Enhanced of Tio_2 Properties by Sn Doping

Fayssal Boufelgha[1,2], Fayçal Labrèche[2,*], Karima Ramdane[2] Nour-Eddine Brihi[2] , Rahima Zellagui[1] and Mohamed-cherif Benachour[1]

[1] Research Center in Industrial Technologies CRTI, P. O. Box 64, Cheraga, Algiers, 16014 Algeria.

[2] Laboratoire Physique de la Matiére Condensée et Nanomatériaux (LPMCN), Département de Physique, Faculté des Sciences Exactes et Informatique, Université Mohammed Seddik Ben Yahia-Jijel, 18000 Algeria

[*] *E-mail:* faycal_labreche@yahoo.fr

Received:11 May 2023; Accepted: 02 August 2023; Published: 30 August 2023

Abstract

Due to their interesting properties: chemical, optical and electrical, titanium dioxide (TiO_2) attracts the attention of several researchers, and many studies have been carried out to control its properties [1, 2]. And because of its wide fields of application such as optoelectronics, photocatalysis, biology…. thin layers of TiO_2 have attracted much attention from industrialists and researchers [3, 6]. In order to improve its properties, we are interested in this work in the development and study of the variation of the properties of TiO_2 by Sn doping at different concentrations. Given its simplicity, speed and cost, the deposition of our layers (on ordinary glass substrates) we have chosen the Sol-Gel method linked to the spin-coating technique. In our study we based on the study of the structural, optical and electrical properties of Sn-doped SnO_2 layers. The XRD spectra show good crystallization of all the layers with the presence of a single anatase phase. Concerning the UV-Visible, the spectra show a high transmittance of the films in the visible with a transmission rate varying between 75% and 95% with a wide optical gap between 3.4eV and 3.7eV. Concerning the optical properties of our films, its resistivity is low (about 10^{-2} Ω.Cm), we still note the minimum value of 4.29 x10-2 Ω.Cm for the 3% doping.

Keywords: TiO_2, sol–gel, thin films, Tin (Sn), optoelectronics.

Tob Regul Sci. ™ 2023;9(1): 5063 - 5072
DOI: doi.org/10.18001/TRS.9.1.352

1. Introduction :

TiO_2 is a unique material due to its remarkable properties : high refractive index, bandgap (3.2 eV), and resistance to physical and chemical impact. As well, TiO_2 has very good semiconducting properties, which has generated significant enthusiasm on the part of scientists for various applications, including photocatalysis, anti-reflective coatings, optical waveguides, photonic crystals, devices based on metal/ferroelectric/insulator/semiconductor structures.

Conductive transparent oxides (TCO) constitute an interesting class of materials and combine two physical properties; high transparency in the visible range and high electrical conductivity leading to several applications in the fields of photovoltaics and optronics [1,2].

Titanium dioxide has been the subject of much research, because it is a cheap, non-toxic material with great chemical and mechanical stability. In addition, it also has a high refractive index and a high transmittance in the visible light range, which makes it a very attractive compound in many of a field of optical applications [3]. Our objective for this work is to study the effect of the doping of thin films of TiO_2 by tin on the structural, optical and electrical properties.

2. Experimental procedure:

The solution leading to the deposition of thin layers of TiO_2 was prepared from the precursor of titanium isopropoxide: Ti $(OCH(CH_3)_2)_4$, isopropanol: $CH_3CHOHCH_3$. In order to dilute the previous compound, nitric acid HNO_3 to stabilize the titanium isopropoxide by complexing it. And finally, methanol is poured into the solution to obtain a less viscous sol. This solution is transparent yellowish in color and slightly viscous. To dope the solution with tin (1%, 3%, 5%, 7%) a suitable precursor was used: tin chloride. It can be added directly before the methanol. The deposition of thin films of TiO_2 on glass substrates by the sol-gel route, via the spin-coating technique. In the latter, a few drops of the solution are distributed uniformly on the surface of the substrate (optical glass) placed on the device, then the rotation of the substrate with a rotation of 2000 rpm for 10 seconds causes the spreading of the liquid. For each layer, the sample is dried on a hot plate at a temperature of 150° C. for 10 min. Drying is necessary to evaporate the solvents trapped in the structure of the wet gel and to continue the condensations between Ti-OH groups present in the gel. The thermal annealing is separated from the drying phase; in our work, the annealing of the layers was carried out in an oven at 525°C for 1h30 min. On the other hand, and in this work we used XRD, UV-Vis and 4Pointes techniques for the characterization of thin layers of titanium oxide (TiO_2).

