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DETERMINATION OF THE OPTICAL CONSTANTS AND THICKNESS OF TITANIUM OXIDE THIN FILMS BY SWANEPOEL METHOD

BY

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Abstract The Swanepoel method is a well-suited method for the study of the thin films optical constants as a function of wavelength. More, this method allows also to obtain, with good accuracy, the thickness of the films. Here, this study was made on a titanium oxide thin film obtained by a dc sputtering technique onto optical glass slides. XRD patterns showed a mixed anatase/rutile structure. Refractive index and extinction coefficient were determined as a function of wavelength in the visible spectral range. The thickness was found to be about 300nm.

1. INTRODUCTION

Sputtering is the most common technique used to deposit optical thin films for a large variety of applications: optical coatings, protective layers, microelectronics application. Regardless of the deposition technique used, it is necessary in the development of coating equipment and coating processes to have the ability to determine the physical and optical properties of the obtained films. Spectral measurements made on thin films can be used to extract some of their optical properties. For instance, the wavelength dependency of the film optical constants can be examined by variable angle spectroscopic ellipsometry [1]. Another method is to obtain the mentioned dependences by performing optical transmission measurements and using the envelope (Swanepoel) method.

In the present work, we describe the Swanepoel method used for the determination of the TiO_2 thin film optical constants and its thickness. The accuracy is of the order of 1%, which is better than the accuracy of few elaborate computational iterations. It can be mentioned that the method doesn't require a dispersion model to determine the film thickness and optical parameters of the film, but it is not accurate when the film has significant dispersion and high absorption.

2. EXPERIMENTAL PROCEDURE

Titanium oxide thin films were deposited by a dc sputtering technique onto glass substrates maintained at 300 °C. Argon and water vapors were

chosen as sputtering gas and reactive gas, respectively. The target to substrate distance was 150 mm, the total pressure ($Ar+H_2O$) being set at $2x10^{-3}$ mbar. The reactive gas partial pressure was kept constant at $0.6 \cdot 10^{-3}$ mbar during the deposition. The deposition rate was about 0.03nm/s.

An Alpha-Step 500 Surface Profiler was used for measuring the thicknesses of the samples, in order to verify the values obtained by Swanepoel method.

X-ray diffraction (XRD) measurements have been carried out at grazing incidence diffraction (5°), with a Rigaku Geigerflex computer-controlled diffractometer, (Cu $K_{\square}$ radiation).

The film transmission was measured in the visible region and near IR range, using a SPECORD UV - VIS spectrophotometer, Carl Zeiss Jena.

3.EXPERIMENTAL RESULTS AND DISCUSSION

XRD patterns revealed a polycrystalline structure (Fig. 1), which is specific for thin films deposited onto heated substrates [2]. Mixed anatase and rutile peaks can be observed in Fig. 1. Using a formula given by Spurr et.al [3], the weight percentage of the anatase phase was calculated (70 %).

The transmission spectrum for the sample under study is given in Fig. 2. The observed fluctuations are connected with the film thickness and consequently with the interference in the layer.

Considering the thickness substrate alone, in the absence of the film, the values of the transmission, T_S, without interference, is given by the well-known expression:

$$T_S = \frac{1-R}{1+R}, \qquad (1)$$

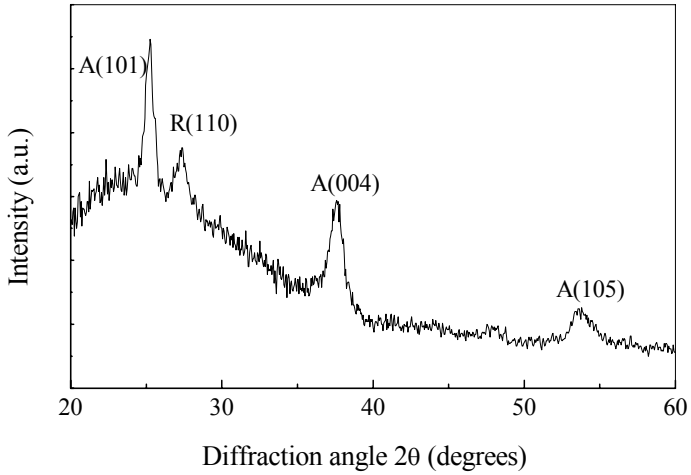

Fig. 1 XRD pattern for the studied sample

where the reflectance R is given by:

