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OPTICAL AND STRUCTURAL PROPERTIES OF TITANIUM OXIDE THIN FILMS PREPARED BY SOL-GEL MERHOD

M.Hemissi*, H. Amardjia-Adnani
Laboratoire de dosage, analyse et characterisation en haute resolution, Université de Paris, France

TiO_2 thin films were prepared by sol gel method. The structural investigations performed by means of X- ray diffraction (XRD) technique, Scanning electronic microscopy (SEM) showed the shape structure at T=600°C. The optical constants of the deposited film were obtained from the analysis of the experimental recorded transmittance spectral data over the wavelengths range 200-3000 nm. The values of some important parameters (refractive index n, dielectric constant ε_∞ and thickness d), and the third order optical nonlinear susceptibility $\chi^{(3)}$ of TiO_2 film are determined from these spectra. It has been found that the dispersion data obey the single oscillator relation of the Wemple-DiDomenico model, from which the dispersion parameters and high – frequency dielectric constant were determined. The estimation of the corresponding band gap E_g, $\chi^{(3)}$ and ε_∞ are 2.57 eV, 0.021×10^{-10} esu and 5.20, respectively

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1. Introduction

Many nanostructured materials are now being investigated for their potential application in photovoltaic, electro-optical, micromechanical and sensor devices [1]. Nanoporous TiO_2 thin films for dye-sensitized and ETA solar cells have been under intensive study for many years [2]. TiO_2 occurs naturally as minerals: rutile, anatase or brookite. The rutile and anatase forms have been intensively studied and have significant technological usefullness, owing, in large measure, to their optical properties: both are transparent in the visible and absorb in the near ultraviolet [3]. The rutile (110) surface serves as a prototype model for basic studies of oxide surfaces, and is the active component in self cleaning cement. It serves as the dye-supporting electron transporting substrate in a promising class of solar cells. Recent interest has been raised for the transparent anatase N-doped films [4].

At room temperature the direct gap E_g is 3.06 eV for rutile and about 3.3 eV for anatase. This paper reports on investigation of optical properties of nanocrystalline TiO_2 anatase films prepared by dip-coating in the frame of the sol-gel method.

Structural properties, morphology and grain sizes are studied. The substate is immersed in the solution four times with speed of 80 mm.mn-^{1} . Each layer was dried at 100 °C for 15 min and annealed at 300°C during 30min. After deposing the fourth layer the film was treated at 400 °C for 20 min.

The film structure was determined by (XRD) Cu K_α Dron- 3m diffractometer [5]. The UV-Visible spectra of samples deposited on glass wafer were recorded in the photo-spectrometer FT- IR Perkin -Elmer SPECTRUM 1000, the surface morphology were analysed by scanning electronic microscopy SEM ESEM XL 30 FEG FEI Company (Philips).The optical study to calculate the refractive index (n), dielectric constant (ε_∞) was carried out for TiO_2 anatase by analyzing the transmission spectra of thin layer (four layers) using the envelope method proposed by Swanepoel [3]. The optical band gap was calculated by Tauc's extrapolation method [6], and compared to the plot of $(\alpha h\nu)^2$ vs $h\nu$ for the determination of direct band gap E_g.

2. Experimental

The sol-gel solution [8] is prepared in the following way:1.6 cm^3 of titanium isopropoxide was considered, to which 4.65 cm^3 of isopropanol are added drop by drop. The solution was left under closed

*Corresponding author: hemissi_melia@yahoo.fr

stirring under heating at 60 °C during 10 minutes. Then 5.15 cm^3 of acetic acid was poured, stirred during 15 minutes under heating at 60°C. Finally 12 cm^3 of methanol and was added and stirred during 2 hours. The samples were immersed in the sol-gel solution with the speed of 80 mm/min, dried at 100 °C during 15 min, and finally annealed at 400 °C during 20 minutes.

