Properties of TiO_2 thin films deposited by RF magnetron sputtering

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TiO_2 thin films deposited by RF magnetron sputtering have been investigated. The films were deposited on glass, ITO/glass and silicon at room temperature. The deposition was carried out in different experimental conditions, starting from a pure Ti target. We studied the influence of the experimental deposition parameters (power sputtering, Ar and O_2 flow rate) on the film properties. The deposition typical conditions were 300-500 W, 10-45 sccm Ar, 3.3-30 sccm O_2, at a pressure around 2.7×10^{-3} mbar. The film structure, morphology, deposition rate, and optical transmission were investigated. Rutile phase was obtained. The titania films deposited with a rate 4-16 nm/minute had 50-1500 nm thickness. Two kinds of TiO_2 films have been obtained depending on the experimental conditions: nanocrystalline films with roughness of 3-10 nm and another one with droplets 2-8 µm. The optical transmission in the visible range was between 70 and 95%.

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1. Introduction

Titanium dioxide films were extensively studied due to their application in fields as solar cells, sensors, photocatalists, etc. Many papers have been devotated to a better understanding of the correlation between experimental parameters and film properties and precise control of the deposition process, as well. A considerable interest has received the development of numerous synthesis techniques, such as sol gel [1-2], electron beam evaporation [3-4], bias assisted cathodic arc deposition [5], oxidation process [6-7], atomic layer deposition [8-9], DC magnetron sputtering [10-16], dip coating process [17], pulsed laser deposition (PLD) [18], physical vapor deposition (PVD) [19-20], medium frequency magnetron sputtering [21-22], plasma source ion implantation [23], RF magnetron sputtering [24-31] .

The magnetron sputtering technique seems to be the most favourable because it offers more freedom in selecting and adjusting deposition conditions. The high energy electrons in the plasma can break chemical bonds and the substrate temperature can be low [24]. The material can be supplied to the growing surface layer in the equal proportions and with sufficient energy to ensure the formation of a dense structure; furthermore, the low temperature of the substrate is another advantage of the method.

In this paper we report the deposited TiO_2 thin films by RF magnetron sputtering technique on glass, ITO/glass and silicon. The influence of the experimental deposition parameters (power sputtering, Ar and O_2 flow rate) on the film properties was investigated.

2. Experimental

The plasma was excited by a RF power supply working at a frequency of 13.56 MHz in a Dressler Ceasar 136 sputtering system with a RF matching network. The films were deposited on glass, ITO/glass and silicon substrates.

As target we used pure titanium (grade 2), 7.5 cm in diameter and 6 mm thickness.

The substrates were placed at a distance of 10 cm from the target. The sputtering chamber was pumped down to 1.7×10^{-5} mbar.

The substrates were cleaned by sonication with acetone and ethanol for 6 minutes.

Before deposition, in order to remove possible contaminations, the substrates were etched in argon at a pressure of 4×10^{-2} mbar. The silicon and glass substrates were etched for 10 minutes while ITO/glass for 2 minutes only, at 600 V bias voltage, 150 mA current, 200 W power, and 20 sccm argon flow rate.

The films have been deposited at a base pressure of about 2.7×10^{-3} mbar, in a mixed pure argon-oxygen atmosphere; the applied power was in the range 300-600 W and the sputtering time was ranging from 6 min. to 120 min.

The argon and oxygen flow rate in the reaction chamber was varied between 3.3 and 45 sccm.

The transmission measurements were performed with a spectrometer Ocean-Optics HR 4000, (spectral range 400-1100 nm, 0.2 nm resolution, and calibrated).

The X-ray diffraction measurements were carried out using an DRON 2,0 X ray diffractometer

and surface morphology with a scanning electron microscope Hitachi model S 2600 N.

For the roughness and thickness measurements was used a profilometer Tokyo Seimitsu Surfcom 130A.

3. Results and discussion

In Fig. 1 is shown SEM image of a TiO_2 film (50 nm thickness) deposited on silicon at 500 W, $Ar:O_2$=20:20 (sccm). One can notice that the film has a high quality, there are no defects on the surface, it is very smooth. The films show a good adhesion and uniformity.

