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| OS | STAMATE, Marius, VASCAN, Ioan, LĂZAR,Iuliana, LAZĂR, Gabriel, CARAMAN, Iuliana and CARAMAN, Mihail. Optical and surface properties TiO2 thin films deposited by DC magnetron sputtering method. *Journal of Optoelectronics and Advanced Materials*. 7(2). April 2005. 771 – 774. Disponibil la / Available at: http :// joam . infim . ro / JOAM / pdf7 _ 2 / Stamate . pdf. |
| OA | STAMATE, M. and VASCAN, I. Variable optical band gap for TiO2 thin films deposited in a D.C. magnetron sputtering system. *Analele ştiinţifice ale Universităţii „Al.I.Cuza" Iaşi, Fizica Stării Condensate*. Tome XLV-XLVI. 1999-2000. 173-175. Disponibil la / Available at: http: // stoner . phys . uaic . ro / old / ANALE / Anale _ 1999 _ 2000 / An _ Univ _ Iasi _ 1999 _ 2000 _ 27 . pdf. |

| Incidența minimă a suspiciunii / Minimum incidence of suspicion | |
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| p.772:Table 1 | p.174: Table 1 |
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# OPTICAL AND SURFACE PROPERTIES $TiO_2$ THIN FILMS DEPOSITED BY DC MAGNETRON SPUTTERING METHOD

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$TiO_2$ thin films were deposited through a d. c. magnetron sputtering method. An analysis of the optical properties of $TiO_2$ thin films deposited on glass is presented. A strong dependence between the values of $TiO_2$ optical band gap and argon/oxygen ratios has been revealed. Changes in optical, properties of $TiO_2$ thin films, with thermal annealing parameters and gas flowing rate were observed. The optical band gap varies from 3 eV > 3.4 eV as a function of oxygen/argon ratios in the flowing gas between 10% to 50%. The surface conductivity was found to depend on the pressure, in the deposition space.

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*Keywords*: $TiO_2$, DC magnetron sputtering method, Optical gap

## 1.Introduction

Titanium dioxide ($TiO_2$) films are extensively used in optical thin film devices, because of their good transmittance in the visible region, high refractive index and chemical stability [1]. Many deposition methods can be used to prepare titanium oxides films: thermal [2] or anodic [3] oxidation of titanium, electron beam evaporation [4], chemical vapor deposition [5], plasma-enhanced chemical vapor deposition [6], sol-gel method [7] and reactive sputtering. Among these methods, reactive magnetron sputtering has a very important position because the stoichiometry of the film can be controlled and a metal target can be used. This paper is focused on the analysis of optical and surface conductivity of $TiO_2$ thin films deposited by a d.c reactive sputtering method.

## 2. Experimental details

The films were deposited in a home built magnetron sputtering system [8]. The vacuum chamber is a stainless steel one with the volume of 80 liters. A circular magnetron with 60 mm diameter erosion zone was used as 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 in the sputtering chamber at oxygen/argon ratios between 10% and 50%. The target substrate distance was 35 mm. The sputtering pressure was kept at $5 \times 10^{-2}$ Torr. Prior the deposition the target was well cleaned in order to remove the surface oxides layers. The substrate temperature was controlled by using a quartz halogen lamp whose power was controlled by varying the input voltage. Titanium oxides films were deposited on well cleaned microscope glass slides ($75 \times 25 \times 1$ $mm^3$) and on KBr crystals substrates. The thickness of the films has been calculated by using a multiple beam interferometer method to an accuracy of ± 10nm.

Visible transmission spectra were recorded with an Specord UV-VIS, Karl Zeiss Jena in the wavelength range: 350-800nm.The refractive index n and extinction coefficient k were calculated by Swanepoel's method [9]. The structure of the films was examined by using X-ray diffraction with Cu $K_{\alpha}$ radiation in a standard X-ray diffractometer (DRON). The conductivity of the films was recorded by a four probe methods that is sensitive for resistivity up to $10^{11}$ Ω.cm

## 3. Results and discussion

X-ray diffraction's analysis revealed that all the $TiO_2$ films deposited under 150 °C were amorphous. The conductivity of the films at room temperature (300 K), was found to be of the order of $10^{-8}$ $\Omega^{-1}cm^{-1}$, that corresponds to the composition of the film close to the stoichiometric one.

Table.1 Sputtering conditions for $TiO_2$ thin films.

| Sample | Sputtering pressure [Torr] | Gas flow $Ar/O_2$ [sccm] | Deposition rate [nm/min] | Support temperature [°C] | Ratio $Ar/O_2$ |
|---|---|---|---|---|---|
| $TiO_2$-D1 | $2.10^{-3}$ | 19.20 | 6.67 | 150 | 50/50 |
| $TiO_2$-D5 | $1.10^{-3}$ | 50.60 | 5.45 | 300 | 75/25 |
| $TiO_2$-F1 | $2.10^{-3}$ | 46.11 | 5.71 | 300 | 90/10 |

There were recorded the transmission spectra for the $TiO_2$ films and the glass substrate. Fig. 1 shows the absorption spectra for three films whose deposition parameters are presented in table 1.

