared at 500 ºC and then, decreased. These results could be explained by taking into account the mechanism for photogeneration of free charge carriers.

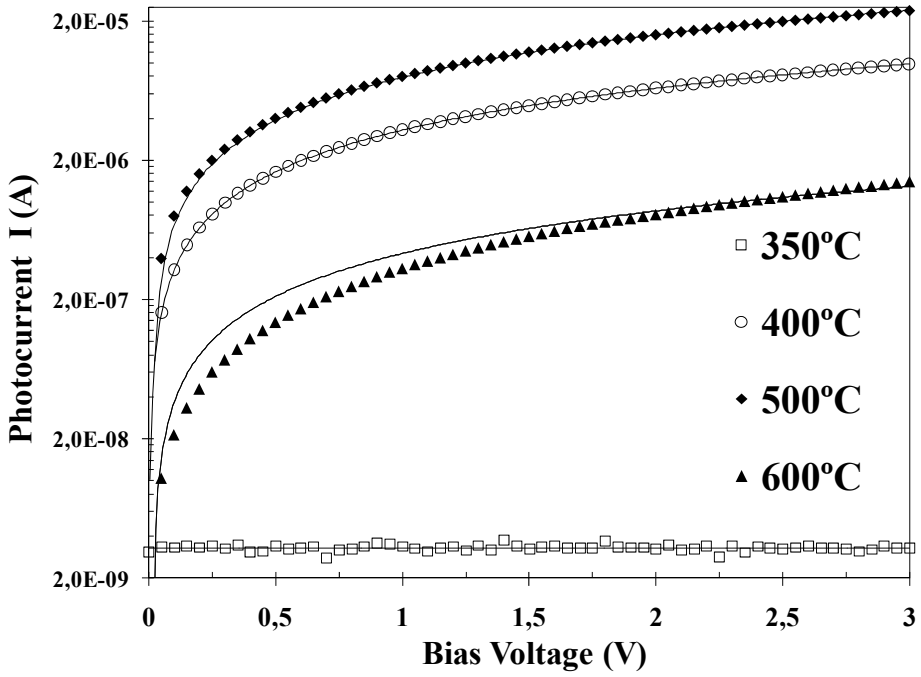

Fig. 6 – I-V characteristics under UV light for TiO_2 thin films heat-treated at various temperatures. The lines are the linear fittings.

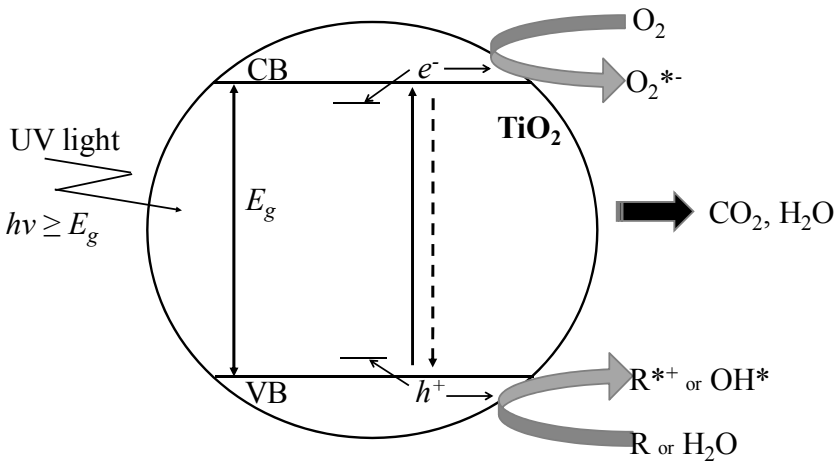

Fig. 7 – Schematic illustration of the band structure and the processes occurred in TiO_2 under UV excitation.

When TiO_2 material is excited by the UV light having the photon energy equal to or greater than the TiO_2 band gap, electron-hole pairs are created and the electrons are promoted from the valence band to the conduction band leaving positive holes in the valence band (Fig. 7). If the electrons and holes do not recombine they can undergo charge transfer processes such as reductive and oxidative reactions on the material surface.[1, 3]

On the other hand the photogeneration rate also depends on the preparation temperature since only high temperatures lead to the requested well-formed crystalline structure of TiO_2 anatase phase as shown in the XRD patterns.

