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ON THE STRUCTURE AND OPTICAL DIELECTRIC CONSTANTS OF TiO_2 SPUTTERED THIN FILMS*

D. Mardare, G. I. Rusu

Faculty of Physics, "Alexandru Ioan Cuza" University, Iasi, R-6600, Romania

TiO_2 thin films were deposited by reactive rf sputtering technique onto glass substrates. Their optical properties have been investigated by spectroscopic ellipsometry in the wavelength range between 360 and 830 nm. By doping with Ce and Nb (low concentrations) TiO_2 structure modifies from mixed rutile/anatase to anatase only. The optical dielectric constant and high frequency electrical conductivity change also. The spectral dependency of the optical dielectric constant and high frequency electrical conductivity have been determined by using a polynomial Sellmeier dispersion function. The surface roughness has been measured by atomic force microscopy and has been taken into account in the ellipsometric model.

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1. Introduction

Among other methods, reactive sputtering [1-4] is one of the most used for obtaining uniform and stoichiometric TiO_2 thin films. Impurities doping induces substantial modifications in electrical and optical properties of semiconductor materials [4-9].

In this paper we present the influence of Ce and Nb doping on the structure of TiO_2 thin films and, as a consequence, on its optical dielectric constant and high frequency electrical conductivity.

2. Experimental

Pure and doped titanium dioxide films were deposited by r.f. (13.56 MHz) sputtering method from a metallic titanium target of 99.5 % purity and 60 mm diameter. High purity oxygen (99.998 %) and argon (99.9997 %) were utilised as reactive and sputtering gases respectively. The target to substrate distance was about 250 mm. To obtain doped TiO_2 thin films, oxide powders like CeO_2 and Nb_2O_5 were used, the method being described in ref. [4]. The total pressure and the partial pressure of oxygen have been set at 1×10^{-3} mbar and 0.3×10^{-3} mbar respectively.

The samples were deposited onto glass substrates. They were labeled A_{gl}, E_{gl}, C_{gl}, D_{gl}. The substrate temperature was 250 °C, except for E_{gl} which was deposited on an unheated substrate (the substrate temperature reaches about 100 °C only because of the sputtering).

X-ray diffraction (XRD) measurements have been carried out with a Rigaku Geigerflex computer-controlled diffractometer, with Cu K_α radiation. The geometry of the diffractometer was the same for all the studied samples (grazing incidence diffraction : 5 °, U = 40 kV, I = 30 mA).

The weight percentage of the anatase phase, W_A, listed in Table I, has been determined using an equation given by Spurr et al. [10] for samples which exhibit mixtures of anatase and rutile phases:

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$$W_A=1/(1+1.265I_R/I_A) \quad (1)$$

Here I_A and I_R are the intensities of A(101) anatase peak and of R(110) rutile peak respectively.

The composition of the films has been investigated by electron probe micro-analysis (EPMA) [5, 6]. We have found that samples A_{gl} and E_{gl} are pure TiO_2 thin films, B_{gl} is a TiO_2 thin film doped with 0.4 at. % Ce and C_{gl} is a TiO_2 thin film doped with 0.35 at. % Nb.

The surface morphology of the films has been investigated by atomic force microscopy (AFM) in non-contact mode (Explorer, TopoMetrix).

The wavelength dependence of the optical dielectric constant and high frequency electrical conductivity films have been examined by variable angle spectroscopic ellipsometry (VASE) (UVISEL, ISA Jobin-Yvon) using a Sellmeier dispersion function, method described in a previous paper [4]. This method provides also the thickness of the films.

The thicknesses of the thin films measured with an Alpha-Step 500 Surface Profiler were found to be the same, 300 nm, except for E_{gl} which has 100 nm. These values have been compared with those obtained by ellipsometry and found to be in good agreement.

3. Results and discussion

The samples deposited onto heated substrates have a polycrystalline structure, as revealed from XRD patterns (Fig. 1) and AFM images (Fig. 2).

