Effect of substrate type on structure of TiO$_2$ thin film deposited by atomic layer deposition technique

R. S. Pessoa[1,2], F. P. Pereira[1], G. E. Testoni[2], W. Chiappim[2], H. S. Maciel[1,2], L. V. Santos[1,2]

[1]Nanotechnology and Plasmas Processes Laboratory, Universidade do Vale do Paraíba (Univap),
São José dos Campos, SP, 12244-000, Brazil
[2] Plasma and Processes Laboratory, Instituto Tecnológico de Aeronáutica (ITA-DCTA),
São José dos Campos, SP, 12228-900, Brazil
e-mail: rspessoa@univap.br

ABSTRACT

This paper discusses about the effect of substrate type on structure of titanium dioxide thin film deposited by atomic layer deposition technique using titanium tetrachloride and deionized water as precursors. The substrates investigated are silicon (100), cover glass and titanium, and the depositions were performed at temperatures ranging from 300ºC to 450 ºC. We observed through Rutherford backscattering spectrometry that the TiO$_2$ thin films grown on both substrates are stoichiometric. Grazing incidence x-ray diffraction showed that rutile phase could be obtained in almost pure phase at temperature of 450 ºC, however only for glass and titanium substrates. For the case of silicon (100) substrate, the anatase phase was preponderant for process temperatures investigated.

Index Terms: atomic layer deposition; thin film; titanium dioxide; elemental composition; material structure.

I. INTRODUCTION

The growth of titanium dioxide (TiO$_2$) thin film has received a great deal of attention in last year's [1-5]. In general, the applicability of this material in thin film form depends on its crystalline phase. As it is known, in bulk form, TiO$_2$ is a polymorphous material that is known to exist in three main crystalline structures: two tetragonal structures, the anatase and the rutile phases; and an orthorhombic structure, the brookite phase. However, in thin film form, only anatase and rutile structures are more easily synthesized [1, 6]. Anatase and rutile phases consist of interconnected TiO$_6$ octahedral chains that are interconnected in different configurations, resulting in different physical and chemical properties [3, 7]. Due this, they are potentially attractive in different areas. For example, the high temperature equilibrium rutile phase is desired for optical and microelectronic applications due its high refractive index (2.62 (|| a) and 2.90 (|| c)) and dielectric constant (86-170, depending of rutile crystal orientations), respectively [8, 9]. Anatase phase exhibits high photocatalytic activity which can be used in a variety of potential applications that include dye-sensitized solar cells (DSSC),

photo-chemical degradation of toxic chemicals, electrode material in lithium batteries, water splitting and photocatalysts of high efficiency [2, 4, 10, 11].

Due to aforementioned properties, TiO$_2$ thin films with rutile structure are considered as promising candidates for DRAM capacitor dielectrics by the International Technology Roadmap for Semiconductors (ITRS) [12, 13]. However, its synthesis is easier at temperatures higher than 500°C for most of the deposition processes of thin films, namely, magnetron sputtering [1, 14], chemical vapor deposition - CVD [15], plasma enhanced chemical vapor deposition - PECVD [16], atomic layer deposition - ALD [17], among others.

Unfortunately, rutile phase often coexists, in TiO$_2$ thin films, with the lower dielectric constant anatase phase, thereby resulting in a reduction of the effective dielectric constant of TiO$_2$ [18]. Usually, post deposition annealing at temperatures above 800°C has been performed to obtain pure rutile phase films. Nevertheless, some recent works indicate the ability of ALD technique to induce the formation of pure rutile phase of TiO$_2$, at lower temperatures, being only needed a seed layer to modify the substrate surface. Aarik et al. used this approach to grow

pure rutile phase on α-Al$_2$O$_3$ [19]. Kim et al. showed that the growth of the rutile phase at low temperature can be stabilized by the RuO$_2$ seed layer [20]. This is possible by ALD process, using the template approach with O$_3$ as oxidant [21], however, O$_3$ can etch the RuO$_2$ seed layer, thus hindering the deposition process [21]. To overcome these drawbacks it is necessary to investigate others materials for inducing the formation of rutile phase at lower ALD process temperatures.

In this work, the structure of atomic layer deposited TiO$_2$ thin films from TiCl$_4$ and H$_2$O precursors were investigated for three different types of substrate: Si(100), cover glass (composed mainly by SiO$_2$) and titanium. For this, grazing incidence x-ray diffraction (GIXRD) and Rutherford backscattering spectrometry (RBS) techniques were used to investigate the structure and stoichiometry/thickness of as-deposited thin films, respectively.

