Optical characterization of thin films TiO_2/SnO_2: F

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***Abstract*— The TiO_2 thin films were prepared on FTO substrates (SnO_2: F) by the sol-gel method (dip coating). To see the influence of annealingtemperature on thin films, we usedthreedifferenttemperatures (350°C, 450 °C and 550 ° C). The thin films elaborated are characterized by two methods: the ellipsometry and UV-VISIBLE.**

Thin films TiO_2/FTO are transparent in the visible (VIS) and opaque in the ultraviolet (UV), also, the transmission decreases with increasing temperature. The refractive index increases with increasing temperature. The study showed that the refractive index and packing density increases with increasing temperature, while the pore volume decrease.

Keywords*— TiO_2, SnO_2: F, Annealing temperature, Refractive index, Spectroscopy, Ellipsometry.

I. INTRODUCTION

The study of the material in the form of thin films is the subject of a growing number of studies since the second half of the 20thcentury, because of technological advances in the development and characterization of these layers. Materials TCO (transparent conductive oxides) such as TiO_2 are very important technological materials because of their multiple applications [1]. They are increasingly used in new applications and play an increasingly important role in our life. The best known TCOs are oxides of indium, cadmium, tin, zinc and gallium. They are the foundation of a new scientific and technological revolution.

The growing interest in using the materials in the form of thin films has led to considerable diversification deposition processes [2-3]. Each process has advantages and disadvantages in terms of complexity of implementation and the quality of the deposit. We are interested in the synthesis by the Sol-Gel TiO_2 thin films that will be deposited on FTO substrates [4]. Compared to other methods of preparation, the Sol Gel has long been known [5], [6]. It offers many advantages to produce materials of greater purity and homogeneity at temperatures lower than those of conventional methods.

This work focuses on the development of titanium oxide TiO_2 thin films. We characterized the layers of titanium oxide deposited on FTO substrates (tin oxide doped with fluorine) with twoopticalmethods (ellipsometry and UV-Visible), we also studied the effect of temperature variation on the optical properties of thin films TiO_2/FTO.

II. EXPERIMENTAL

In the present work, we aim primarily the development and characterization of thin films of titanium oxide (deposited on a FTO substrate), obtained by the sol-gel method (dipcoating) from the titanium isopropoxide. We study in particular the optical properties of these layers. We seek the optimal conditions for preparation of TiO_2 thin films quality. Therefore, to obtain TiO_2 thin films with good adhesion, we evaluate the influence of some experimental parameters such as annealing temperature.

A. Substrate

We used the FTO (tin oxide doped with fluorine) deposited on a flat glass panes ordinary (soda lime) of dimension ($30x10x3mm^3$).

B. The manufacturing process of TiO_2 thin films

The solution leads to the deposition of TiO_2 thin films were prepared from the precursor titanium isopropoxide 97% produced by **Aldrich**: Ti (OCH (CH_3) 2) 4, isopropanol: $CH_3CHOHCH_3$ to dilute the above compound, acetic acid: CH_3COOH to stabilize titanium isopropoxide by complexing. Finally, we pour methanol in the solution to obtain a less viscous sol (Figure 1). This solution is transparent yellowish, slightly viscous. When glass plate (FTO / glass) is carefully washed and dried dipped in this clear solution and then removed of it at a speed of 4 cm / min, it becomes covered with a thin layer of whitish color.

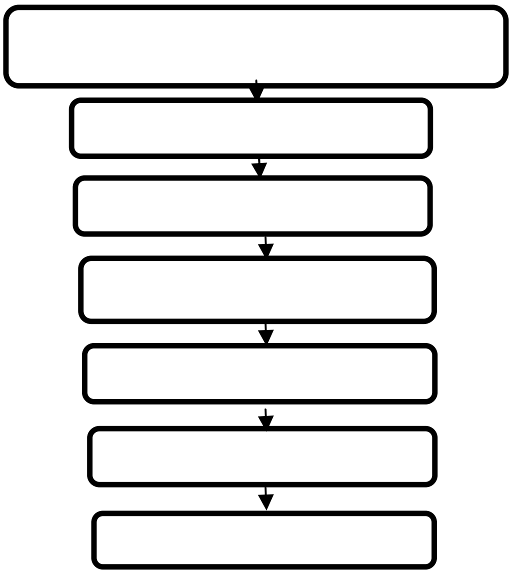

Fig. 1 The manufacturing process of TiO2 thin films.