3. Results

Fig. 1, shows the X-ray diffraction (XRD) patterns of TiO_2 thin film annealed at 400°C during 20 mn, it is seen that the elaborate TiO_2 thin layer has a crystalline structure after annealing under oxygen O_2 flux at 400 °C for 20 min, It has been observed two phases, the anatase phase with the preferential orientation of the crystallites along the [101] direction, and the appearance of a very small peak of rutile phase at 2θ =47.67°.

According to Sabataityteÿ and al.[2] who used sol-gel method and spray pyrolysis technics for film deposition, the structure obtained is anatase at 500 °C. On the other hand *spin-coating* [7] method lead to the formation of the configuration Ti-O-Ti anatase. This modification was observed after an annealing of 450 °C. The rutile crystalline structure was observed after an annealing at temperatures higher than 700 °C.

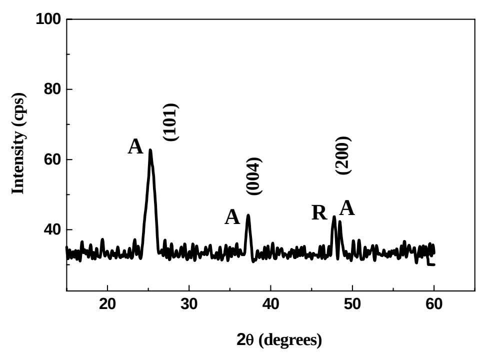

Fig.1. X-ray diffraction spectra of TiO_2 thin layer (four layers) annealed at 400°C during 20 mn

The surface morphology of the as-prepared TiO_2 nanoparticle film, annealed at 600°C for 30 min has been studied by scanning electronic microscopy SEM. It is clearly observed from the micrography that nanoparticles are extra-fine, with an average grain size of 20 nm.

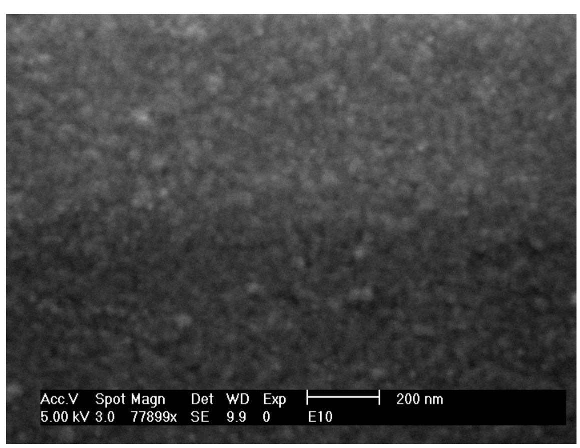

Fig. 2. SEM microscopy of the as-prepared TIO_2 nanoparticles annealined at 600 °C for 30 min.

Analysis of optical transmission spectra is one of the most productive tools for understanding of the band structure and energy band gap, E_g, of the crystalline structure.

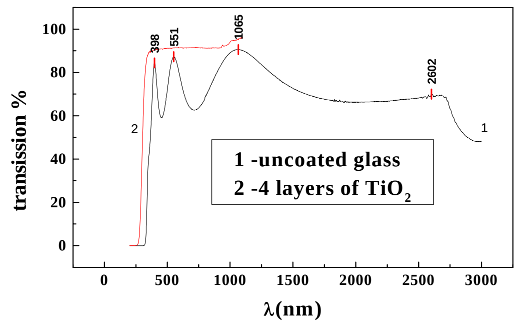

Fig .3 Transmittance spectra of TiO_2 thin film deposited by sol-gel method and annealed at 400°C during 20 min.

With the aim to study the optical transmission of TiO_2 thin film, the dependence of transmittance, T, on the wavelength, λ, in the spectral range 200 nm - 3000 nm, was recorded. Figure 3 shows the transmittance spectra at normal light incidence for as-prepared TiO_2 samples before and after calcination at 400 °C. for 20 min.