Sample A_{gl} has a mixed phase with anatase predominating over the rutile phase. Adding low dopant concentrations: Ce (0.4 at. %) (B_{gl}) or Nb (0.35 at. %) (C_{gl}), pure anatase TiO_2 films have been obtained. This could be explained on the basis of results obtained in the previous paper [6], where it was found that the coordination number of the cation (titan) that is the nearest neighbor to the anion (oxygen) modifies from 5.5 for the undoped sample to 5.36 and 5.12 for Ce doped sample and Nb doped samples, respectively. Thin films deposited onto unheated substrates (E_{gl}) have an amorphous structure (Fig. 1), which could be connected with the fact that the atom condensation takes place near the point of impingement [11], because the adatom mobility on the unheated substrate is negligible.

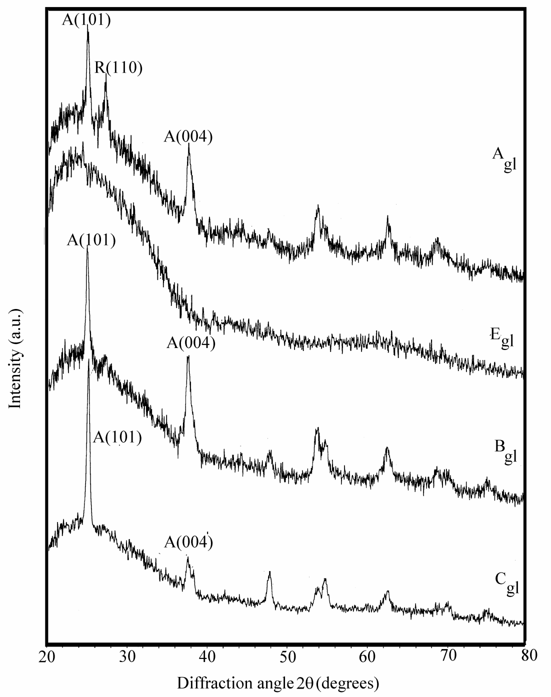
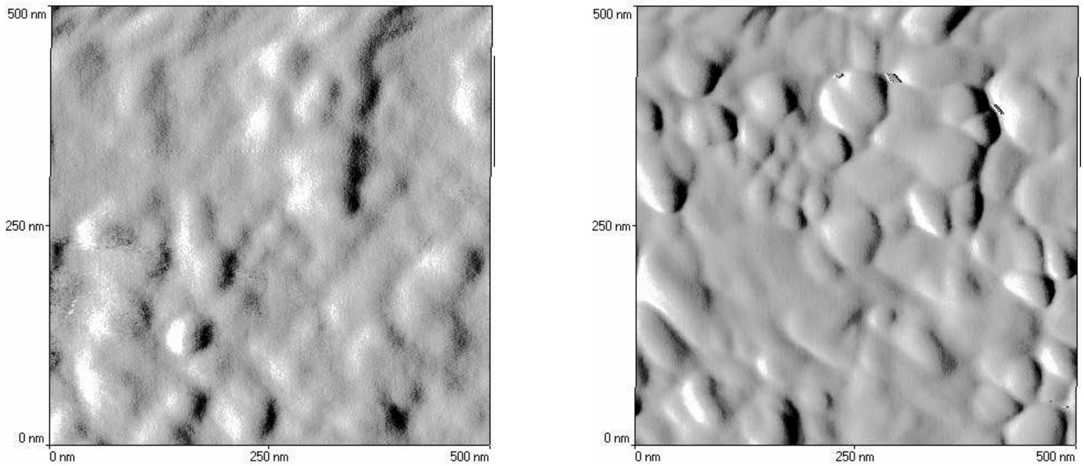


Fig. 1. XRD patterns for samples A_{gl}, E_{gl}, B_{gl} and C_{gl}.



a) b)

Fig. 2. Surface morphology by AFM for: a) amorphous TiO_2 thin film (sample E_{gl}) and b) Ce doped TiO_2 thin film (sample C_{gl}). The scanned area is 0.5×0.5 µm.

Thin film surfaces are relatively smooth as can be seen from the values of roughness ($R_{AFM} \leq 5.5$ nm) presented in Table I.

