Optical study of titanium dioxide thin films prepared by R.F. sputtering.

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Optical response of TiO_2 layers, prepared by R.F. sputtering from TiO_2 target, was studied as a function of target state, oxygen partial pressure and sputtering power. We have found that TiO_2 layers deposited from a used target exhibit a high absorptance which decreases greatly when an oxygen partial pressure is introduced. Whereas an increase of sputtering power leads to an absorbent TiO_2 matrix.

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I. INTRODUCTION

TiO_2 thin films are the most widely used coatings because of their desirable properties, such as good transmission in the visible and near infrared regions, good adhesion, and high stability against mechanical abrasion, chemical attack, and high temperatures [1,2]. Therefore they are used very often as single-layer or multilayer optical coatings [3]. However, the characteristics of TiO_2 films are strongly dependent on the preparation methods and the deposition parameters.

Our goal in this work is to optimize the optical properties of TiO_2 thin films prepared by R.F. sputtering in order to use them as a matrix for Ag-TiO_2 nanocermet thin films which will be published elsewhere.

Many techniques have been used to prepare TiO_2 thin films such as evaporation [4], ion beam technique [5], chemical vapour deposition [6] and reactive (D.C., magnetron) sputtering [7-8]. In our case, we have used R.F. diode sputtering as a preparation technique because it is an industrial process and leads to high adherent films even at low substrate temperature.

II. EXPERIMENTAL TECHNIQUES

Titanium dioxide TiO_2 thin layers were prepared by R.F. (13.56 MHz) sputtering under a base pressure (or argon + 1 % O_2) of 15 mTorr. TiO_2 target with a purity of 99.998 % and 13.54 cm as diameter was used. The target-substrate distance was fixed at 6 cm.

During the same pulverization different types of substrates nature were used such as silica (SiO_2), silicon (Si) and sodium chloride (NaCl). To obtain homogeneous films, periodic motion of the substrates was adopted.

Reflectance R and transmittance T measurements under near-normal incidence in the spectral range 200-2600 nm were performed by using a Varian Cary 5 spectrophotometer. Ellipsometric measurements between 350 and 900 nm were performed, under 70° incidence angle, by using a Sopra ESG 4 spectroscopic ellipsometer with rotating polarizer. The films thickness were deduced from grazing angle X-ray reflectometry and ellipsometric measurements.

Samples morphology and electronic diffraction pattern were performed using Transmission Electron Microscopy (T.E.M.). Rutherford Back Scattering (R.B.S.) was performed to determine the films composition.

III. RESULTS AND DISCUSSION

In figure 1, we have plotted transmittance T, reflectance R and absorptance A (A = 1-R-T) spectra for TiO_2 thin layers deposited on SiO_2 substrates with a thickness of 150 nm. One can note that T spectrum exhibits a high transmittance in the spectral range 500–2600 nm. The absorptance presents interference fringes due to the large value of the film thickness (three times the mean wavelength). The mean absorption appears around 350 nm (3.54 eV). The A quantity is not the intrinsic absorption of the material. It still contains multiple internal reflectance effects in the layer. The edge at 3.54 eV gives thus only an approximate value of the absorption edge in the TiO_2 semiconductor. Moreover the small oscillations observed in A, at the bottom of this edge and beyond, are only due to these internal interference effects in the thin film, conjugated with a weak residual absorption.

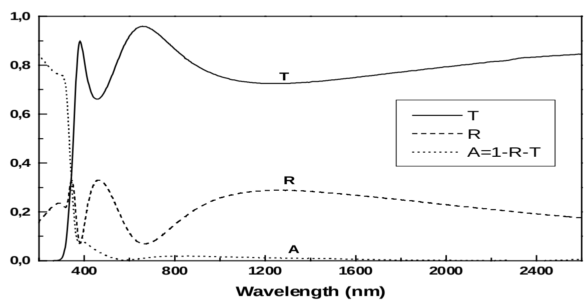

Fig. 1 : Transmittance T, reflectance R and absorptance A spectra for a TiO_2 thin film deposited on a silica substrate, with a thickness of 150 nm and 1.85 O/Ti atomic ratio.

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We want to point out an important effect, well known in the sputtering community, but seldom explicitly presented : the evolution of the stoichiometry of oxide targets along the sputtering process, i.e. after several depositions. Three precursor conditions were adopted to prepare TiO_2 thin layers :

-TiO_2 (NT) from a New Target.

-TiO_2 (UT) from a Used Target (after four depositions using the same target).

-TiO_2 (UTO) from a Used Target but under Ar + 1% Oxygen pressure.

All of the condition parameters were fixed. The sputtering power was 150 W. Figure 2 presents absorptance spectra for these three layers deposited on SiO_2 substrates.