The transmittance of the uncoated glass substrate is greater than 93% over the whole spectral region excepting for wavelengths below 1000 nm where a slight increase of transmission of about 95% is observed, an effect that due to light scattering by bubbles inside the substrate [8]. The transmittance of TiO_2 thin film is slightly less than that of the uncoated substrate. Relatively high transmittance of the film is an indication of low surface roughness and good homogeneity [9]. The spectrum can be roughly divided into two regions: a transparent region with the interface pattern and a strong absorption zone in the UV range. In the region of low absorption, the incident light traverses and reflects in film several times and produces the interference fringes. The four observed peaks in the spectra are related to each layer.

From the experimental data of the optical transmittance of the TiO_2 thin film, the refractive index has been calculated.

The complex refractive index for the homogeneous film, with uniform thickness, d, is defined by the relation $n_c = n - i.k$ [10], where n is the refractive index and k is the extinction coefficient.

The refractive index, n[11] has been obtained from the relation (1). In order to evaluate the extinction coefficient k [12] the relation (2) was used.

$$\frac{1}{T_m} - \frac{1}{T_M} = \frac{1}{4}\frac{(n^2-1)(n^2-n_S^2)}{n^2 n_S} \qquad (1)$$

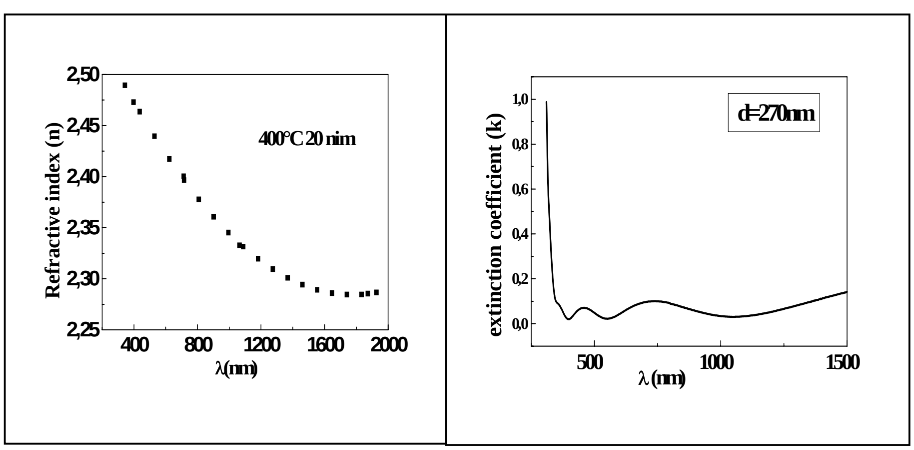

Fig .4. Dispersion of n and k for TiO_2 film on glass substrate.

where n_S is the refractive index of glass substrate, T_M and T_m are the maximum and minimum values of the transmittance at the same wavelength, respectively. The spectral dependence of refractive index n, and k for TiO_2 film is shown in Fig 4.

$$k = \frac{\alpha\lambda}{4\pi} \tag{2}$$

$$\alpha = \frac{Ln(1/T)}{d} \tag{3}$$

The absorption coefficient α [13] have been determined from the spectra using the formula (3), where T is the transmittance and d is the thickness of the film. This coefficient is slightly affected by the change of structure at lower energy values. This behavior is probably due to the crystallization process occurring in the films [14].

