The Influence of Reactive Gaseous Flow Rate and Composition on the Optical Properties of TiO₂ Thin Films Deposited by Dc Magnetron

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In the paper there are shown the changes in optical properties of TiO₂ thin films prepared by dc magnetron sputtering at different gas flow rates. We found that there is a drastic change in optical properties such as optical transmission, refractive index, extinction coefficient and optical band gap with the gaseous flow rate and composition. We observed an improvement in optical properties of the films that had been deposited at higher gaseous flow rate and at a certain gaseous composition.

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1. Introduction

Titanium dioxide has very promising properties for many applications. The high value of the optical transmission and refractive index combined with high chemical stability are very suitable properties for optical coatings [1–4]. TiO₂ films are used to build interference filters, antireflections coatings. New domains of applications were recently found for TiO₂ based gas sensors [5]. Lately, a high demand of high permittivity thin films appeared, primary for the replacement of silicon oxide in high density dynamic memories applications. New applications were found in heterogeneous photocatalytic purification of water and air [6]. TiO₂ thin films with rutile or anatase structure investigated with modern optical techniques have revealed one [7] of the highest values for non-linear refractive index, $n_2 = 132 \times 10^{-14}$ ($n(E) \approx n_0 + n_1 E + n_2 E^2 + \dots$). Among other oxides this value is the third value which comes after PbO (185×10^{-14}) and Sb₂O₃ (134.4×10^{-14}), and it is at least one order of magnitude greater than all other oxides non-linear refractive index [8]. This high value for non-linear refractive index leads to new possible applications for TiO₂ thin films in non-linear optics devices. Titanium oxide films are extensively used in optical thin film device applications owing to their desirable optical properties and good stability in adverse environments [9]. Many deposition methods can be used to prepare titanium oxide films [10, 11]. Among these methods, reac-

tive magnetron sputtering has a very important position because the stoichiometry of the film can be controlled and a metal target can be used. In this paper, we have studied the effect of the gaseous flow rate on the optical properties of TiO₂ thin films in order to establish the concrete influence of the reactive gaseous flow rate to the films optical properties.

2. Experimental details

TiO₂ thin films were deposited on glass and KBr by reactive sputtering using a dc magnetron sputtering system. The films were deposited in a home built magnetron sputtering system [12]. The vacuum chamber is 80 litres volume stainless steel chamber, a circular magnetron with a 60 mm diameter erosion zone was used as the cathode. The discharge characteristics have been controlled using a variable dc power supply (3 kV and 500 mA). Pure titanium (99.5) of 130 mm diameter and 3 mm thickness has been used as a sputtering target. Pure argon (4N) and oxygen were used as the sputtering and reactive gases, respectively. The gases were mixed prior the admission to the sputtering chamber at different proportions Ar/O₂: 90%/10%/; 75%/25%/, and 50%/50%. Gaseous flow rate was varied by a correlate vacuum pumping power with the gaseous inlet system in order to control the sputtering pressure. Sputtering current and cathode potential were kept at 300 mA and 550 V, respectively. Total pressure was maintained at 0.3 Pa, the substrate temperature was 300°C. Titanium oxides films were deposited on well cleaned microscope

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glass slides ($75 \times 25 \times 1 \text{ mm}^3$) and KBr crystals. The deposition time was 1 hour and the sputtering power was of about 155 W ($300 \text{ mA} \times 550 \text{ V}$). The thickness of the films has been calculated by using a multiple beam interferometer method to an accuracy of $\pm 10 \text{ nm}$. The structure of the films was examined by using X-ray diffraction with $\text{Cu } K_\alpha$ radiation in a standard X-ray diffractometer.

Visible transmission spectra were recorded with a Specord UV-VIS, Carl Zeiss Jena over the wavelength ranges 350–800 nm.

The refractive index n and extinction coefficient k were calculated by Swanpoel's method [13].