3. Results and discussion :

3.1. XRD analysis:

As part of this study, the incident X-rays were produced from a CuKα radiation source, having the wavelength λ = 1.54060 A°. The identification of the DRX spectra obtained is carried out using HighScore software using the JCPDS No 21-1272 card.

Figure 1 presents the diffraction spectra of the different pure and tin-doped samples.

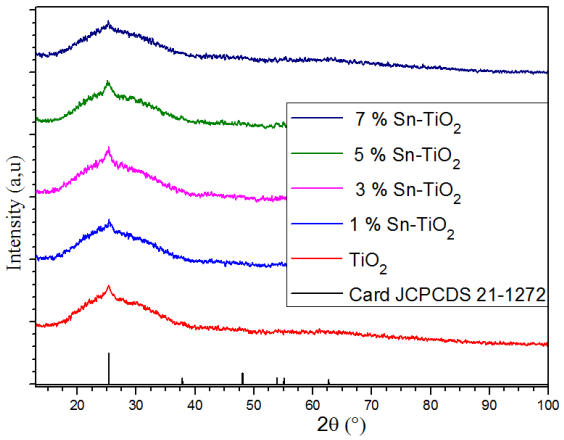

Fig. 1. Diffraction spectra of pure and doped thin films.

The absence of parasitic diffractions indicates the purity and good dispersion of the dopant in the matrix. The XRD diffractograms show good crystallization of the different samples and the peaks located at around 2θ=25.28° confirm the presence of the anatase phase alone.

3.2. UV-Vis:

Optical transmission spectra of pure and tin-doped TiO_2 thin films deposited on glass substrates were performed and recorded as a function of wavelength in the 200-800 nm range. The exploitation of this type of spectra allows us to access the determination of the optical characteristics: optical absorption coefficient, extinction coefficient, optical gap and refractive index. The figure 2 shows the transmission spectra of pure and doped TiO_2 thin films at different tin concentration rates (1%, 3%, 5% and 7%) as a function of the wavelength.

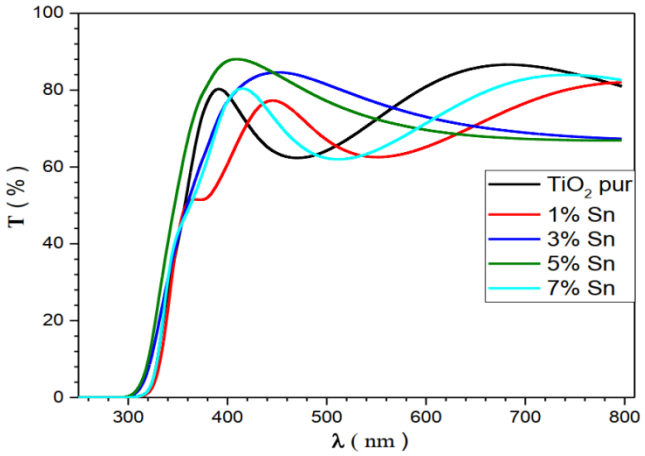

Fig.2. Transmittance spectrum as a function of wavelength.

The curves show the influence of the dopant content on the optical properties of the thin films of TiO_2, they are composed of two regions:

• a region characterized by strong absorption located at 360 nm. It encompasses the Ultra-Violet range. It is essentially due to the electronic inter-band transition, which largely justifies its use in determining the optical gap of films.

• a region of high transparency. It encompasses the visible and near infrared range, so over a wide range of wavelengths from 400 to 800 nm, the transmission values are around 70 to 90%. This high transparency is the interest in TiO_2 thin films. Also, the transmittance is more than 65% in the visible region for all the samples and the maximum of the average value of the transmittance exceeds 80%.

The absorption coefficient of the α layers can be calculated by the formula [4]:

$$\alpha = \frac{1}{d} \ln(1/T)$$

Where: d is the film thickness and T being the transmittance.

The figure 3 shows the variation of the absorption coefficient as a function of the wavelength.