Table 1. Substrate temperature T_S during deposition, film thickness d, surface roughness determined by AFM, R_{AFM}, and by ellipsometry, R_{SE}, dopant concentration, and the weight percentage of the anatase phase, W_A, of the studied TiO_2 thin films.

Sample	T_S (°C)	d (nm)	R_{AFM} (nm)	R_{SE} (nm)	Doping (% at.)	W_A (%)
A_{gl}	250	300	5.5	9.1	-	60
E_{gl}	≤100	100	2.0	3.0	-	-
B_{gl}	250	300	5.4	5.4	0.4 at. % Ce	100
C_{gl}	250	300	-	4.0	0.35 at. % Nb	100

From the theory of the electromagnetic waves propagating in a homogeneous, isotropic, non-magnetic medium characterized by a complex dielectric constant $\bar{\varepsilon}$, one can obtain the relations between the optical constants (n, k) which also characterized the medium and the real and imaginary parts of $\bar{\varepsilon}$ (ε_1, ε_2) [12]:

$$\begin{cases} n^2 - k^2 = \varepsilon_1 \\ 2nk = \varepsilon_2 \end{cases} \tag{2}$$

where ε_1 is the optical dielectric constant of the medium, and ε_2 is given by:

$$\varepsilon_2 = \frac{\sigma}{\varepsilon_0 \omega} \tag{3}$$

Here, σ represents the high frequency electrical conductivity, ε_0 is the vacuum absolute permitivitty and ω is the frequency of the wave.

VASE technique offers both the dependences $n(\lambda)$, $k(\lambda)$ [6] and $\varepsilon_1(\lambda)$ and $\sigma(\lambda)$ (Figs. 3, 4) in the wavelength range between 360 and 830 nm.

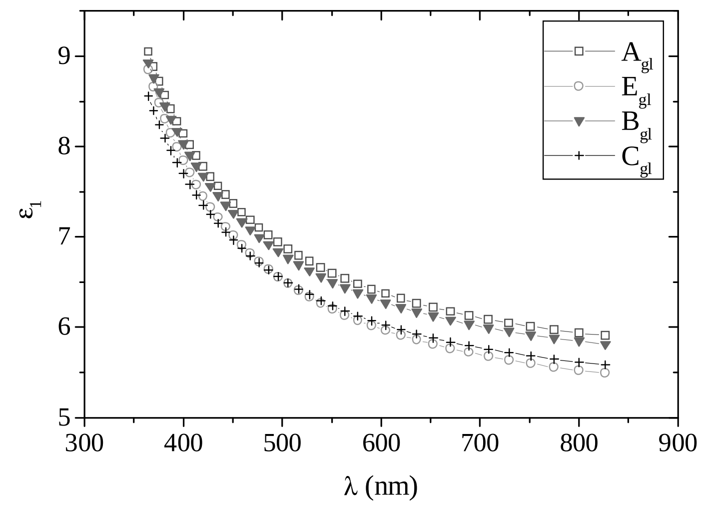


Fig. 3. Optical dielectric constant ε_1 versus the wavelength λ of the light in the transparent region of the studied samples.

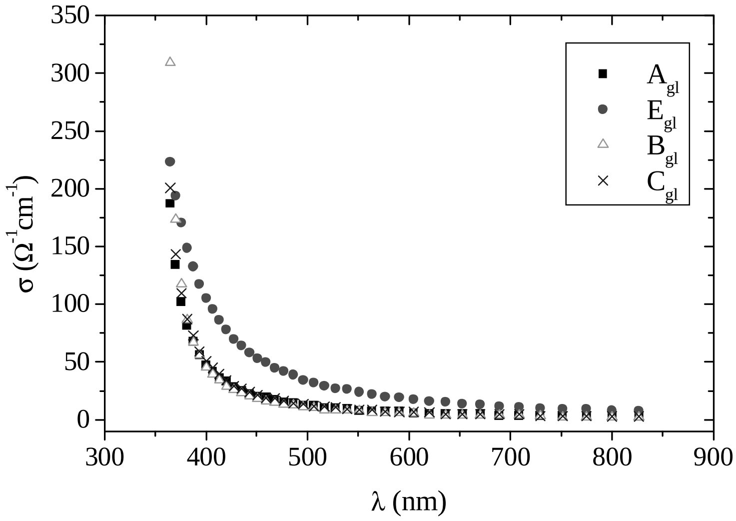


Fig. 4. High frequency electrical conductivity σ versus the wavelength λ of the light in the transparent region of the studied samples.