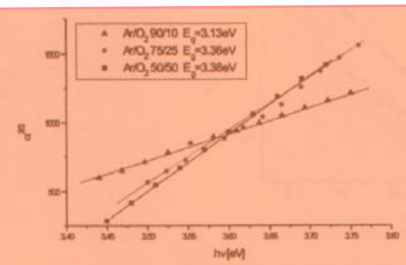


Fig .1. The absorption $\alpha^{2/3}$ versus hν for $TiO_2$ thin films.

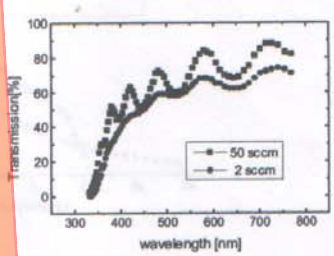


Fig. 2. Transmission spectra for $TiO_2$ films deposited at various flow rates.

For low $Ar/O_2$ ratio the band gap is 3.13 eV, while for higher values of the $Ar/O_2$ the $TiO_2$ band gap increases up to 3.38 eV.

In Fig. 2 there are shown the transmissions spectra for two films deposited at various flow rates. The first film was grown at high gas flowing rate, about 50 sccm (standard cubic centimeter per minute) and the second one was prepared at a low gas flowing rate, ~ 2 sccm. The gaseous mixture, consisting of 75% argon and 25% oxygen, was admitted in the vacuum chamber at various flow rates by varying the absorption power of the diffusion pump. The thicknesses of the films deposited at different gaseous flow rates was about 0.6 μm. The interference fringes in the transmission spectrum of the films grown at a flowing rate of 50 sccm prove a very different thickness as compared to that of the second film.

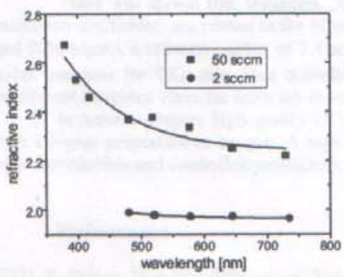


Fig. 3. Refractive index coefficient for $TiO_2$ films deposited at various flow rates.

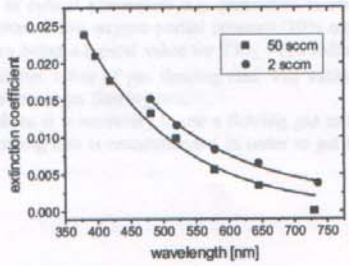


Fig. 4. Extinction coefficient for films deposited at various flow rates.

In Fig. 3 and Fig. 4 are shown the refractive index and extinction coefficient for $TiO_2$ films deposited at various flow rates.

From Figs. 2 - 4 one observes that there is a drastical modification in optical parameters of $TiO_2$ thin films when low gas flowing rate is changed with a high flowing rate. This change could be related to the poor oxidation of titanium at the substrate surface, for high gas fllowing rate.

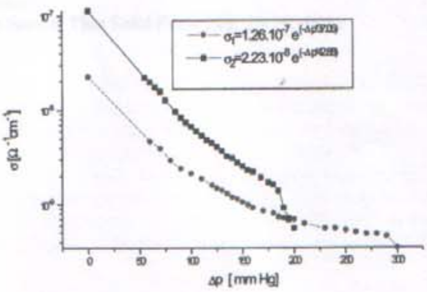


Fig. 5. Electrical conductivity versus pressure of $TiO_2$ thin films.

Fig. 5 shows a surface desorption behavior of $TiO_2$ thin films as a function of the pressure in the deposition space. One observes a strong modification in electrical conductivity with the pressure. This behavior was observed only for air and was not observed for inert gases ($N_2$, $O_2$, $CH_4$).

An activation pressure of about 35-40 mm Hg, for this effect was found.

## 4. Conclusion

The properties of $TiO_2$ thin films deposited by DC magnetron procedure are reported. There was shown that it is possible to grow films with different band gap width. The method is suitable for the preparation of separate films with different band gap width or for $TiO_2$ sandwich based structures with different band gap width films for optical or electrical purposes.

There was shown that important changes in optical parameters e.g. (refractive index and extinction coefficient) are related to the films deposited at low oxygen partial pressure (10% oxygen and 90% argon), a refractive index of 2.8 at 400 nm being a typical value for $TiO_2$. The refractive index increases for $TiO_2$ thin films deposited at higher value of gas flowing rate. The extinction coefficient increases when the films are deposited at lower gas flowing rate.

In order to prepare high quality $TiO_2$ thin films it is necessary to use a flowing gas mixture with a higher proportion in oxygen. A high gas flowing rate is recommended in order to get films with reproducible and controlled parameters.

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