3. Results and discussion

TiO_2 thin films deposited in the dc magnetron sputtering without the support heating were amorphous and X-ray diffraction analysis proved that the crystalline diffraction peaks corresponding to the anatase crystalline phase of titanium dioxide appear only for films that are annealed in air at a temperature greater than 350°C . The anatase crystalline phases appear for films prepared with the support temperature higher than 300°C . In Fig. 1 there are revealed the X-ray diffraction data for TiO_2 films as deposited without the support heating and with the support heated at 300°C .

Fig. 1. The X-ray diffraction spectra for TiO_2 as deposited and annealed at 500°C .

The thickness of the films was measured by an interferometer method and revealed that there is a strong dependence in the deposition rate with the gaseous composition. In Table there are shown the data for deposition rate variation with gaseous composition. From the data we noticed that the gaseous composition which is corresponding to a mixture of Ar 75% and O_2 25% presents the higher value for the TiO_2 deposition rate. We have chosen this composition to make the gaseous flow rate analysis. In Fig. 2 there are shown the transmission spectra for two TiO_2 films deposited at various gas flow rates. One was grown at high gaseous flow rate, of about 50 sccm and the other was prepared at a low gaseous flow rate, about 2 sccm. The thicknesses of the films de-

TABLE
The TiO_2 deposition rates for different gaseous compositions.

Gaseous composition [Ar%/O ₂ %]	Deposition rate [Å/min]	Sputtering pressure [Pa]	Support temperature [°C]
50/50	50.2	0.3	300
75/25	93.6		
90/10	71.0		

posited at different gaseous flow rates were about $0.6 \mu\text{m}$, and were not influenced by the flow rate.

Fig. 2. Transmission spectra for TiO_2 thin film deposited at different flow rates.

In Fig. 2 it is revealed that there is a drastic change in the optical transmission of TiO_2 thin films with the gaseous flow rate. This change may be correlated with the insufficient oxidation of titanium at the substrate surface. Due to the fact that the sputtering current was kept constant, we assume that the sputtering target was bombarded with the same intensity. Therefore the insufficient oxidation of the titanium clusters sputtered from the target is connected with the low value in gaseous flow rate.

In Fig. 3 there is shown the dispersion of TiO_2 refractive index and in Fig. 4 there is revealed the wavelength variation of the absorption coefficient for TiO_2 films deposited at various flow rates. From Fig. 3 it is shown that the refractive index is strongly dependent with the gaseous flow rate. At a lower gaseous flow rate there is a smaller value for refractive index while at higher gaseous flow rate the refractive index increases more than 30% in absolute value at the same wavelength. If we look at Fig. 4 we also observe that the dielectric loss is smaller when the films are prepared at higher gaseous flow rate. We also have calculated the optical band gap for films deposited on KBr crystals and we have found that the film prepared at lower gaseous flow rate have a smaller value for the optical gap, around 3.12 eV, while the TiO_2 films prepared at higher gaseous flow rate have an optical

Fig. 3. Refractive index for films deposited at various flow rates.

Fig. 4. Extinction coefficient for films deposited at various flow rates.

gap value around 3.29 eV. We think that this behavior is due to the insufficient oxidation of the titanium films during the sputtering process.

4. Conclusions

From the above figures we may conclude that there are important changes in optical parameters i.e. refractive index and extinction coefficient with the gaseous flow rate. Refractive index of a value of about 2.8 at 400 nm

is typical value of TiO_2 . The refractive index increases for TiO_2 thin films deposited at high value of gaseous flow rate. As for the extinction coefficient we find that it increases for the films deposited at low gaseous flow rate. We also found a shift in the optical band gap towards the visible spectrum, which may be useful in devices that are working with visible light.

Finally, we conclude that controlling the gaseous flow rate is an important technique to manipulate TiO_2 structures. We expect that for films with nanometric dimensions where the surface/volume ratio is larger, the gaseous flow rate is a strong technique in developing new types of material properties.

Acknowledgments

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