High quality TiO_2 deposited by reactive sputtering. Structural and electrical peculiarities influenced by the specific experimental conditions

J. Libardi[1], K.G. Grigorov[1,2], M. Guerino[1], A. S. da Silva Sobrinho[1], H. S. Maciel[1,3], J. P. Soares[4], M. Massi[1,5]

[1]Technological Institute of Aeronautics (ITA), Physics Department, São José dos Campos-SP, Brazil

[2]Space Research and Technology Institute, Acad. G.Bonchev Str. Bl.1, 1113, Sofia, Bulgaria.

[3]IP&D, University of Vale do Paraiba – S. J. dos Campos, SP, Brazil.

[4]National Institute of Spatial Research - São José dos Campos – SP, Brazil

[5]Federal University of São Paulo - ICT, São José dos Campos - SP, Brazil

***Abstract*— Titanium dioxide (TiO_2) thin films were deposited on silicon p type (100) substrates by reactive magnetron sputtering technique at different oxygen partial pressures. The film structure was studied by X-Ray Diffraction (XRD), while the film composition was examined by Rutherford Backscattering Spectroscopy (RBS). Finally, Metal-Oxide Semiconductor (MOS) capacitors were manufactured and some important physical constants were analyzed as function of the oxygen content in the films. It was found that the films deposited at lower oxygen partial pressure exhibited better crystalline structure and higher dielectric constant.**

Keywords—TiO_2; dielectric constant, oxygen partial pressure.

I. Introduction

The reactive magnetron sputtering deposition technique is widely used to grow titanium dioxide (TiO_2) thin films with dense and well controlled stoichiometry [1-3]. The three major polymorphs of TiO_2 films are: anatase and rutile, which have tetragonal structure and also brookite with rhombohedrical structure. Each crystal configuration exhibits unique properties i.e., anatase is the most photoactive, on the other hand its dielectric constant is about 12-40, while rutile dielectric constant values are around 80. Anatase is thermally instable and it transforms into rutile stable phase above 600°C [4,5].

The deposition of TiO_2 thin films with different crystal configuration can be achieved by controlling the parameters applied during the discharge, such as: power supply, oxygen partial pressure, working pressure, substrate temperature etc. The sputtering technique allows the adjustments of deposition parameters and consequently the obtention of desirable electrical, optical and physical properties [6].

The present work investigates the effect of oxygen partial pressure in the dielectric properties and crystalline structure of the TiO_2 films. It's already known from literature that oxygen has main role in the properties of TiO_2 thin films. Some characteristics as deposition rate and surface morphology are markedly changed as well the optical and electrical properties [5,7]. In order to determine the dielectric constant MOS capacitors were build and capacitance versus voltage (C-V) measurements were performed. The Rutherford Back Scattering (RBS) and X-Ray Diffraction (XRD) techniques were employed to investigate the stoichiometry and crystalline structure of titanium dioxide. Furthermore, the surface morphology was studied by AFM technique.

II. Experimental

Titanium dioxide thin films were deposited on Si (100) p-type substrates with resistivity about 1-10 Ω by reactive d.c. magnetron sputtering system. The deposition chamber was equipped with mechanical and turbo vacuum pumps which provided background pressure of 6.67 x 10^{-4} Pa. Titanium metallic plate (99.6 %) with diameter of 2.4 cm located at 25 mm from the substrate holder was used as cathode target. The silicon substrates were previously cleaned with a solution of H_2SO_4 - H_2O_2 (4:1) and then with H_2O - HF (20:1). In order to remove the target oxide layer, 10 min of a pre-sputtering in argon atmosphere was done.

Ultra-high purity argon (Ar) and oxygen (O_2) were used as sputtering and reactive gases. During the deposition the oxygen partial pressure (pO_2) was varied as follow: 0.07; 0.2; 0.27 and 0.4 Pa, which corresponds to 10%, 30%, 40% and 60% of gas content in the discharge. The working pressure pAr + pO_2 were kept at 0.67 Pa by total gas flux of 20 sccm. All films were deposited at 150 W dc power supply during 30 minutes.

The MOS structures Al/TiO_2/Si/Al were fabricated using photolithographic process with well defined top electrode area of 200μm x 200μm. Thus, current-voltage (C-V) relations were performed in high frequency (1MHz) using a Keithley model 82 CV system. The dielectric constants were calculated from the C-V curves.

The film thicknesses were determined in an edge of the film obtained by a mechanical mask using a Tencor Instruments Alpha-Step 500 perfilometer. The TiO_2 crystallography was investigated by Grazing Incident X-Ray

978-1-4799-0518-8/13/$31.00

Diffraction (Philips X'Pert) technique and the surface morphology of the films was revealed by Atomic Force Microscope (AFM) operating in tapping mode.