C. *Analysis method of thin films TiO_2/SnO_2: F*

After developing the TiO_2 thin films, it then proceeded to their optical characterization. The ellipsometry and UV-Visible spectrophotometry are the main analytical techniques implemented.

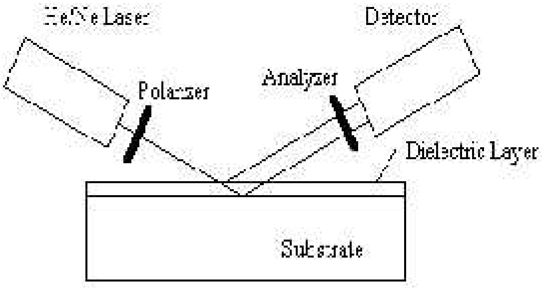

Fig. 2 Theellipsometrymeasurement technique.

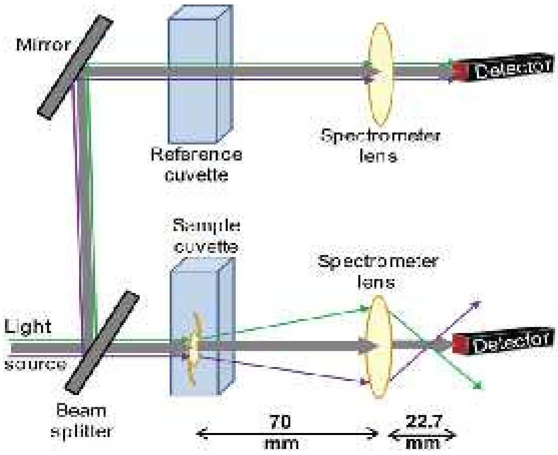

Fig. 3SpectrometerUV-Visible double beam.

D. *Thermal treatment*

This is the most important part, on the one hand to show that the deposition is successful, and on the other hand, the total evaporation of the solvents so the only possibility to have the titanium oxide. To see the influence of annealing temperature on thin films (TiO_2/SnO_2: F) we have chosen three temperatures 350 ° C, 450 ° C and 550 ° C.

III.RESULTS AND DISCUSSION

A. *Results of ellipsometry*

The ellipsometry is to send a polarized light beam with an oblique incidence to be analysed after interaction with the sample. The evolution optical indexes of the samples according to the wavelength and annealing temperature are shown in figure 4 and figure 5.

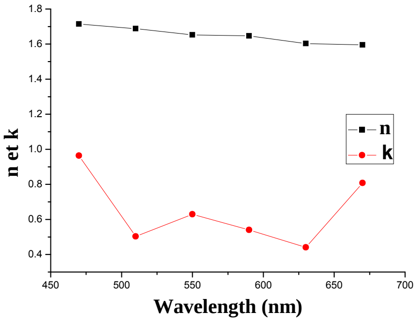

Fig. 4.aOptical indices of TiO2 / FTO depending on the wavelength obtained ellipsometry at: 350 ° C.

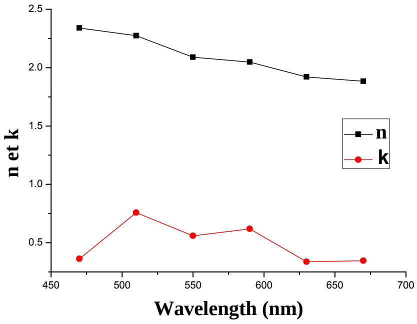

Fig. 4.bOptical indices of TiO2 / FTO depending on the wavelength obtained ellipsometry at: 450 ° C.

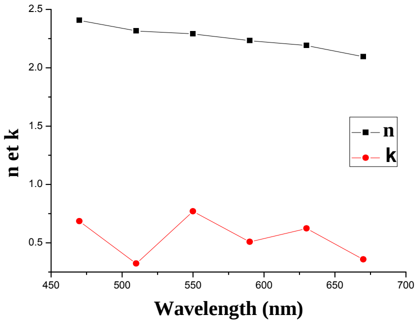

Fig. 4.c Optical indices of TiO2 / FTO depending on the wavelength obtained ellipsometry at: 550 ° C.