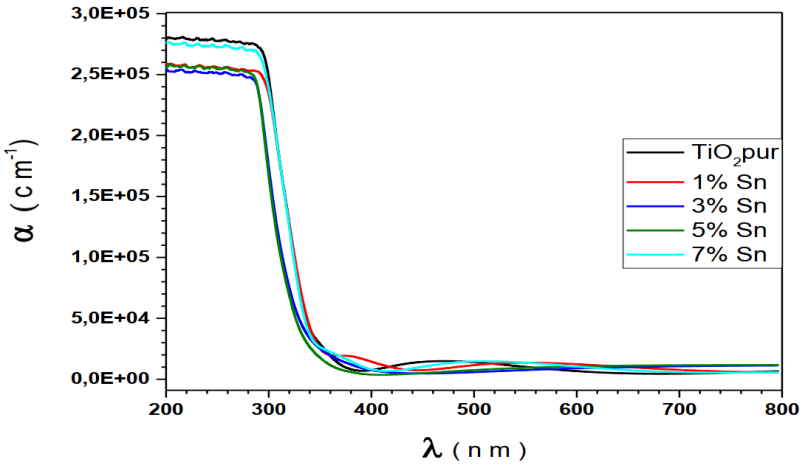

Fig. 3. Absorption coefficient as a function of wavelength.

We note that the values of the absorption coefficient are of the order of 10^5 cm-1 in the ultraviolet region, whereas in the visible region, it is of the order of 10^3 cm. In addition, the sample doped with 3% Sn has the lowest coefficient.

The extinction coefficient k is defined as a fraction of energy lost by scattering and absorption per unit thickness. Coefficient is calculated from the relationship [5]:

$$k = \frac{\alpha \lambda}{4 \pi}$$

The evolution of the extinction coefficient is shown in Figure 4.

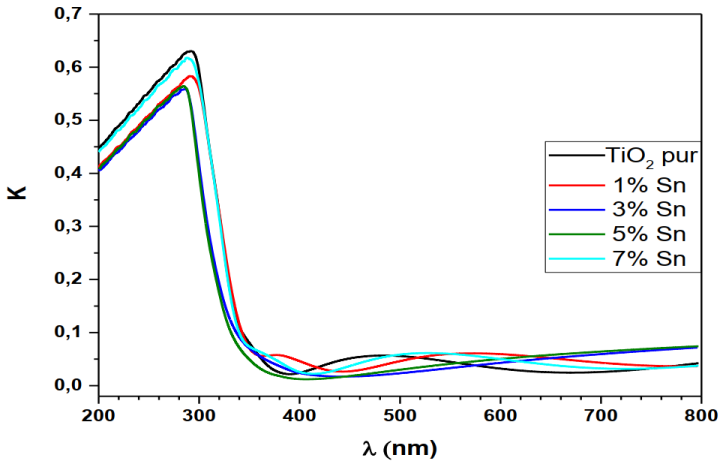

Fig. 4. extinction coefficient as a function of length.

It is clear that the average values of the extinction coefficient k(λ) in the visible region are low. The maximum value is obtained for the sample doped with 7% Sn and is worth k = 0.61 while the minimum value is obtained for the film doped with 5% and is worth k =0.012.

The optical gap was calculated from the first derivative with respect to the energy, this variation is illustrated in Figure 5. The relation between the energy in (eV) and the wavelength λ in (nm) is given by [6]:

$$E = \frac{hC}{\lambda} = \frac{1240}{\lambda}$$

Where :

h: Planck's constant.

C: speed of light in vacuum.

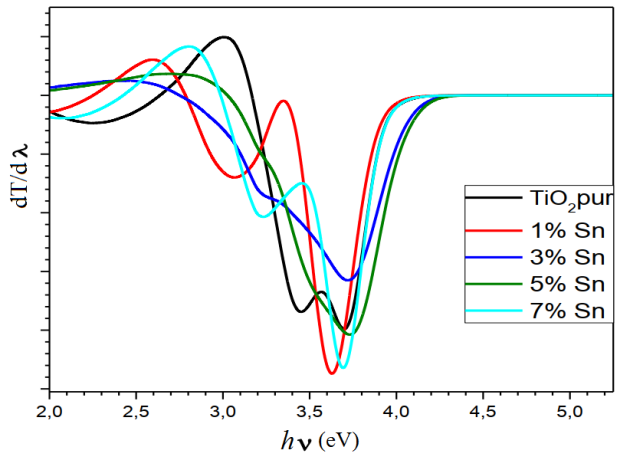

Fig. 5. Variation of the first derivative of transmittance as a function of photon energy (eV).

The table 1 below groups together the values of the gap calculated from the first derivative.

Table .1: Gap energy values of pure and Sn-doped TiO_2 thin films.