The film compositions were investigated by Rutherford Back-Scattering (RBS) technique, using the RUMP simulation code.

III. Results and discussion

Fig. 1 shows the TiO_2 deposition rate as function of oxygen partial pressure in the discharge for working pressure of 0.67 Pa. The significant decrease of the deposition rate observed at 0.2 Pa is attributed to the target poisoning by oxygen leading to an important reduction of the sputtering yield [5, 6].

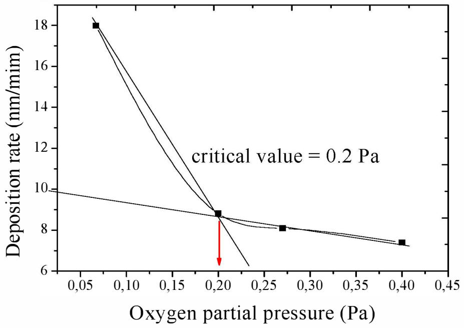


Fig. 1. TiO_2 films deposition rate in function of different oxygen partial pressure.

Interpolating the two deposition rates trends by a straight line, one can obtain the critical oxygen pressure value which leads to the poisoning of the titanium target that is 0.2 Pa in this case. In the literature close values for oxygen partial pressure were reported [8, 9], however, these values depend upon the applied power to the magnetron and the total gas pressure.

Fig. 2 shows the typical RBS spectrum of the TiO_2 film deposited with 60% of oxygen content in the discharge.

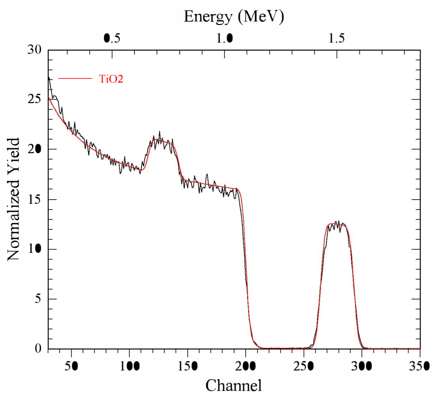


Fig. 2. RBS spectrum of 300 nm TiO_2 /Si together with the simulated curve for film deposited at 60% discharge oxygen content.

The others spectra are not show since all the films obtained with different oxygen partial pressures are stoichiometric and have the same characteristic spectra.

Fig. 3 shows the XRD patterns of the TiO_2 films grown on Si (100) substrates at room temperature. The patterns indicated by a, b, c and d correspond, respectively, to 10%, 30%, 40% and 60% of oxygen content in the discharge.

All diffraction peaks show the anatase (A) phase as predominant (101) orientation at 2θ =25.45°. However, for high oxygen content (60%) in the plasma, there is an important decrease in the intensities of the titanium dioxide peaks indicating a degradation of crystalline structure.

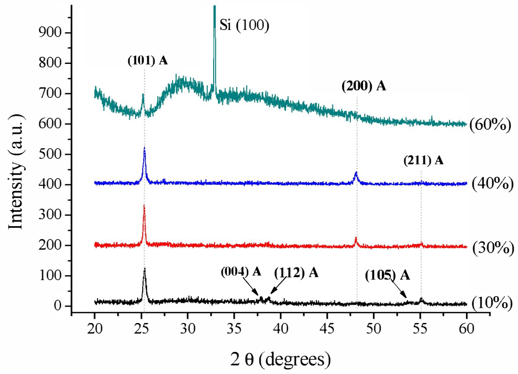


Fig. 3. XRD patterns of TiO2 thin films deposited by different oxygen partial pressure

The former can be caused by increasing of oxygen flow into the discharge. As the oxygen partial pressure increases the cathode target is poisoned (see Fig 1) and the current toward target decreases. In order to maintain power supply constant, the tension in the discharge increases from 420 volts at 10% oxygen up to 435 volts at 60% of oxygen content in the discharge. This results in higher bombardment rate and energy of the ionized species accelerated towards the substrate. As a consequence the deposited film undergoes damages such as; points defects, interstitials and lattice displacements.

Pattern (d) show the Si (100) peak as consequence of the low film thickness.

Fig. 4 show the curves of capacitance as function of the voltage (C-V) of MOS capacitors fabricated using TiO_2 as dielectric layer. The curves show the typical three regions accumulation, depletion and inversion of p-type capacitors. The dielectric constant (k) values were determined from the maximum capacitance C_{max} ($C_{max}.d/E_o.A$), where A is the aluminum plate area, d is oxide thickness, E_o is the vacuum permittivity. The capacitances were normalized due to the different films thickness [6].

As stated before, the film crystalinity is degraded as oxygen content increases in the discharge as consequence higher substrate bombardment which causes structure damage of the films.