$$R = \left(\frac{n_s - 1}{n_s + 1} \right)^2 \tag{2}$$

n_s being the refractive index of the substrate. Consequently, T_S can also be written as:

$$T_S = \frac{2n_s}{n_s^2 + 1}, \tag{3}$$

and the refractive index of the substrate, at each λ, is given by:

$$n_s = \frac{1}{T_S} + \left(\frac{1}{T_S^2} - 1 \right)^{1/2}. \tag{4}$$

The basic equation for interference fringes is:

$$2nd = m\lambda, \tag{5}$$

where the order number m is an integer for maxima and half integer for minima.

According to Swanepoel's method [4], considering the theory for an infinite substrate, a first value of the refractive index of the film n_1, in the spectral region of medium and weak absorption, can by calculated by the expression:

$$n_1 = \left[N_1 + \left(N_1^2 - n_s^2 \right)^{1/2} \right]^{1/2}, \tag{6}$$

where

$$N_1 = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2}. \tag{7}$$

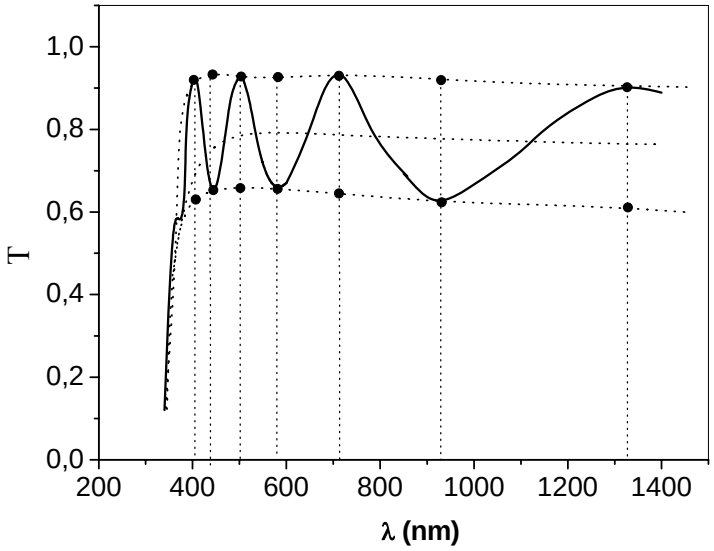

Fig. 2 Transmission spectrum for the studied TiO_2 thin film

T_M and T_m are the transmission maximum and the corresponding minimum at certain λ wavelength, one being measured and other calculated. The smooth envelopes of TiO_2 film and the intermediate values are plotted by a suitable computer program (Origin 7.5) with parabolic interpolation between the three nearest experimentally measured points (Fig. 2).

The refractive index of the substrate in the region of medium and weak absorption can be determined by means of transmission spectrum for the clean substrate alone and using equation (4) to calculate n_s. For our sample we have obtained that n_S = 1.47 with T_S = 0.93. Table 1 designates the values at the extremes of the spectrum, T_M and T_m, at different λ obtained from Fig. 1. The refractive index values, n_1, are calculated from equation (6) and listed in Table 1.

Table 1. Values for wavelength corresponding to different maxima and minima, transmission maximum T_M and the corresponding minimum T_m at certain λ, first values of the refractive index of the film n_1 at certain λ, first values of the thickness d_1, the order numbers, m_0, for the different extremes, exact integer or half integer values, m, second values of the thickness, d_2, second calculated values of the refractive index of the film n_2, T_α *as a* geometric mean of T_M and T_m.