Doping rate (Sn)	0	1	3	5	7
Eg (eV)	3.70	3.62	3.71	3.72	3.69

We note that the value of the gap for the pure sample is equal to 3.7 eV, then this value is reduced for the film doped with 1% tin from which we obtain the minimum and which is worth 3.62 eV. Afterwards, we notice an increase in the value of the gap for the samples doped with 3% and 5% Sn. This increase is due to the filling of the lower states of the conduction band by the electrons coming from the dopant. The maximum value of the gap is observed for the sample doped with 5% Sn. Thereafter, we notice a second decrease in the value of the gap for the doping at 7% Sn.

3.2.1. The refractive index: Thickness calculation

The thickness of the layer is determined from the following relationship [7]:

$$d = \frac{\lambda_1 \quad \lambda_2}{2(\lambda_1 \quad n_2 - \lambda_2 \quad n_1)}$$

The refractive indices n1 and n2 of the layer for the wavelengths λ_1 and λ_2 are taken from the relationship:

$$n_{1,2} = \left[N + (N^2 - S^2)^{1/2}\right]^{1/2}$$

Where :

S: refractive index of the substrate (S = 1.45)

And $N_{1,2}$ are calculated by the relation:

$$N = 2\,S\left(\frac{T_M - T_m}{T_M\,T_m}\right) + \frac{S^2 + 1}{2}$$

Where :

T_M: Maximum transmittance

T_m: The minimum transmittance

3.3. Electrical characterization of thin layers: 4 Points:

The electrical properties of our samples are measured at room temperature using a 4-point device of the N-0272086 type.

The four-point method is used to measure the resistance of films

thin. The resistance of the film is defined by [8]:

$$R_s = \frac{\pi}{ln2}\left(\frac{V}{I}\right)$$

The conductivity of the film $\sigma\ (\Omega.cm)^{-1}$ is given by the relation:

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s\, d}$$

The results of the thicknesses, resistivities and conductivities of the various samples are presented in table 2.

Table .2: The values of thickness, resistivity and conductivity as a function of the doping rate of TiO_2 thin films.

Sample	Thickness (nm)	Resistivity (Ω.cm).10 $^{-2}$	Conductivity $(\Omega.cm)^{-1}$
Pur	315.92	6.70	14.91
1 % Sn	343.78	4.88	20.49
3 % Sn	349.10	4.29	23.28
5 % Sn	342.90	5.14	19.45
7 % Sn	321.78	6.32	15.79

Figure 6 shows the influence of tin doping on the electrical properties (resistivity and conductivity) of titanium oxide thin films.

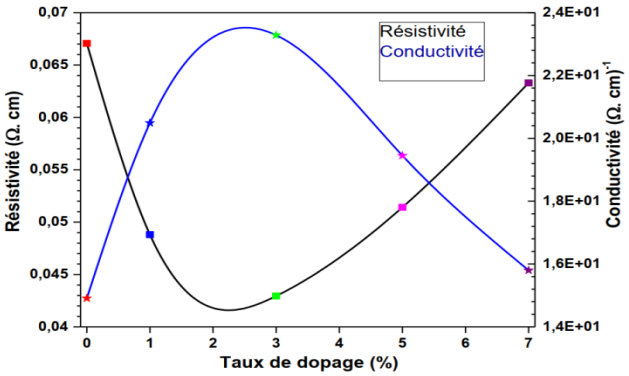

Fig. 6. Variation of resistivity (conductivity) as a function of pure and Sn-doped TiO_2 thin films.

We note the resistivity of the samples decreases with the increase in the doping rate and reaches its minimum value of 0.05 Ω. cm For a rate of 3% tin. This decrease in resistivity can be interpreted by the increase in the number of charge carriers (electrons) coming from the Sn^{+2} donor ions incorporated in the substitutional or interstitial sites. For the sample doped at 5% and above, we notice an increase in the resistivity of probably due to the decrease in the mobility of the electrons. It should be noted that the resistivity of an n-type semiconductor is given by the relation [9,10]:

$$\rho = \frac{1}{e\,\mu\,n}$$

Where :

e: elementary charge $1.6\ 10^{-19}$ C.

n: concentrations of electrons per unit volume.

μ: electron mobility.

3.4. Merit factor:

The performance of TCO films can be assessed through two crucial parameters, namely sheet strength (Rs) and optical transmittance (T). It is always desirable to have low resistance with high transmittance. In order to determine the optimal combination between the optical transmittance, we used the figure of merit defined by Hackee [11]:

$$\varphi = \frac{T^{10}}{R_s}$$

Where :

T: Average transmittance around 550 nm.