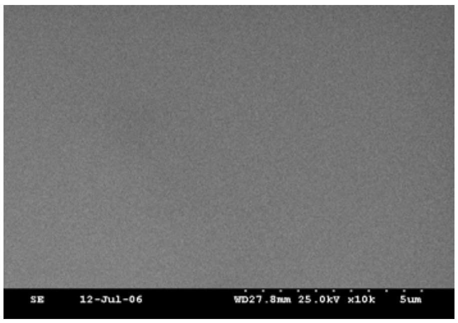

Fig. 1. SEM image of a TiO_2 film deposited on silicon at 500 W; $Ar:O_2$=20:20 (sccm); 50 nm thickness; 1.9×10^{3} mbar.

Changing the deposition conditions, (increasing the pressure and decreasing the sputtering power), from SEM images it can be noticed that the films presented some droplets on the surface (figure 2). There can be observed a number of approximately 30,000 droplets/cm^2 with a maximum size of 8 µm. In figure 2, one can also see some holes that are caused by the detachment of the droplets from the substrate. Because of the formation of some cracks around the droplets, these are dislocated and in their place appear the holes.

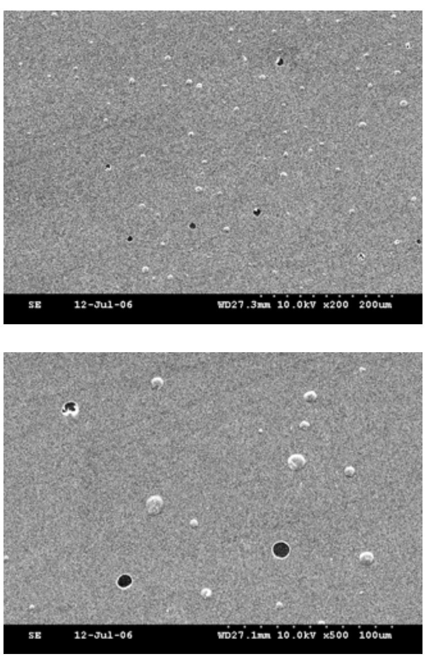

Fig. 2. SEM images of a TiO_2 film deposited on silicon at 300 W; $Ar:O_2$=10:3.3 (sccm); 500 nm thickness; 3.2×10^{-2} mbar.

In Table 1, are presented the roughness data of the films deposited at the same duration of time and pressure, different argon and oxygen flow rates (arithmetic roughness evaluated on 2 cm long path), on the silicon. It can be seen that the roughness of the films is significantly influenced by the argon and oxygen flow rate. The best value of the roughness was 3 nm for the films deposited at 500 W, $Ar:O_2$=10:3.3 (sccm) and 2.7×10^{-3} mbar.

Table 1. The values of roughness of TiO_2 films deposited at 500 W; 12 min; 2.7×10^{-3} mbar

Pressure [mbar]	Argon [sccm]	Oxygen [sccm]	Deposition time [min.]	Roughness [nm]
2.7×10^{-3}	10	3.3	12	3
2.7×10^{-3}	15	5	12	4
2.7×10^{-3}	30	10	12	10

From XRD measurements resulted that TiO_2 film structure corresponds to the rutile phase. Figure 3 ilustrates a XRD diagrame of a film prepared at 300 W ; $Ar:O_2$=30:10 (sccm); 250 nm thickness; 6.5×10^{-2} mbar. It exhibits (111), (211), (221) peaks which are typically for rutile phase. Using Debye Scherrer formula, we determined the size of nanocrystalline grain of 5 nm. A closed value reported Andres et al in [26], as well.

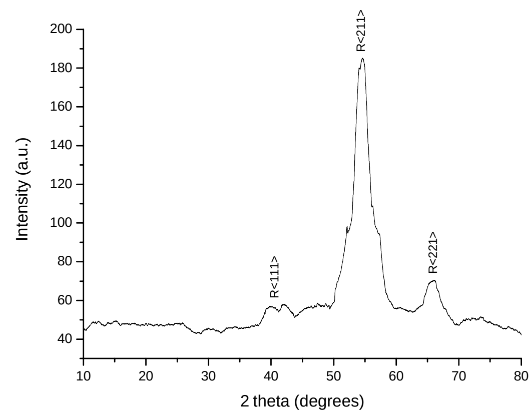

Fig. 3. XRD spectrum of TiO_2 thin films deposited on glass (300 W ; $Ar:O_2$=30:10 (sccm); 250 nm thickness; 6.5×10^{-2} mbar).