λ (nm)	T_M	T_m	n_1	d_1 (nm)	m_0	m	d_2 (nm)	n_2	T_α
407	0.922	0.623	2.421	335.3	3.88	4.00	289	2.421	0.757
445	0.919	0.629	2.393	393.5	3.42	3.50	340	2.393	0.761
503	0.929	0.644	2.360	363.1	2.93	3.00	302	2.360	0.774
584	0.932	0.652	2.339	391.5	2.46	2.50	333	2.339	0.780
713	0.926	0.655	2.319	386.9	1.96	2.00	315	2.320	0.779
932	0.927	0.657	2.315	389.0	1.43	1.50	326	2.316	0.780

An absolute error of 1% in T_M leads to a relative error of about 0.5% in n in the region of weak absorption, but increases to about 1% in the region of medium absorption.

If n_{c1} and n_{c2} are the refractive index at two adjacent maxima (or minima) at λ_1 and λ_2, it follows from equation (5) that the thickness is given by:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}. \quad (8)$$

The average value of d_1, ignoring the last values because it was affected by errors, is $d_1 = 373{,}15$ nm. The value of d_1 can now be used, with the value of n_1, to calculate the order numbers m_0 for the different extremes using equation (5). The accuracy of d can now highly increased by account the corresponding exact integer or half-integer values of m associated with each extreme point. The thickness values d_2 obtained from equation (5) are showed in Table 1. The average thickness of TiO_2 thin film was found to be 317nm, a very close value to that obtained by the profilometric method (300nm). In fact, the number of the

available fringes from Fig. 2 gives the accuracy of this method, since the final thickness is the average value over the thickness obtained at each fringe position [5].

The curve $n(\lambda)$ presented in Fig. 4 shows a Sellmeier dispersion type dependence as reported in literature [1] for the visible spectral range, where the sample is transparent.

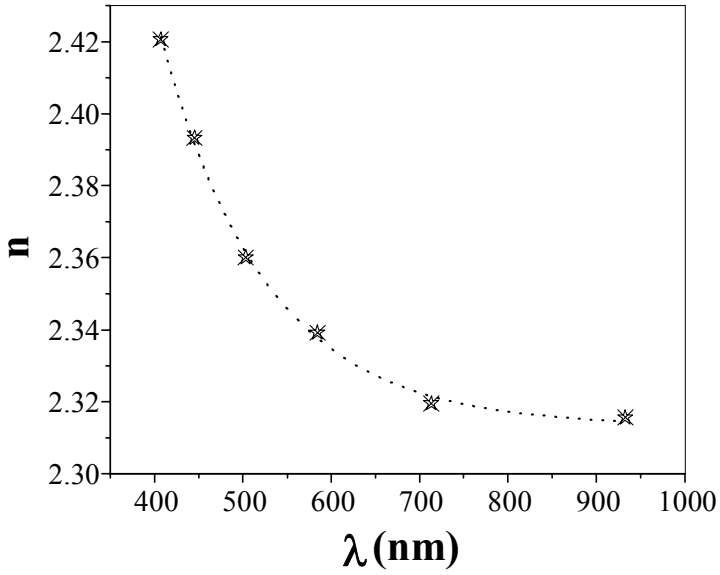

Fig. 3 The refractive index n vs. λ for the studied TiO_2 film

One can observe the high values of the refractive index of these films, which make them suitable in a great number of applications, such as antireflection coatings, interferential filters, etc.. These values agree well with those corresponding to anatase predominantly films [6].

Using an equation proposed by Connel and Lewis [7], we can calculate from transmission spectra without interference, the absorbance $A(\lambda)$:

$$A = \left\{ P + \left[P^2 + 2QT_\alpha (1 - R_2 R_3)^{1/2} \right] \right\} / Q, \tag{10}$$

where

$$P = (R_1 - 1)(R_2 - 1)(R_3 - 1) \tag{11}$$

and

$$Q = 2T_\alpha (R_1 R_2 + R_1 R_3 - 2R_1 R_2 R_3), \tag{12}$$

where R_1, R_2 and R_3 are the reflectances of the air-film, film-substrate and substrate-air interfaces: $R_1 = [(1-n)(1+n)]^2$, $R_2 = [(n-n_s)/(n+n_s)]^2$ and $R_3 = [(n_s-1)(n_s+1)]^2$, respectively.