RS: Thin film resistance.

The results obtained are listed in Table 3 (Tab.3).

Table .3. Values of the Factor of Merit (quality) as a function of the tin doping rate of TiO_2 thin films.

Doping rate	0	1	3	5	7
$\Phi\ (\Omega)^{-1}.10^{-5}$	1.860	0.646	5.765	2.655	0.620

The variation of the figure of merit (quality) as a function of the tin doping rate is represented in figure 7.

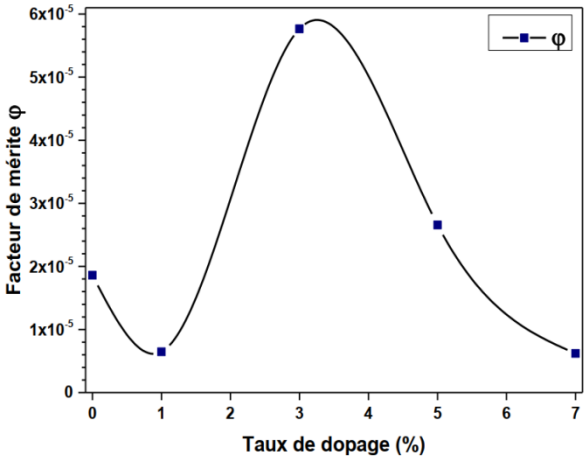

Fig. 7. Merit factor according to the doping rate of the different samples.

It is noted that the maximum value of the quality factor corresponding to a better correlation between the high transmittance and the low resistivity is that of the film doped at 3%.

4. Conclusions :

In this study, we studied the properties (structural, optical and electrical) of thin films of pure and tin-doped titanium oxide (Sn-TiO_2) deposited on glass substrates by the spin-coating method. Several techniques were used for the characterization of the samples: X-ray diffraction, UV-Vis spectroscopy and the four-point method. The XRD spectra show good crystallization of the different samples and the presence of only the anatase phase. The UV-Vis measurements show a high transparency in the visible of the thin films greater than or equal to 70% with a maximum of transmittance which exceeds 90% for the sample doped with 5% tin. Also, the values of the optical gap vary between 3.60 and 3.72 eV, and the study of the electrical properties show that the electrical resistivity is of the order of 10^{-2} Ω. cm with a minimum of resistivity for the sample doped with 3% Sn (5.28 10^{-2} Ω.cm) and a better correlation between transmittance and resistivity for the sample doped with 7% tin proved by the figure of merit by Hackee.

References

[1] H. E. Doghmane and al, Synthesis and Characterization of Tio_2 Thin Films for Photovoltaic and Optoelectronic Applications, Springer Proceedings in Energy (SPE) ICREEC , 317 (2019).

[2] Y-J Ma and al, Fabrication of TiO_2 thin films with both anatase and rutile structures together using the ion-implantation method, Optical Materials Express, **8 (3)**, 540 (2018).

[3] M.I. Khan and al, Structural, electrical and optical properties of multilayer TiO_2 thin films deposited by sol–gel spin coating, Results in Physics, **7**, 1437 (2017).

[4] Yu. M. Evtushenko and al, Optical Properties of TiO_2 Thin Films, Physics Procedia, **73**, 100 (2015).

[5] V. Zharvan and al, Study on fabrication of TiO_2 thin films by spin–coating and their optical properties, AIP Conference Proceedings, **1719 (1)**, 1 (2016).

[6] P. Ellappan and L. R. Miranda, Synthesis and Characterization of Cerium Doped Titanium Catalyst for the Degradation of Nitrobenzene Using Visible Light, International Journal of Photoenergy, **2014**, 1 (2014).

[7] S. G. Pawar et al, Effect of annealing on microstructural and optoelectronic properties of nanocrystalline TiO_2 thin films, Journal of Experimental Nanoscience, 8(4), 500 (2013).

[8] Fujshima et K. Honda, Electrochemical Photolysis of Water at a Semiconductor Electrode, Nature, 238, 37 (1972).

[9] Gultekin, Effect of Au Nanoparticles Doping on The Properties of TiO_2 Thin Films, Materials Science, **20 (1)**, 10 (2014).

[10] V. Kumar, J.K. Singh, Model for calculating the refractive index of different materials, Ind. J. Pure Appl. Phys. **48**, 571 (2010).

[11] Ravindra, N.M. Auluck, S. Shrivastav, V.K. On the Penn gap in semiconductors. Phys. Stat. Sol. (b), **93**, 155 (1979).