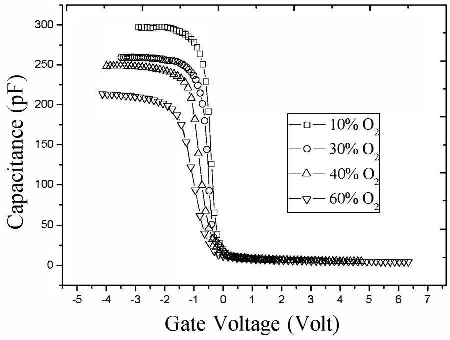


Fig. 4. Capacitance versus gate voltage of MOS capacitors fabricated with TiO_2 thin films as insulating layer deposited at different oxygen content.

In Figure 5 the decrease of the dielectric constant is attributed to the gradual deterioration of the crystallinity of the growing film when increasing the oxygen content in the discharge. The consequent degrees of crystal cell imperfection lead to lower ability of the unity-cell to maintain charge locked. As a consequence under lower values of the external electric field the unity-cell is broken resulting in leakage current between electrodes. This decrease is surprisingly high – more than 3 times. This peculiarity was not previously discussed in the related literature and should be considered as an important when such kinds of dielectrics are deposited.

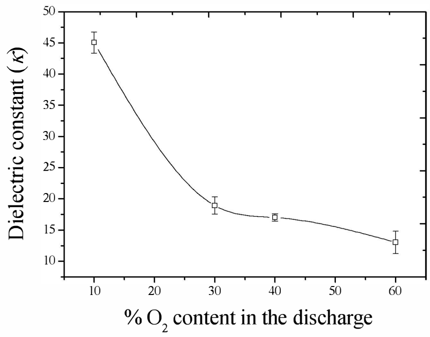


Fig. 5. Dielectric constant (k) of TiO_2 thin films deposited with different oxygen partial pressures.

It is possible to verify a shift in the flat band voltage (V_{FB}) to negative gate voltage, for all C-V curves, as the oxygen content increases. This trend can be caused, and/or presence of defects in the films and high values of the effective charge density. Table 1 shows dielectric constant, effective charge density and flat-band voltage for the discussed MOS capacitors. More details about the methodology to obtain these values are described at [13]. The high effective charge density can be correlated with the presence of oxygen vacancies, moreover, as the values are negative and higher than $1{,}0x10^{11}$ charge/cm^2 indicates that oxide charges are connected with trapped electrons [5, 6].

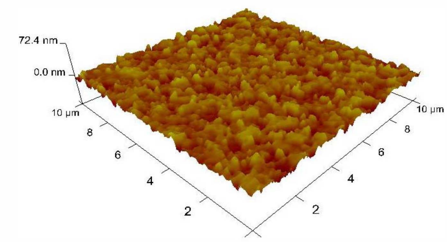
TABLE I. Parameters calculated from C-V curves

Oxygen content in the discharge	**Parameters Calculated from C-V curves**		
	Dielectric constant(k)	**Effective charge density (charge/cm^2)**	**Flat band Voltage (Volt)**
10%	45.0±1.7	$-2.58x10^{11}$	-0.22
30%	18.9±1.4	$-1.71x10^{11}$	-0.35
40%	17.0±0.6	$-1.50x10^{11}$	-0.37
60%	13.4±1.8	$-1.04x10^{11}$	-0.45

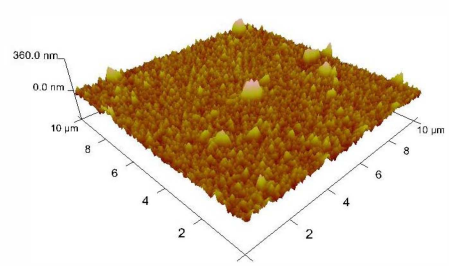
Fig. 6 shows the AFM images of films deposited at different oxygen content in the discharge. For the oxides deposited with 10%, 30%, 40% and 60% the surface roughness are, respectively, 4.05 nm, 13.9 nm, 14.2 nm, 18.5 nm. It is observed a significant difference in the surface topography once the root mean square roughness increases as the oxygen film content increases. The large dots observed in AFM images of films deposited with 30%, 40% and 60% may be attributed to imperfect substrate cleaning or to cluster formation in the plasma discharge.

The oxygen concentration in the discharge has effects on the plasma kinetics mechanisms as the oxygen is an electronegative gas and produces negative ions. The bombardment of substrate due to higher concentrations of negative ions can promote the damages to the deposited film surface which increases the roughness. Very often higher oxygen content is related to cluster formation which could also significantly affect the degree of the film surface roughness [10, 12].