In the polycrystalline thin films, the transport mechanism of charge carriers is strongly influenced by the presence of grain boundary effects. An increase of the preparation temperature will cause at this level the increase in grain size and lowering of the barrier potential energy. Further the effect at the grain boundaries will be a decrease in the charge carrier scattering and a higher conductivity. This happened for the samples heated at 350 and 500 ºC. At a temperature higher

than 500 ºC, the TiO_2 film easily loses oxygen from the surface and bulk leaving oxygen vacancies which can act as traps not only for the already present free charge carriers but also for the photogenerated electrons.[28,29] Therefore, the lower photoconductivity for the samples prepared at 600 ºC can be explained by a lower number of free charge carriers due to a higher recombination rate.

EXPERIMENTAL

The TiO_2 thin films were prepared using the sol-gel method as follows: titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) used as a titanium alkoxide precursor was dissolved in a solvent, buthanol (C_4H_9OH), and mixed by stirring for half hour at room temperature. Then, an alcoholic solution was obtained by mixing of the anhydrous n-butanol with H_2O and HCl as a catalyst. The molar ratio was: $Ti[OCH(CH_3)_2]_4$:C_4H_9OH: H_2O: HCl = 1:25:1:0.3. The final solution was transparent and colorless. To obtain TiO_2 thin films, the sol-gel was coated on commercial alkali free glass (Corning 7059) by spin coating at 4000 rpm for 60 sec. After each coating, the wet films were introduced in to a Supertherm STC 18.06 oven and subjected to a thermal treatment in air in two steps: (1) heating from room to the prescribed temperature with 10 ºC/min; (2) maintaining the sample at the prescribed temperature for 1 h. This temperature varied from 350ºC to 600 ºC (Fig. 8).

The thickness and the refractive index were measured by the ellipsometry technique using an EL X-02 Spec spectroscopic ellipsometer with variable wavelengths. The optical band gap of TiO_2 thin films was determined from Tauc's plot using the optical transmittance spectra measured with a UV-Vis SPECORD 200 Analytik Jena spectrophotometer. The crystalline structure was analyzed by X-ray diffraction (XRD) with a Bruker AD8 Advance X-ray diffractometer with Cu $K\alpha_1$ line of 1.54 Å operated at 40 mA and 40 kV. The X-ray diffraction spectra were recorded in the 20° to 60° 2θ range in steps of 0.02°.

The electrical measurements were carried out in air at room temperature by the two-probe method set-up with a Keithley 6517A electrometer. The photo-excited electrical measurements were done using an UV light source with λ= 365 nm (4 W/ 230 V/ 50 Hz). The I-V curves of TiO_2 thin films were driven with a bias voltage from 0 to +3.0 V.

CONCLUSIONS

TiO_2 thin films were coated on glass substrate by sol-gel spin coating technique and thermally treated at different temperatures. The structural, optical and electrical properties were proved to strongly depend on the thermal treatment. The experimental results indicated that the optimum temperature is 500 ºC and can be used to obtained TiO_2 thin films with nano-sized crystallite (20 nm), a very high transmittance (89 %), a refractive index of 2.2, a low porosity (13 %) and a photocurrent of 2.3 x 10^{-5} A.

Acknowledgements: The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement n°264115-STREAM.

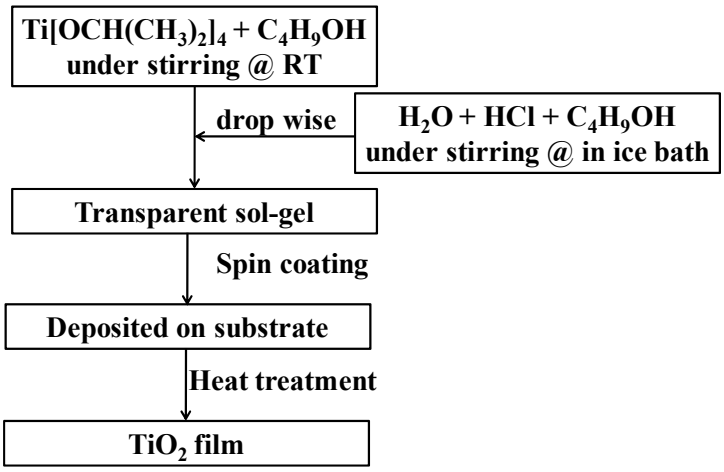

Fig. 8 – Preparation of TiO_2 thin films using sol-gel method.

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