II. EXPERIMENTAL

A. TiO$_2$ film deposition

Pieces from a 350 μm thick Czochralski Si wafer (p-type, 4 Ωcm, (100)-orientation), cover glass (for microscopy) and titanium foil (purity 99.9% and thickness of 0.5 mm) were used as substrates. Fort he case of titanium substrate, due to considerable surface roughness, before the TiO$_2$ thin film deposition the substrate underwent a polishing process (using sand paper grits from 800 to 2000) in order to achieve a low surface roughness. They were individually cleaned in ultrasonic bath using acetone and deionized water for 5 min, and then dried with N$_2$ gas before the introduction in the ALD reaction chamber. The TiO$_2$ films were deposited by a TFS-200 ALD system from Beneq Oy operating in thermal mode. Figure 1 show a schematic diagram of ALD reactor as well as a picture of the whole system. Here, the following ALD cycle time steps for deposition of films were used: 0.25–2–0.25–2 s, i.e. the TiCl$_4$ pulse of 0.25 s, the first purge of 2 s, H$_2$O pulse of 0.25 s and the second purge of 2 s. Nitrogen (N$_2$) of 99.999% purity was used as purge gas. The vapors of TiCl$_4$ and H$_2$O were led into the reactor from external reservoirs kept with liquid TiCl$_4$ (Sigma-Aldrich 99.95% purity) and deionized water at temperature of 21°C. A capillary was used to control the precursors flow, inserted into the reactor, by only action of their own pressure vapor, i.e., no bubbling systems were used. During the deposition the gas pressure in reactor chamber was maintained around 100 Pa through the insertion of 300 sccm of N$_2$ in reaction chamber.
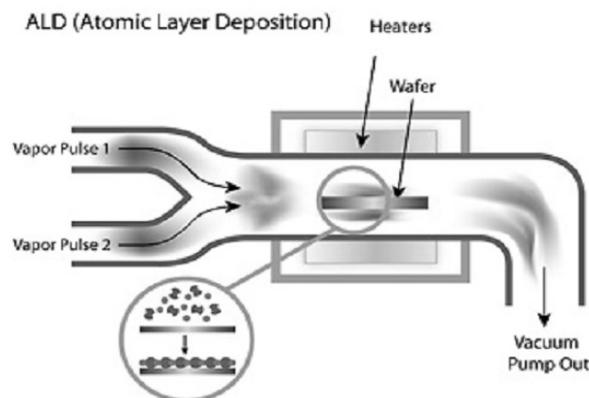
(a)

(b)

Figure 1. (a) Schematic diagram of thermal ALD chamber and (b) picture of the ALD system.

Finally, some process temperatures were investigated in the range of 300-450 °C for a reaction cycle number fixed at 2000. The instability of the substrate temperature did not exceed 3 °C for all conditions investigated.

B. Film characterization

Rutherford backscattering spectroscopy (RBS) was used to measure the thickness and chemical composition of the film. The measurements were carried out using a 2.2 MeV ⁴He⁺ beam from a Pelletron accelerator type with a particle detector positioned at 170° to the incident beam. For data evaluation of the RBS spectra, the computer code SIMNRA [22] was used was used taking into account the electronic stopping power data by Ziegler and Biersack, Chu + Yang's theory for electronic energy-loss straggling and Andersen's screening function to Rutherford cross-section. The contribution from a multiple scattering into the RBS spectra were taken into account using the calculating facilities of SIMNRA. The simulated RBS areal density

values (10^{15} atoms/cm^2) were converted into the layer thickness value (nm) by using the theoretical film density taking account of the crystal structure of the film.

In order to characterize the crystal structure, grazing incidence x-ray diffraction (GIXRD) method was used. The GIXRD patters were obtained at room temperature in a Shimadzu XRD 6000 goniometer using cooper target (CuKα radiation 1.5418Å), 2θ from 10° to 80°, at a scanning speed of 0.02°/s, a voltage of 40 kV, and a current of 30 mA. The samples were mounted in a rotating aluminum sample holder (60 rpm). Moreover, the GIXRD studies were carried out at an incidence angle of 0.29°. This angle was close to the optimum values for anatase and rutile films and allowed efficient reduction of the reflections from the substrate [23].

III. RESULTS AND DISCUSSION

Figure 1 shows the experimental and simulated RBS spectrum of TiO$_2$ deposited on Si(100) at temperature of 300 °C. As can be seen, the film does not have impurities arising from the deposition process, such as the presence of chlorine. The measured thickness of the film was 190.2 nm. For condition of 450 °C the film thickness was 141.6 nm. Although not shown here, the thicknesses of films deposited on glass and titanium substrates are approx. the same as that grown on silicon. Other important information obtained from this RBS analyze is about the stoichiometry, namely, the investigated ALD conditions allow the growth of stoichiometric TiO$_2$ thin films.