The thickness has been calculated from the relation [11]

$$d = \frac{M\lambda_1\lambda_2}{2[n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1]} \tag{4}$$

Through the above calculation, n and d of the film were obtained. The film thickness d was found to be about 270 nm, which is in good agreement with the value measured by ellipsometer Jobin-Yvon UVISEL. The value is about 280 nm

Figure 4 shows the refractive index n and extinction coefficient k of TiO_2 film as a function of wavelength. The dispersion curve of refractive index is fairly flat in the long wavelength region and rises rapidly towards shorter wavelengths, showing the typical shape of dispersion curve near an electronic inter band transition. the refractive index is 2.32 at 800 nm near the visible region. The extinction coefficient decreases gradually with the shortening of wavelength.. therefore, the calculated k value actually included the total optical losses caused by both absorption and scattering, this factor is 8.9×10^{-2} at 800 nm, the low value of extinction coefficient (of the order of 10^{-2}) in visible and infrared region is a qualitative indication of excellent surface smoothness of the TiO_2 thin film [15].

4. Discussion

Based on the single-oscillator model, wemple- DiDomenico [16] is a semi-empirical dispertion relation for determining the refractive index n at photon energies ($h\nu$) can be written as follows:

$$n^2(h\nu) - 1 = \frac{E_0 E_d}{E_0^2 - (h\nu)^2} \tag{5}$$

where h is the Plank constant, ν is the frequency, E_o is the oscillator energy and E_d is the dispersion energy which is measure of the average strength of inter-band optical transition or the oscillator strength.

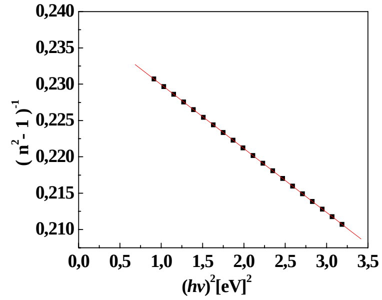

Fig 5. Plot of $(n^2 – 1)^{-1}$ against $(h\nu)^2$

By plotting $(n^2 - 1)^{-1}$ against $(h\nu)^2$ and fitting a straight line as shown in Fig (5) $(E_0\ E_d)^{-1}$, and the intercept E_0/E_d , on the vertical axis. The oscillator energy, E_0 , is related to the optical band gap, E_g in close approximation by $E_0 \approx 2E_g$

Using the curve above the estimated values of the oscillator parameters E_o is 5.59 eV, E_d is 23.51 eV, and band gap E_g is 2.79 eV. It is known that that inter-crystallites boundaries contain structural defects and impurities, these factors having a strong influence on the absorption processes[14]. The value of the refractive index, n(0), for $(h\nu)\to 0$, extrapolated from the Wemple-DiDomenico model fitted with the high-frequency dielectric constant $\varepsilon_\infty = n(0)^2$ [17], is about, respectively, 2.28 and 5.20.

It has been pointed out that the oscillator strength E_d obeys a simple empirical eq. [18,19]:

$$E_d = \beta N_c Z_a N_e \text{ (eV)} \tag{6}$$

where N_c is the effective coordination number of the cation nearest-neighbour to the anion ($N_c(TiO_2) = 6$), Z_a is the formal valency of the anion ($Z_a(TiO_2) = 2$), N_e is the effective number of the valence electrons per anion excluding the cores ($Ne(TiO_2) = 8$), and β is a constant that depends on the inter-atomic bond (β $(TiO_2) = 0.27$ eV). The parameters required to calculate E_d give 25.92 eV. One can remark that a good agreement between the two calculated values is obtained.

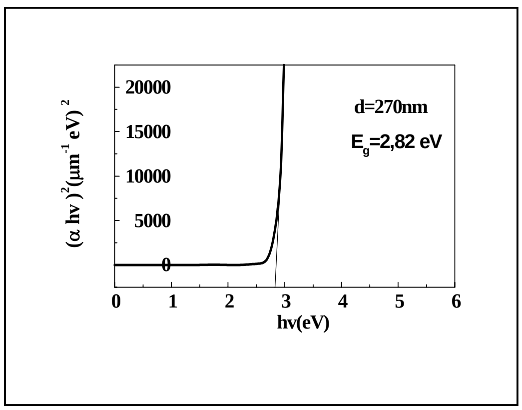

Fig 5. plot of $(\alpha\ h\nu)^2$ vs hν plot for determination of direct gap, E_g

For photon energy hν falling on the material and assuming direct transitions between the valence band and conduction bands, the absorption coefficient is related to the band gap E_g in the following manner

$$(\alpha\ h\nu)^2 = C\ (h\nu - E_g) \tag{6}$$

where C is a constant. The E_g value was estimated to be 2.82 eV by extrapolating the linear part of $(\alpha\ h\nu)^2$ vs $h\nu$ in Fig.5. This value is similar to the value 2.79, found through the equation (3) .