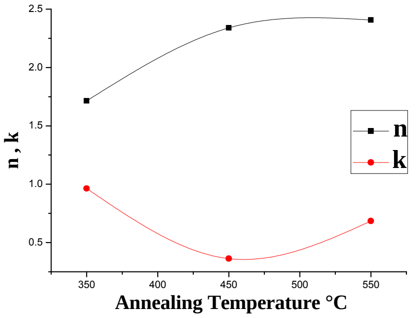

Fig. 4.aVariation of the refractive index n and the extinction coefficient k as a function of the annealing temperature for 470 nm.

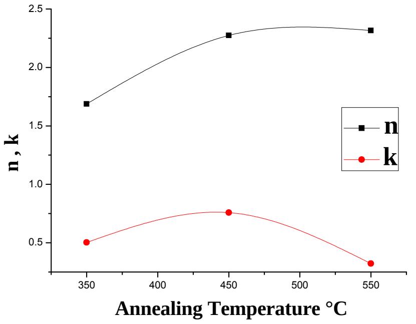

Fig. 5.b Variation of the refractive index n and the extinction coefficient k as a function of the annealing temperature for 510 nm.

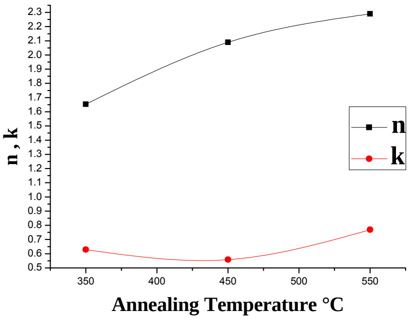

Fig. 5.cVariation of the refractive index n and the extinction coefficient k as a function of the annealing temperature for 550 nm.

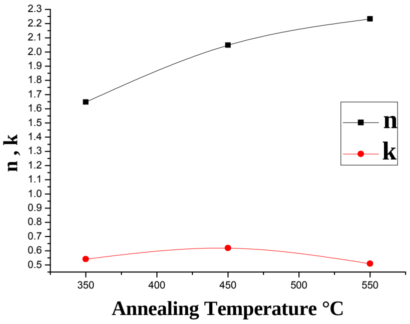

Fig. 5.dVariation of the refractive index n and the extinction coefficient k as a function of the annealing temperature for 590 nm.

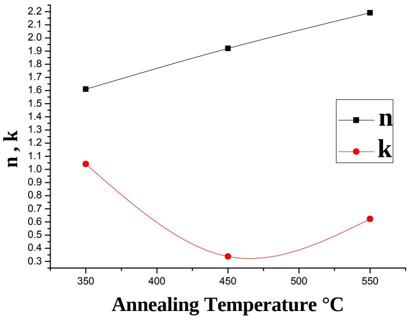

Fig. 5.eVariation of the refractive index n and the extinction coefficient k as a function of the annealing temperature for 630 nm

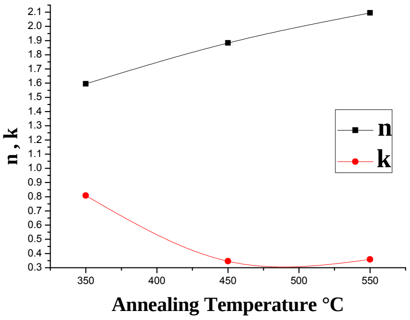

Fig. 5.f Variation of the refractive index n and the extinction coefficient k as a function of the annealing temperature for 670 nm.

Experimental measurements (Figure .5) show a remarkable increase in the values of the optical indexes with increasing annealing temperature. After thermal annealing performed on the sample at 350 ° C, the refractive index reaches the value of 1.72. Note that the samples treated at 350 °C, are at the beginning of crystallization. They have a low value of the refractive index. It is known in the sol-gel methods, the organic material (does not yet evaporated) have a considerable influence on the crystallinity and optical properties of titanium oxide films. The thermal treatment at T = 450 ° C causes an increase in the index which reaches a value of about 2.33. Treatment at T = 550 ° C causes a slight increase in the index, n = 2.40. Therefore, these samples treated between 350 ° and 550 ° C are perfectly crystallized. It should also be noted that the ellipsometric response is sensitive to surface roughness. Therefore, the variation of temperature during thermal treatment causes mechanical stress on the surface. This affects the roughness that, in turn, affects the response of the ellipsometric refractive index.

For the absorption coefficient k, there are unforeseen variations in all treated samples (outliers), these variations may be due to the quality of the deposit or assembly used.