Figure 2 shows the GIXRD patterns of TiO$_2$ thin films deposited on Si(100) substrate for process temperatures of 300 °C and 450 °C. These tempera-
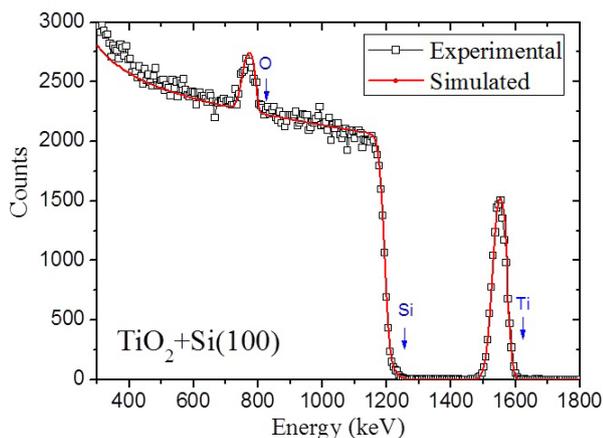
tures were selected based on literature [12, 19, 23] and observations by us as the optimum temperatures to obtain the anatase (around 250-300°C) and rutile phase (higher than 400°C) with a high degree of crystallinity. It is possible to see from Fig. 2 that pure anatase phase can be obtained on Si substrate for 300 °C. When the temperature was increased to 450 °C, some diffraction peaks relative to rutile phase begin to appear together with anatase phase but yet with very low intensity. Cheng et al. also observed this feature and attributed the appearance of rutile phase on Si substrate as due to change of grain size of TiO$_2$ thin film at temperatures higher than 400 °C [25].

Figure 3 shows the x-ray diffraction pattern of the TiO$_2$ films grown on glass substrate. Additionally, it is presented the GIXRD spectrum of glass substrate, confirming its amorphous condition. Differently of the case of Si substrate, the rutile phase initiates its formation, for temperature of 300 °C, concomitantly with the growing of metastable anatase phase. Only for the temperature of 450 °C, the rutile phase became predominant with relation to anatase phase. Aarik et al. showed that growing TiO$_2$ films on polycrystalline RuO$_2$ on Si allows the formation of rutile phase at process temperature of 425 °C. They stated that this obtained rutile structure was due to epitaxial growth on the RuO$_2$ seed layer [18]. However, even so, the rutile phase was not obtained with high intensity or pure form.

It is surprising, as we can infer from Fig. 3, that the present ALD process promotes the synthesis of almost pure rutile TiO$_2$ on glass, which is basically a SiO$_2$ type substrate. This result rises the conjecture that SiO$_2$ substrate or even a SiO$_2$ seed layer on another

Figure 2. RBS spectrum of TiO$_2$ thin film deposited on Si(100) at temperature of 300 ºC. The red line represents the simulation by SIMNRA code.
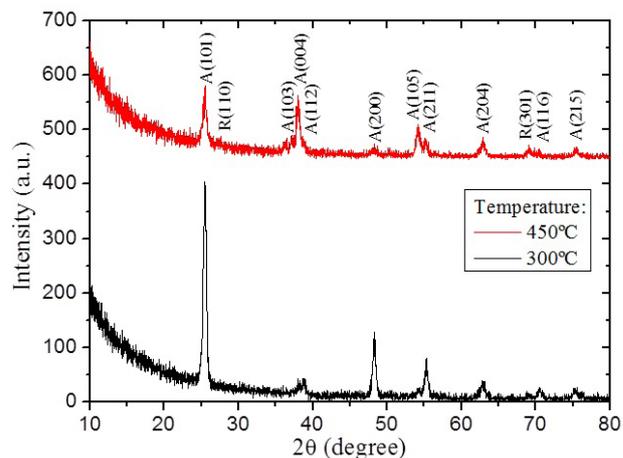
Figure 3. GIXRD patters for TiO$_2$ thin films deposited on Si(100). For comparison, the relative intensities of x-ray reference diffractions of anatase powder are: (101)/100, (200)/35, (004)/20, (105)/20, (211)/20, (204)/14, (103)/10, (112)/10, (116)/6, (215)/4 [24].

substrate could act as a good platform for growth of good quality rutile TiO_2 phase. Moreover, the SiO_2 is resistant to etching by the precursors used in the present process, on the contrary of other used seed layers, like RuO_2 [18]. Anyway, these potential advantages of SiO_2 substrate to support an easy and handy growing of pure rutile TiO_2, must be demonstrated by further investigations on this ALD process.