According to Wagner et al. [20] the Miller rule is very convenient for visible and non linear and near infrared frequencies, which equalize the third order non linear polarizability parameter, $\chi^{(3)}$, the so-colled non linear optical susceptibility, and the linear optical susceptibility, $\chi^{(1)}$, through the equation:

$$\chi^{(3)} = A\ (\chi^{(1)})^4 = A[E_0\ E_d/4\pi(E_0^2 - (h\nu)^2\ ]^4 = A/(4\pi)^4(n^2 - 1)^4 \tag{7}$$

where the constant is $A = 1.7\times10^{-10}$. The covalency and ionicity of the chemical bonds strongly influence the magnitude of the non-linearity.

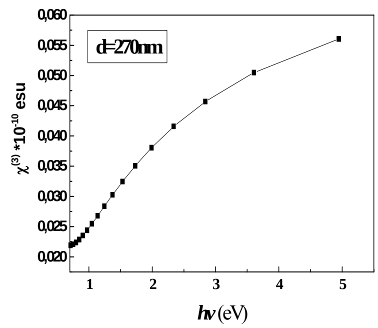

Fig 6. The third order optical non linear susceptibility of TiO_2 film annealing at 400 °C for 20 mn

The third order nonlinear susceptibility of TiO_2 film is calculated from the equation.(7), which is shown in Fig.6. One can see that $\chi^{(3)}$ increases when the photon energy $h\nu$ increases. That begins from 0.021×10^{-10} esu,. The estimated value of the third order nonlinear susceptibility $\chi^{(3)}$ using the equation (7) is for n(0) = 2.28. The limit value is 0.056×10^{-10} esu.

Table 1: The estimated values of the oscillator parameters of TiO_2 thin films.

Film	T °C	T_{anneal}	Tech	d (nm)	E_o (eV)	E_d (eV)	E_g (eV)	n (0)	ε_∞
TiO_2	400°C Inder O_2	20 min	Sol-Gel	270 Experim. 280	5.59	23.51 Equation (6) 25.92	2.79 Extrapolated 2.82	2.28	5.20
TiO_2 [20]sintered substrate (250°C)	450°C inder N_2	1h	APCVD	80.4				2.08	3.81

5. Conclusions

TiO_2 thin films have been deposited on glass substrate by sol-gel method. X–ray diffraction patterns have shown that the films are non-crystalline. The envelope method was used to calculate their optical constant (n, d) from the transmittance spectra. The dispersion of the refractive index in film follows the single electronic oscillator mode relation. Using this method, the values obtained for the oscillator strength E_d and the oscillator energy (E_o) have been got: 23.51 eV and 5.59 eV respectively. The optical band is estimated to be 2.79 eV compared to 3.2 eV in [4] and the dielectric constant ε_∞ was estimated to be 5.20. The refractive index was estimated about 2.28, and the thickness was found equal to 270 nm, compared to that measured ellipsometrically, 280 nm. The third order nonlinear susceptibility $\chi^{(3)}$ has been calculated using Wagner model and the obtained value was 0.021×10^{-10} esu.