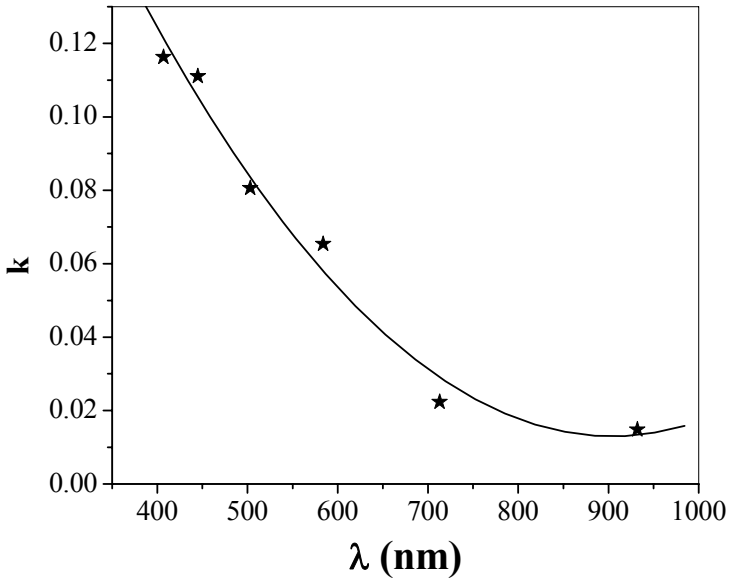

Fig. 4 The extinction coefficient k vs. λ for the studied TiO_2 film

From Ref. [4], T_α is defined, in the spectral region with interference fringes, by the geometric mean of T_M and T_m, i.e. $T_\alpha = (T_M T_m)^{1/2}$. The curves $T_M(\lambda)$, $T_m(\lambda)$ and $T_\alpha(\lambda)$ converge to a single curve in the high absorption range, where the interference fringes disappear. The absorption coefficient α is calculated from equation:

$$\alpha = -\frac{1}{d}\ln A\,. \tag{13}$$

Using the formula:

$$k = \frac{\alpha\lambda}{4\pi}, \tag{14}$$

we can obtain the values of the thin film extinction, k, as a function of λ (Fig. 5).

4. CONCLUSIONS

TiO_2 thin films were obtained by a d.c. sputtering technique onto glass substrates. The films are mainly anatase, as seen from XRD patterns. By using the envelope method proposed by Swanepoel we have calculated the optical constants as a function o wavelength and the thickness of the film. The values agree well with those reported in literature for these kind of films (2.42 at 400nm). The thickness of TiO_2 film was found to be about 317 nm a very close value to that obtained with the profilometric method (300nm).

5. REFERENCES

[1] D.Mardare and P.Hones - *Mater.Sci.Eng*., B68, 42 (1999).
[2] D.Mardare, M.Tasca, M.Delibas and G.I.Rusu - *Appl. Surf. Sci*., 156, 200 (2000).
[3] R.A.Spurr,H.Myers - *Anal. Chem*. 29, 760 (1957).
[4] R. Swanepoel, *J. Phys. E: Sci. Instr*, 16, 1214 (1983).
[5] Y.Laaziz, A.Bennouna, M.Y. Elazhari, J.Ramiro-Bargueno, A. Outzourhit, N. Chahboun, E.L.Ameziane, *Thin Solid Films*, 303, 255 (1997).
[6] Diana Mardare, *Romanian Journal of Physics*, 45(7-8), 571 (2000).
[7] G. A.N. Connell, A.J. Lewis- *Phys. Status Solidi B*, 60, 291 (1973)