We have deposited films with thickness in the range 50-1500 nm at 500 W, 2 V bias voltage and at the pressures from 0.8 to $3.3x10^{-3}$ mbar . The deposition rate was from 4 to 16 nm/min.

From the Fig. 4, it can be observed that the deposition rate strongly depends on the argon-oxygen flow rate and the pressure in the sputtering chamber; it increases when the ratio multiplied by the pressure also increases.

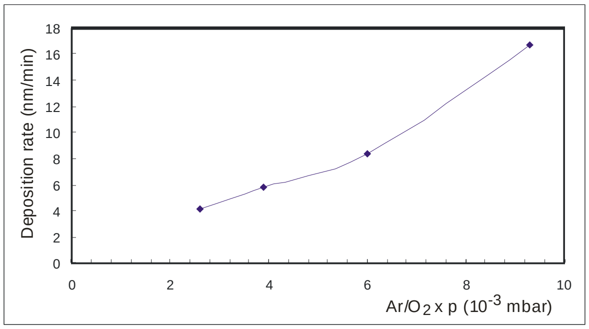

Fig. 4 Dependence of deposition rate as a function of argon and oxygen flow rate at 500 W; 2 V;0.8-3.3×10^{-3} mbar.

In Fig. 5, we present the optical transmission spectra of TiO_2 films with different thickness values, deposited on glass at 500 W, Ar:O_2=40:10 (sccm), 2.7×10^{-3} mbar. In some cases, the transmission curves have an wavy aspect which is related to the values of refractive index of the glass and TiO_2 film, and the film thickness. At 620 nm wavelength, the transmission of the film with 500 nm thickness is over 95% while at the same wavelength and at 50 nm thickness, the transmission is decreasing at 80% .

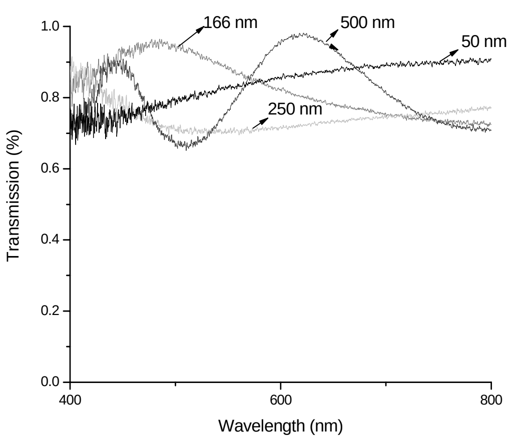

Fig. 5. Transmission of TiO_2 on glass substrate as a function of thickness (500 W; Ar: O_2 = 40:10 (sccm); 2.7×10^{-3} mbar.

In figure 6 are shown the transmission spectra as a function of flow rates. It can be seen that the transmission of the TiO_2 film is 80 % at 650 nm for the flow rate of Ar=10 sccm and O_2=3.3 sccm, while at the same wavelength and if the flow rate of gases increases, Ar =30 sccm and respectively O_2=10 sccm, the transmission is higher by few percents.

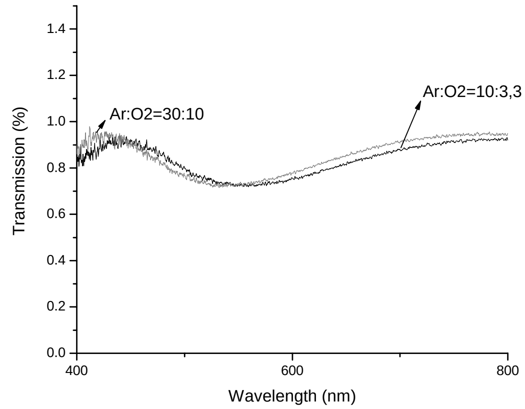

Fig. 6. Transmission of TiO_2/ITO as a function of flow rate at the same Ar/O_2 proportion (500 W; thickness 100 nm).

4. Conclusions

We have successfully deposited rutile TiO_2 thin films using RF magnetron sputtering method on the glass, ITO/glass and silicon.

We have obtained films with thickness in the range 50-1500 nm. The deposition rate was from 4 nm/min to 16 nm/min. The transmission of the films in the visible domain was between 70—95% being strongly influenced by variation of the deposition parameters.

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