B. Analysis of UV spectra

The optical measurements are to trace the transmission spectra of the thin films TiO_2/FTO obtained at various annealing temperatures ranging from 350 to 550 ° C. Figure 6 shows the transmission spectra of thin TiO_2/FTO: layers treated at annealing temperatures ranging from 350 to 550 ° C. These spectra show that these thin films are transparent in the visible. Calculations have yielded a coefficient of transmission medium between 60% and 75% for $\lambda \geqslant 350$ nm, the results are shown in figure 6.

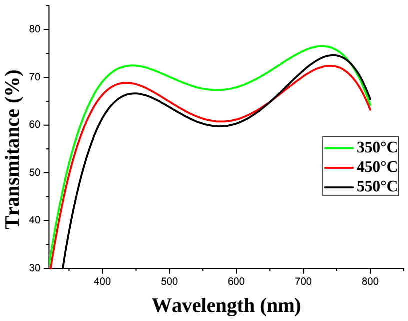

Fig. 6transmission spectra of thin films of TiO2/FTO.

Figure 6 shows that the transmittance of thin films TiO_2/FTO decreases with the annealing temperature and, at the same time, it moves to larger wavelengths. This can be attributed firstly to structural change and the increase of the grain size and, on the one hand, a significant increase in the values of extinction coefficient k with increasing temperature.

C. Packing density

The packing density is given by the following relationship [7].

$$\rho = \frac{\rho_f}{\rho_b} = \left(\frac{n_f-1}{n_f+2}\right)\left(\frac{n_b+2}{n_b-1}\right) (1)$$

ρ_f, and $\rho_b$are the densities of thin film material and solid respectively, n_f and n_b are the indexes of thin film material and solid respectively (in the case of TiO_2, n_f is the value corresponding to the peak, and n_b is the value corresponding to the solid material estimated equal to 2.57), the results are shown in figure 7.

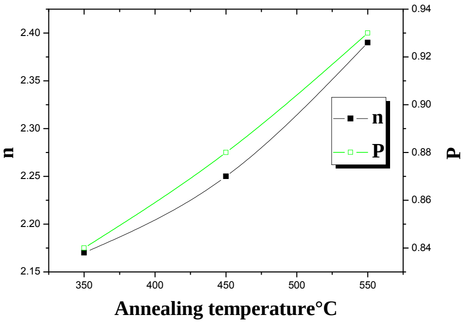

Fig. 7 Variation of the packing density and the refractive index as a function of the annealing temperature.

Figure 7 shows an increase in packing density of the films made with the temperature rise (ie the density increases with the refractive index). This is reflected by the fact that the densification of the film tends to progressively increase.

D. Volume porosity

An estimate of the volume porosity *Vp* can be obtained from the refractive index $n_f$of the layer and the value of the index $n_b$of the solid material (from the packing density) using the relationship Lorenz - Lorentz [8]:

$$V_p = 1 - \rho (2)$$

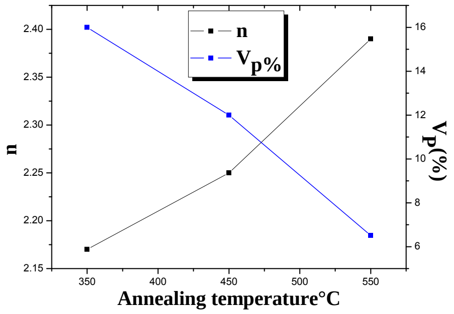

Fig. 8Variation of the volume porosity and refractive index as a function of the annealing temperature.

From Figure 8, the volume porosity *Vp* shows a linear variation as a function of the temperature. The behavior of this parameter is certainly a direct consequence of structural change caused by the high annealing temperature. Therefore, it is found that the refractive index varies in a manner inversely proportional to the porosity of the layer. We suppose that changes in the refractive index reflect a significant change in the degree of densification of the layers. Layers treated at 450 ° and 550 ° C are better densified than those treated at 350 ° C.

III. CONCLUSIONS

The study of optical properties of thin films TiO_2/FTO showed that they are transparent in the visible and opaque in the UV. Also, the transmission decreases with increasing temperature. The study showed that the refractive index increases with increasing temperature. In this context, we found that the two methods used for the characterization of these layers confirm the relationship between the refractive index of thin films TiO_2/FTO and wavelength (dispersion).

The study showed that the refractive index and the packing density increases with increasing temperature, while the volume porosity decreases.

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