SPECTROSCOPIC FT-IR STUDY OF TiO_2 FILMS PREPARED BY SOL-GEL METHOD

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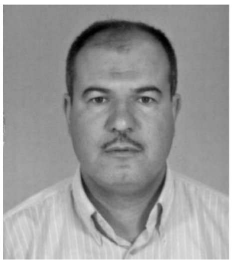
Received: 26 Jul 2007; accepted: 30 Aug 2007

TiO_2 thin films used like a photoanode in dye sentisitized solar cells (DSSC), were prepared on conductor glass (FTO) by sol-gel method. They were studied by FT-IR spectroscopy in order to determinate a film composition and structural properties. The results showed that the thin layers of TiO_2 achieved with speed of 16 cm/min and annealed at 400 C° present important morphological and structural properties.

Keywords: structural materials; solar energy; TiO_2, sol-gel, dip-coating, DSSC.



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Publications: 2.

Introduction

These last years the protection of the environment became major preoccupation. Numerous ways of research moved therefore toward the investigating in the renewable energies, of which the solar energy, nevertheless on a terrestrial scale applications of the solar generators remain limited because of the method of the photobattery production that is laborious and difficult, therefore too dear. Scientists wanted to find an alternative to constituted traditional solar cells of semiconductor as silicon, who permits the conversion of light in electricity. These materials although steady must be to elevated temperature constituted of an atom network very pure, what returns their costly manufacture and therefore their difficult on a big scale use. It appears however laborious to increase the output or to reduce costs of production. The solar cell of Graetzel or dye cell appear then in 1990, to palliate to this problem. The professor Michael Graetzel of Swiss Federal Institute of Technology, put to the point for the first time a solar cell that uses the principle close to the photosynthesis. It replaces the mechanism used by plants to transform rays of the sun in electric energy.

Our work has for objectives, the survey and the characterisation of materials nanocrystallines semiconductors that is used in the Graetzel cell as the TiO_2 [1]. TiO_2 film can be prepared by methods such as ion beam assisted deposition (IBAD) or chemical vapor deposition etc… However, it's difficult and expensive to deposit a uniform layer of TiO_2 on the substrate with complex shapes or geometry by these methods. Sol-gel technology is a low temperature method of preparing film from chemical routes. The advantages of using a sol gel dip coating technique are that it is independent of the substrate shape, and can achieve a good control of surfaces properties such as composition, thickness and topography [2]. Our gait consists in synthesizing the oxide of titanium by sol gel way, then to make some thin layer deposits on supports in conductor glass (FTO) with different speeds of immersion, and in very controlled humid atmosphere, with technical deep-coating. In order to study morphologic and microstructuralesproperties of our samples, we have proceed to the application of FT-IR analysis method.

Experimental details

Film preparation

Titanium isopropoxyde ($Ti(OC_3H_7)_4$ from Aldrich 97 %, was used as TiO_2 precursor [3]. First, 1.6 ml of $Ti(OC_3H_7)_4$ was dissolved in 4.65 ml of isopropanol. The solution was let under agitation to plug closed during 10 min with heating to 60 °C. Then one adds 5.15 ml of acetic acid, while letting agitate during 15 min under heating to 60 °C. One finally adds 12 ml of methanol and one lets agitate during 2 h. The second phase of synthesis consists in preparing the thin layers of TiO_2 by dip-coating process. The deposit of the thin layers of TiO_2 is achieved on blads of conductor glass (Fluor Tin Oxide, FTO) in device dip-coating. This device (achieved in our laboratory) is constituted of a surrounding wall squared in glass permitting nevertheless the passage of a flux of the Ar gas through two cracks on the lateral faces. The Humidity inside it limps is controlled by thermohygrometre (C62916, Bioblock Scientific, French), because the conditions of deposit influence on the quality of layers. It limps is surmounted of a motor permitting the control of the speed of immersion and withdrawal of the sample in the solution. The dip-coating sol-gel process consist in the immersion to a weak speed of an oblong plate of glass conductor (FTO) substrate [4]. Inside the solution of TiO_2 and to make take it with the same speed. For our work we achieved some thin layers with speeds of immersion of: 4, 8, 12, and 16 cm/min. The obtain samples were dried at 100 °C for 10 min, after they are annealed at 400 °C for 1 h.

Surface characterization

The film thickness and refractive index were measured by spectroscopic ellipsometre SOPRA GESP5, and the IR spectra of the samples on silicon wafers were recorded on the Nicolet 6700 FT-IR spectrometer.

Results and discussion

Formation of TiO_2 film

According to the literature [5] a rate of humidity of 20 % and temperature of 25 °C represent the best conditions for the adhering, transparent and homogeneous deposit obtaining. For the same conditions of deposit and of anneal, we varied the speed of immersion in order to study the effect of this last on thickness of layers, on their refractive index, on their structures and morphology. The thickness of the TiO_2 film is very important for the transportation of electrons as well as adsorption of the dye and it's another crucial factor contributing to cell efficiency. Although a thinner film has high transmittance, and the thicker ones have high dark current, it's workable and necessary to achieve optimum film thickness for energy conversion efficiency [6]. The thickness of the compacts films obtained from a sol gel in different speeds was measured by Ellipsometre according to the Table 1.