References

[1] R. S. Singh, V. K.Rangari, S. Sanagrapalli, V. Jayaraman, S. Mahendra, V. P. Singh, Nano-stuctured CdTe,CdS and TiO_2 for thin film solar cell applications, under print.
[2] Julija Sabataityté, Ilona Oja, Frank Lenzman,Olga Volobujeva, Alle Krunks, Characterization of nanoporous TiO_2 films prepared by sol-gel method C.R Chimie **9** (2006).
[3] R. Zallem, M.P.Moret, Solid State Communications **137**, 154 (2006).

[4] A simple method to synthesize light active N-doped anatase (TiO_2) photocatalyst, Bulletin of the Catalysis Society of India, **4**, 131 (2005).
[5] M.Hemissi, H.Amardjia-Adnani, J.Cplenet, B.Cannut, and J.M.Pelletier, Influence of annealing time on structural and electrical properties of Sb doped SnO_2 films, Revue des energies renouvelables **10**, 233-279 (2007).
[6] Pankaj Sharma, S.C.Katyal, Influence of replacing Se in $Ge_{10}Se_{90}$ glassy alloy by 50 at .% Te on the optical parameters, Journal of Ovonic Research, **2**, N° 6, 105, December 2006.
[7] Julija Sabataityteў, Ilona Oja, Frank Lenzmann, OlgaVolobujeva, Malle Krunks, Characterization of nanoporous TiO_2 films prepared by sol–gel method, C. R. Chimie (2005).
[8] Hu Z, Hang Z, Lai Z, Wang Gand Chu, Thin Solid Films **437**, 223 (2003).
[9] R. Thomas, D. C. Dube D C, Jpn. Appl. Phys. **39** 1771 (2000).
[10] Li –Jian Meng, Andrischky, M.P. dos Santos, The effect of substate temperature on properties of d.c reactive magneton sputtered titanium oxide films, Thin Solid films **223**, 242, 1993.
[11] R.Swanepoel, Determination of thickness and optical constants of amorphous silicon, J. Phys E : Sci. Instrum. **16**, 1214 (1983).
[12] P. Sharma, S.C. Katyal , Influence of replacing Se in $Ge_{10}Se_{90}$ glassy alloy by 50 at% Te on the optical parameter, Journal of Ovonic Research **2**(6), 105, December 2006.
[13] G. Hirankumar, Thermal, electrical and optical studies on poly (vinyl alcohol) based polymer electrolytes, in print.
[15] N.Tigau, V.Ci7upina, G.I.Rusu, G.Prodan,E.Vasile ,influence of substrate temperature on the structural and optical properties of Sb_2S_3 thin films, Rom. J. Phys. Vol **50** N°7-8 p859-868, Bucharest, 2005
[16] S. Bhaskar, S. B. Majumder, M. Jain, P. S. Dobal, R.S. Katiyar, Studies on the structural, microstructural and optical properties of a sol-gel derived lead lanthanum titanate thin films, Materials Sciences and Engerineering, **B57**, 178 2001.
[17] H.S.Soliman, D.Abdel-Hady, E.Ibrahim, Optical properties of thermally vacuum evaporated $AgSbSe_2$ thin films J.Phys Condens Matter, **10**, 647,1984.
[18] W. C. Tan, K.Koughia, J. Singh, and S.O. Kasap Fundamental optical properties of materials.
[19] E Marquez, J.B Ramirez-Malo, P. Villares, R . Jimenez-Garay, R. Swanepoel, Optical characterisation of wedge-shaped thin film of amorphous arsenic trisulphide based only on their shrunk transmission spectra, Thin Solid Films, **254**, 83 (1998).
[20] T. Wagner, M.Krbal, J. Jedelsky, Mil. Vlcek, B.Frumarova, M.Frumar, Kinetics of optically and thermally induced diffusion and dissolution of silver in PLD $As_{40}S_{60}$ amorphous films: their properties and structure, J. Optoelectron. Adv. Mater. **7**(1), 153 (2005).
[21] B. S. Richards, Single material TiO_2 double layer antireflection coatings, Solar Energy Mat. & Solar Cells, **79**, 369-390 (2003).