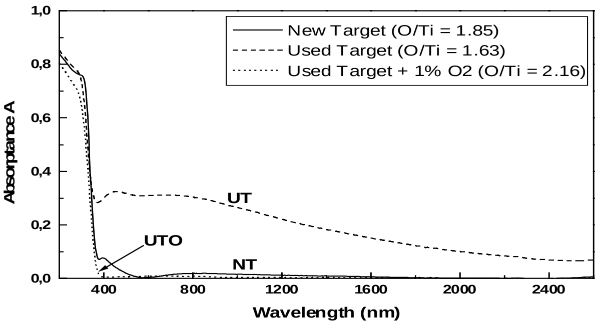


Fig. 2 : Absorptance spectra of TiO_2 films, with a thickness of 150 nm, deposited on SiO_2 substrates from a TiO_2 New Target (NT, O/Ti = 1.85), a TiO_2 Used Target (UT, O/Ti = 1.63) and a TiO_2 Used Target + 1% Oxygen (UTO, O/Ti = 2.16).

One can note that TiO_2 (UT) exhibits a very high absorptance comparative to TiO_2 (NT) and (UTO). This behavior is in agreement with O/Ti atomic ratios obtained from R.B.S. and nuclear microanalysis of the TiO_2 films deposited on Si substrates. O/Ti ratios were respectively 1.85 (NT), 1.63 (UT) and 2.16 (UTO). The last value, which is greater than 2, is due to the total measured oxygen (from TiO_2 matrix, SiO_2 native layer and humidity occupying the films pores). The R.B.S. spectrum of the NT layer is presented in figure 3.

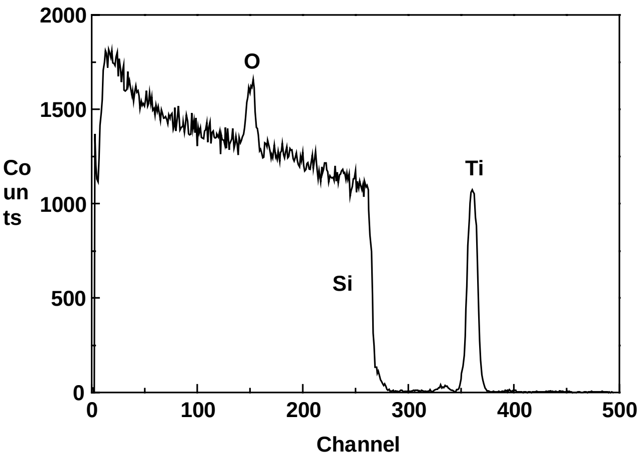


Fig. 3 : R.B.S. spectrum of a TiO_2 thin film, with a thickness of 150 nm, deposited on a Si substrate from a TiO_2 New Target.

In figure 4, we have presented refractive index n determined from ellipsometric measurements for (NT) and (UT) layers and a bulk rutile polycrystalline TiO_2 (curve R) [9],])., which shows the densification effect between the samples.

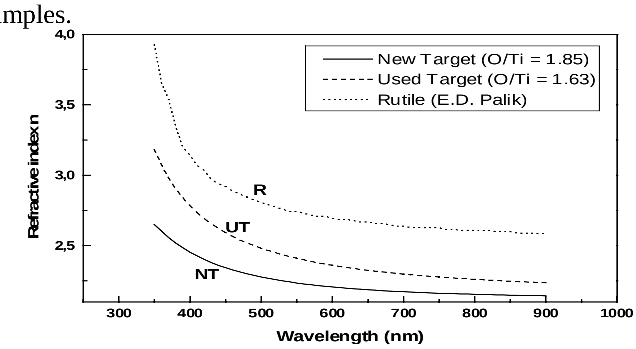


Fig. 4 : Refractive index n determined from ellipsometric measurements, of TiO_2 thin films, with 150 nm thickness, deposited from a new TiO_2 target (NT, O/Ti = 1.85) and a used TiO_2 target (UT, O/Ti = 1.63) compared to those of rutile polycrystalline TiO_2 (R) (E.D. Palik [9]).

In fact, NT and UT layers have a low refractive index compared to rutile polycrystalline TiO_2 case. This result can be explained by : (i) the columnar structure of our films clearly shows up by T.E.M. micrograph of figure 5.