Table 1

Indicate the variation of refractive index and thickness of layers of TiO_2 according to the speed of immersion

The speed (cm/min)	4	8	12	16
Refractive index	1.8	2.15	2.40	2.55
Thickness (nm)	113.63	115.35	121.27	123.55

One also notices that when the speed increases the refractive index increases also. This proportionality between (speed, thickness, refractive index) is bound to the weight. That is to say that more the speed is big and more the set down matter quantity on our samples is big. Therefore, more thickness of layers is important more the refractive index is important and more matter is dense. This densification of layers is obtain after annealed it [7]. Nanostructures layers of TiO_2 obtain by sol-gel process are spongy, indeed they are constituted of grains of gleams and of holes or empty.

This densification is therefore the report between the total volume of the layer, that it's thickness multiplied by the surface of the layer and the volume of the nanocrystal of TiO_2. Thus, if we have to choose the best deposit for the photovoltaic use take the case where we have a large domain in the visible where the transmittance is maximal. In our case we will take the case where the speed is 16 cm/min. This case allows the large spectra of light to cross the layer of TiO_2 to arrive to the dye and so to excite him.

IR Study 3-2

The IR spectra of TiO_2 films deposited by dip-coating at 16 cm/min, dried at 100 °C and annealed at 300, 400 and 500 °C under oxygen atmosphere are presented in Figs.1, 2, 3 and 4.

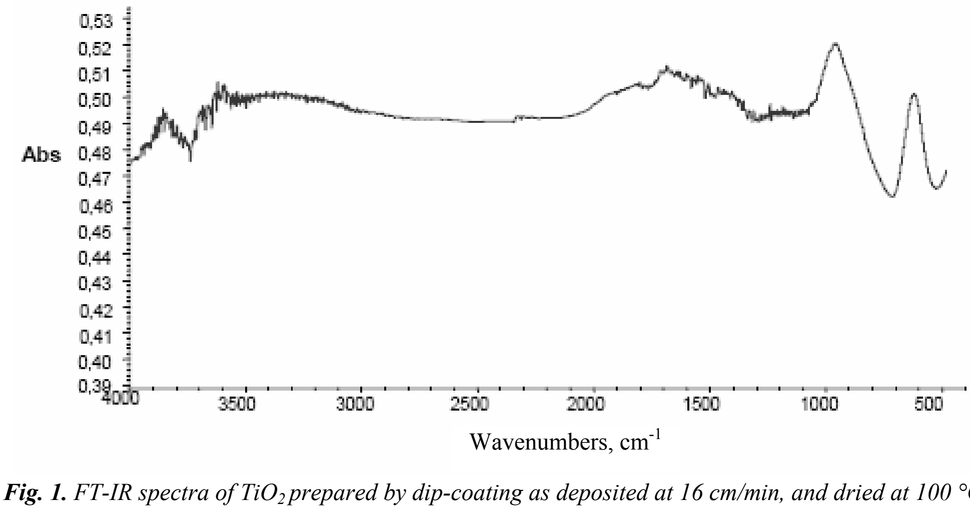

Fig. 1. *FT-IR spectra of TiO_2 prepared by dip-coating as deposited at 16 cm/min, and dried at 100 °C*

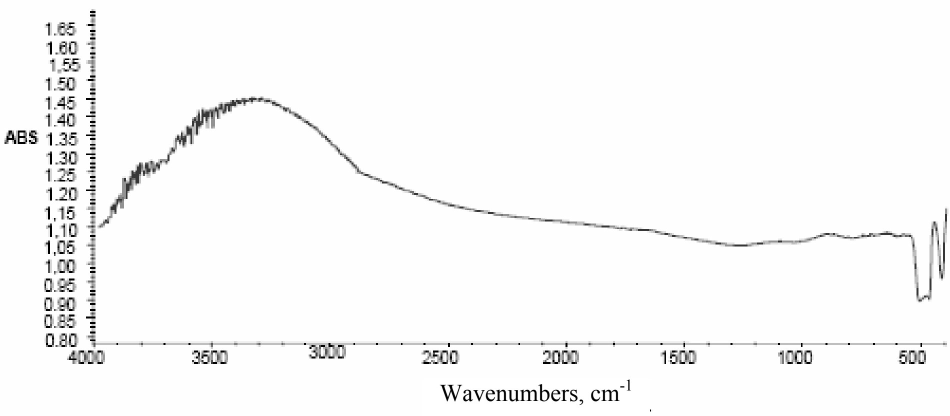

Fig. 2. *FT-IR spectra of TiO_2 prepared by dip-coating as deposited at 16 cm/min, dried at 100 °C and annealed at 300 °C*