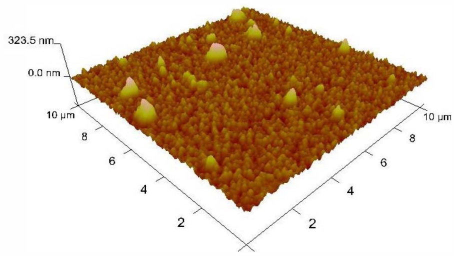
(a) 10% oxygen content



(b) 30% oxygen content



(c) 40 % oxygen content



(d) 60% oxygen content

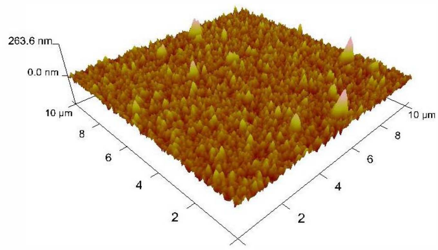


Fig. 6. TiO2 thin films surface AFM images deposited with different content in the discharge.(a) 10%, (b) 30%, (c) 40% and (d) 60%.

I. Conclusion

In this work the dielectric constant of MOS structures are markedly reduced from 45.06 to 13.40 between the lowest (10%) and higher (60%) oxygen content in the dielectric TiO_2 layer. The decrease of the dielectric constant is attributed to the gradual deterioration of the crystallinity of the growing film caused by the higher bombardment rate of the substrate. The bombardment effect also promoted the increase of the surface roughness.

Acknowledgment

The authors acknowledge the financial support of the programs the State of São Paulo Research Foundation (*FAPESP*) Process 2010/11294-7; CAPES/PVE (process BEX9796/12-6) and CAPES/ PNPD nº 02765/09-8. We also thank to the Associated Laboratory of Sensors and Materials (LAS-INPE), Laboratory of Integrated System (LSI-USP), Laboratory of Materials and Ions Beans (LAMFI - USP) and Laboratory of Semiconductor and Devices Characterization (LCDS-IEAv) for the support on the film and the MOS capacitor characterization.

References

[1] W.D. Sproul, D.J. Christie, D.C. Carter. "Control of reactive sputtering processes, " Thin Sol. Films, vol. 491, pp.1 – 17, July 2005.

[2] O. Banakh, P.E. Schmid, R. Sanjinés, F. Lévy, "Electrical and optical properties of TiOx thin films deposited by reactive magnetron sputtering," Surface and Coatings Technology, vol. 151 –152, pp. 272–275, March 2002.

[3] H. Toku, R.S. Pessoa, H.S. Maciel, M. Massi, U.A. Mengui, "The effect of oxygen concentration on the low temperature deposition of TiO2 thin films," Surface & Coatings Technology, vol. 202, pp. 2126–2131, February 2008.

[4] U. Diebold, "The surface science of titanium dioxide", Surface science reports, vol. 48, pp. 53-229, October 2002.

[5] K.F. Albertin, I. Pereyra, "Study of reactive sputtering titanium oxide for metal-oxide-semiconductor capacitors," Thin Solid Films, vol. 517, pp. 4548–4554, June 2009.

[6] I. Safi, "Recents aspects concerning DC reactive magnetron sputtering on thin films: a review", Surface and Coatings Technology, vol. 127, pp. 203-219, February 2000.

[7] S. Simeonov, E. Kafedjiiska, A. Szekeres, C. Parlog, M. Gartner, "Electrical characterization of MIS structures with sol-gel TiO2(La) dielectric films," J. Opto. and Adv. Mat., vol. 7, pp. 545-548, February 2005.

[8] N. Martin, C. Rousselot, C. Savall, F. Palmino, "Characterizations of titanium oxide films prepared by radio frequency magnetron sputtering", Thin Solid Films, vol. 287, pp. 154-163, February 1996.

[9] G.S. Chen, C.C. Lee, H. Niu, Welson Huang, Robert Jann, T. Schütte, " Sputter deposition of titanium monoxide and dioxide thin films with controlled properties using optical emission spectroscopy", Thin Solid Films, vol. 516, pp. 8473–8478, May 2008.

[10] Mark C. Barnes, Andrea R. Gerson, Sunil Kumar, Nong-Moon Hwang, " The mechanism of TiO deposition by direct current magnetron reactive," Thin Solid Films, vol. 446, pp. 29–36, September 2004.

[11] K.G.Grigorov, D.Bouchier, G.I.Grigorov, J-L Vignes, J-P Langeron, ¨A simple estimate of the deposited energy and concentration profiles in films produced by Ion-Assisted physical vapour deposition¨, Appl. Phys A 58 619-622 (1994)

[12] J.C. Sagás, D.A. Duarte, S.F. Fissmer, "Effect of oxygen concentration and system geometry on the current-voltage relations during reactive sputter deposition of titanium dioxide thin films", Vaccum, vol. 45, pp. 1042-1046, March 2011.

[13] Sheng S. Li, "Semiconductor Physical Electronics" 2nd ed, Springer, 2006, pp. 567-582.