The undoped TiO_2 thin film (A_{gl}) is characterized by the highest value of the refractive index [6] and also of the optical dielectric constant ε_1. At the wavelength λ = 633 nm, the values of the optical dielectric constant ε_1 range from 5.87 for the amorphous sample (E_{gl}) to 6.2 for the undoped sample (A_{gl}), having intermediate values of 6.18 for cerium doped sample (B_{gl}) and 5.93 for niobium doped sample (C_{gl}). The structural differences explain the different values of the optical dielectric constant ε_1. Amorphous phase is less dense than anatase, which is less dense than rutile. This could explain the lowest values for ε_1 and for the refractive index [6] obtained for the amorphous sample, repectively the lower values obatined for Ce and Nb doped samples compared to the undoped one.

For the polycrystalline samples (A_{gl}, B_{gl} and C_{gl}), at the same wavelength, λ = 633 nm, ε_2 and σ have approximately the same values, 0.01 and 5.7 $\Omega^{-1}cm^{-1}$ respectively. Doping doesn't significantly influence the high frequency electrical conductivity. These values reache at 0.06 and

15.7 $\Omega^{-1}cm^{-1}$ for the amorphous sample, at λ = 633 nm.

Surface roughness, even in the range below 10 nm, significantly influences the ε_1 and σ values. So, the fitting results must be checked with an appropriate complimentary roughness analysis, as is AFM. In the least square refinement procedure it has been found that the simple 50% TiO_2 / 50% void EMA model satisfactorily describes the small surface roughness of the relatively smooth films of this study [6] (Fig. 5).

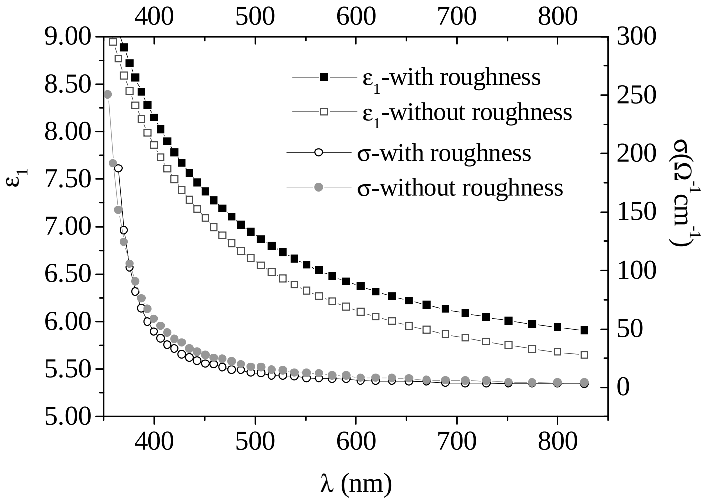


Fig. 5. Optical dielectric constant and high frequency electrical conductivity versus the wavelength λ of the light for sample A_{gl} with and without taking the surface roughness into account.

4. Conclusions

Reactive r.f. sputtering method has been used to obtain pure and doped TiO_2 thin films onto unheated and heated glass substrates. By doping TiO_2 with low concentrations of Ce and Nb, the structure changes from mixed anatase and rutile to pure anatase. The values corresponding to the surface roughness are quite small and lead to the conclusion that thin films obtained by this technique are very smooth (R_{AFM} between 2 and 5.5 nm). The undoped film, with a mixed anatase and rutile phase, is characterized by higher values of the optical dielectric constant ε_1 than the doped anatase films. This is explained by the higher density of rutile compared to anatase. Doping doesn't significantly influence the high frequency electrical conductivity, but the values corresponding to the amorphous film increase significantly.

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