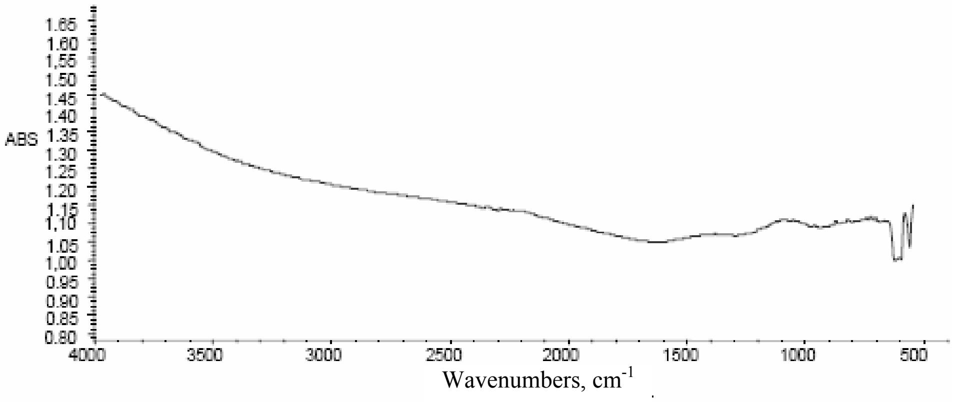

Fig. 3. *FT-IR spectra of TiO_2 prepared by dip-coating as deposited at 16 cm/min, dried at 100 °C and annealed at 400 °C*

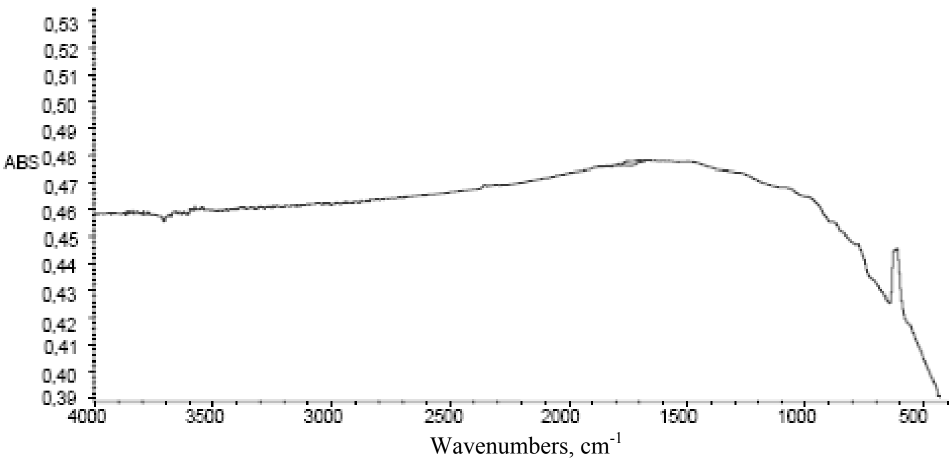

Fig. 4. *FT-IR spectra of TiO_2 prepared by dip-coating as deposited at 16 cm/min, dried at 100 °C and annealed at 500 °C*

For the sample prepared at 16 cm/min and dried at 100 °C (Fig. 1), the absorption bands at 500 cm^{-1} are assigned for aliphatic bonds of type C-C and the absorption bands between 560 and 700 cm^{-1} are assigned for O-N=O deformation which are very intense in IR spectra. The absorption bands at 1097 cm^{-1} are assigned for C-O-Ti. The acetyl and hydroxyl bonds were determinate at 1300 and 3600 cm^{-1} successively. For the sample prepared at 16 cm/min, dried at 100 °C and annealed at 300 °C (Fig. 2), we let's notice the presence of hydroxyl bonds and the disappearence or the shrinkage of organic origin. But the important fact is the apparition of pick at 430 cm^{-1} assigned for Ti-O-Ti bonds.

Let's note that J.Sabataityté et al had determined the strip of absorption of the Ti-O-Ti bonds at 440 cm^{-1} [8]. We find also the O-N=O bonds. Further annealing at temperature of 400 °C, (Fig. 3) we note the disappearance of hydroxyl bonds, what confirms himself distinctly in Fig. 4, for the sample prepared at 500 °C and where one only finds the Ti-O-Ti bonds.

Conclusion

Through results of survey spectroscopic in FT-IR, we notice that our samples undergo amore and more important purification, every time hat one increases the temperature until 500 °C. We can conclude that the nonporous film of TiO_2 in thickness is 123.55 and have been prepared by sol-gel method with speed of immersion of 16 cm/min with and annealed at 500 °C has a perfect crystalline structure. The formation of the Ti-O-Ti bonds in films is observed after annealing at 300 °C. However the film became crystalline after annealing at 500 °C. But we show the sample prepared at 400 °C present a good absorbance (1.45) than a sample prepared at 500 °C (0.45).

Acknowledgements

The authors wish to acknowledge the financial support from the both department of Physics and Genius Process of Ferhat Abbas University. Our consideration for team of Unit of Development of Silicon Technique , UDTS, Algiers.

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