Figure 4 shows the x-ray diffraction pattern of the TiO_2 films grown on pure titanium substrate. Additionally, it is presented the GIXRD spectrum of titanium. The crystalline patterns of titanium is correspondent to its α-phase [24]. Compared with other substrates, it can be noted that intensity of the diffraction peaks of titanium are still strong in the GIXRD spectra when TiO_2 thin film is present. This appears to be a characteristic observed for metal substrates, where even with low-angle XRD, the reflections relative to the substrate can shadowed some reflections of thin film [27]. As observed to cover glass substrate, for temperatures of order or higher than 400 °C the rutile phase is preponderant, indicating that the use of Ti seed layer on another substrate type can be other interesting alternative to induce the formation of rutile phase. Furthermore, it is noteworthy the effect of substrate on crystalline phase of TiO_2 thin film, where in this work were investigated an insulant (SiO_2), a semiconductor (Si) and a metallic (Ti) substrate, and for insulant and metallic substrates the kinetics of crystallization is almost the same. A detailed investigation needs to be performed in order to better understand this effect and answer why for silicon substrate is necessary more energy to change the metastable anatase phase to rutile phase.
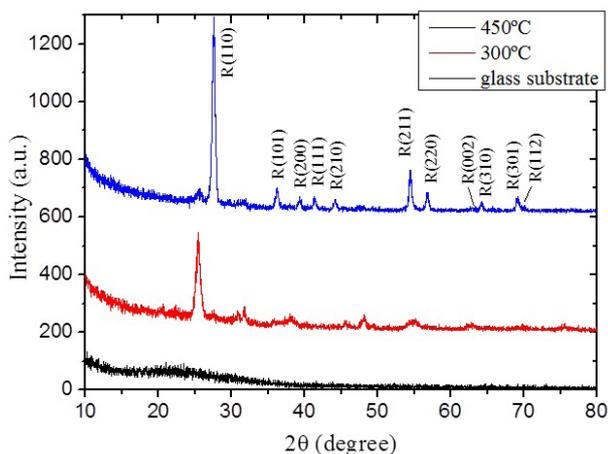

Figure 4. GIXRD patters for TiO_2 thin films deposited on cover glass. For comparison, the relative intensities of x-ray reference diffractions of rutile powder are: (110)/100, (211)/60, (101)/50, (111)/25, (220)/20, (301)/20, (112)/12, (210)/10, (002)/10, (310)/10, (200)/8, (221)/2 [26].
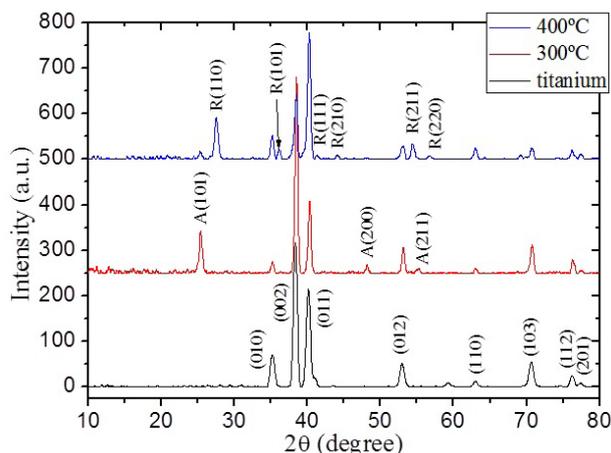

Figure 5. GIXRD patters for titanium substrate and TiO_2 thin films deposited at temperatures of 300 °C and 400 °C.

IV. CONCLUSION

This paper presents preliminary results concerning the effect of substrate type on the crystallinity of TiO_2 thin films synthesized by atomic layer deposition (ALD) process.

The substrates investigated are silicon (100), cover glass and titanium, and the depositions were made at temperatures ranging from 300 °C to 450 °C. We show through the use of GIXRD and RBS techniques that rutile phase can be obtained, in almost pure phase, at temperature higher than 400 °C, however only for glass substrate and titanium. For the case of silicon (100) substrate, it was observed that the anatase phase is preponderant for both process temperatures investigated. These results allow us to highlight that less expensive SiO_2 or Ti thin film could act as a good seed layer for growth of good quality rutile TiO_2 phase, by using ALD process on Si substrate and using precursors such as $TiCl_4$ and H_2O.