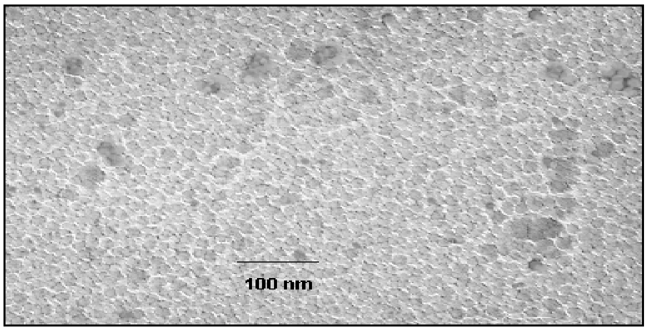


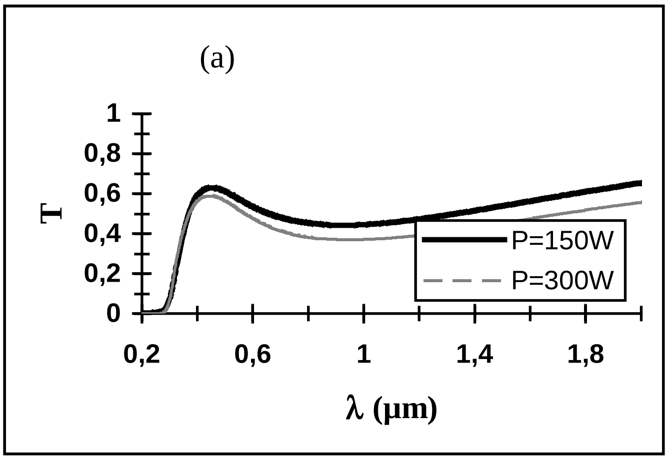
Fig. 5 : T.E.M. bright field image of a TiO_2 thin film, with a thickness of 100 nm prepared from a new TiO_2 target.

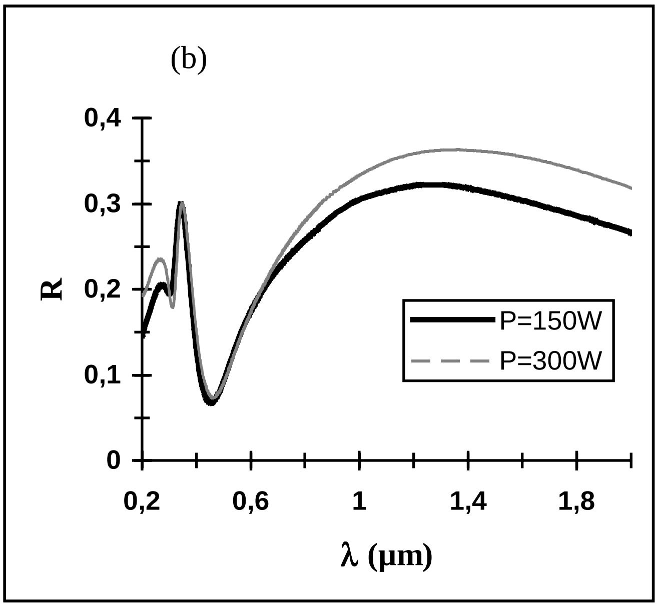
Resulted voids of this porous films lead to a decrease of refractive index; (ii) the amorphous structure of our films which clearly shows up on the electron diffraction pattern (figure 6).

Fig. 6 : Electron diffraction pattern of a TiO_2 thin film, with a thickness of 150 nm, deposited from a new TiO_2 target.

We have also observed that the reference and NT layers are not absorbent in a wide range, while UT layer presents a certain absorptance (k is around 0.05) due to its low O/Ti atomic ratio reported above.

Transmittance, reflectance and absorptance spectra for (UT) TiO_2 layers deposited on glass substrates with 100 nm as thickness under two different sputtering powers (150 W and 300 W) are reported in figure 7.





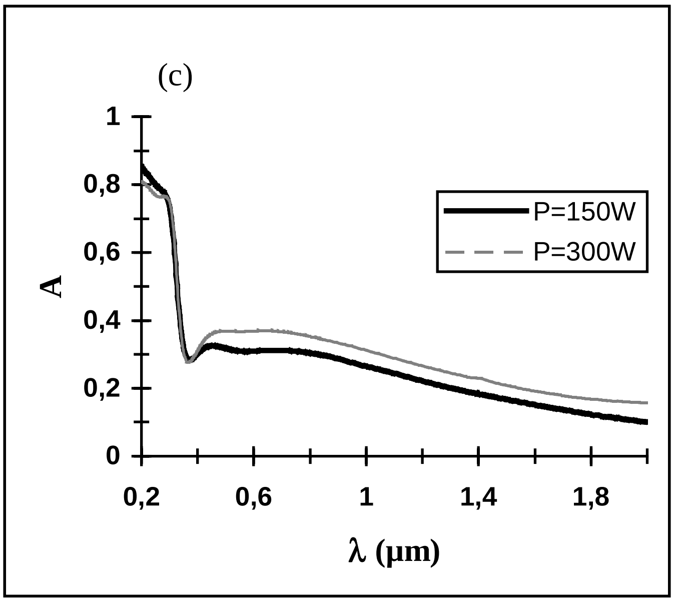


Fig. 7 : Sputtering power effect on T, R and A spectra of TiO_2 thin layers deposited on glass substrates with 100 nm as thickness

All of the layers present a very high absorptance A (A=1-R-T) which increases with sputtering power. In fact, high sputtering power increases the substrate temperature which induces a heat treatment of the layers allowing a decrease of oxygen condensation on substrate. For our following experiments, we have adopted 150 W as the pulverization power.

VI. CONCLUSION

We have found that our TiO_2 layers are amorphous and present a low refractive index comparative to that of the literature. From a used target, we have obtained TiO_2 layers with a high absorptance which decreases greatly when an oxygen partial pressure is introduced. Whereas an increase of sputtering power leads to an absorbent TiO_2 matrix.

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