ACKNOWLEDGEMENTS

REFERENCES

[1] B. Agnarsson, F. Magnus, T. K. Tryggvason, A.S. Ingason, K. Leosson, S. Olafsson, J.T. Gudmundsson, "Rutile TiO_2 thin films grown by reactive high power impulse magnetron sputtering", Thin Solid Films, vol. 545, pp. 445-450, 2013.

[2] M. A. Henderson, "A surface science perspective on TiO$_2$ photocatalysis", Surface Science Reports, vol. 66, pp. 185-297, 2011.

[3] U. Diebold, "The surface science of titanium dioxide", Surface Science Reports, vol. 48, pp. 53-229, 2003.

[4] R. S. Pessoa, M. A. Fraga, L. V. Santos, M. Massi, H. S. Maciel, "Nanostructured thin films based on TiO$_2$ and/or SiC for use in photoelectrochemical cells: A review of the material characteristics, synthesis and recent applications", Materials Science in Semiconductor Processing, vol. 29, pp. 56-68, 2015.

[5] Z. F. Yin, L. Wu, H. G. Yang, Y. H. Su, "Recent progress in biomedical applications of titanium dioxide", Physical Chemistry Chemical Physics, vol. 15, pp. 4844-4858, 2013.

[6] M. D. Wiggins, M. C. Nelson, C. R. Aita, "Phase development in sputter deposited titanium dioxide", J. Vac. Sci. Technol. A, Vol. 14, pp. 772-776, 1996.

[7] J. Lee, S. J. Lee, W. B. Han, H. Jeon, J. Park, W. Jang, C. S. Yoon, H. Jeon, "Deposition temperature dependence of titanium oxide thin films grown by remote-plasma atomic layer deposition", Phys. Status Solidi A, vol. 210, pp. 276-284, 2013.

[8] J. Szczyrbowski, G. Bräuer, M. Ruske, J. Bartella, J.Schroeder, A. Zmelty, "Some properties of TiO$_2$ layers prepared by medium frequency reactive sputtering", Surf. Coat. Tech., vol. 112, pp. 261-266, 1999.

[9] M. Es-Souni, I. Oja, M. Krunks, "Chemical solution deposition of thin TiO$_2$-anatase films for dielectric applications", J. Mater. Sci. Mater. Electron., vol 15, No 6, pp. 341-344, 2004.

[10] S.-Y. Lee, S.-J. Park, "TiO$_2$ photocatalyst for water treatment applications", Journal of Industrial and Engineering Chemistry, vol. 19, pp. 1761-1769, 2013.

[11] E. Serrano, G. Rus, J. Garcıa-Martınez, "Nanotechnology for sustainable energy", Renewable and Sustainable Energy Reviews, vol. 13, pp. 2373-2384, 2009.

[12] T. Arroval, L. Aarik, R. Rammula, H. Mändar, J. Aarik, B. Hudec, K. Hušeková, K. Fröhlich, "Influence of growth temperature on the structure and electrical properties of high-permittivity TiO$_2$ films in TiCl$_4$-H$_2$O and TiCl$_4$-O$_3$ atomic-layer-deposition processes", Phys. Status Solidi A, vol. 211, No. 2, pp. 425-432, 2014.

[13] International Technology Roadmap for Semiconductors 2012 edition, Front End Processes: http://public.itrs.net.

[14] H. Toku, R. S. Pessoa, H. S. Maciel, M. Massi, U. A. Mengui, "The effect of oxygen concentration on the low temperature deposition of TiO$_2$ thin films", Surface and Coatings Technology, vol. 202, pp. 2126-2131, 2008.

[15] F. Maury, J. Mungkalasiri, "Chemical vapor deposition of TiO$_2$ for photocatalytic applications and biocidal surfaces", Key Engineering Materials, vol. 415, pp. 1-4, 2009.

[16] S. S. Huang, J. S. Chen, "Comparison of the characteristics of TiO$_2$ films prepared by low-pressure and plasma-enhanced chemical vapor deposition", Journal of Materials Science: Materials in Electronics, vol. 13, pp. 77-81, 2002.

[17] R. L. Puurunen, "Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/water process", J. Appl. Phys., vol. 97, pp. 121301, 2005.

[18] K. Fröhlich, J. Aarik, M. Ťapajna, A. Rosová, A. Aidla, E. Dobročka, K. Hušková, "Epitaxial growth of high-k TiO$_2$ rutile films on RuO$_2$ electrodes", J. Vac. Sci. Technol. B, vol. 27, No 1, 266-270, 2009.

[19] J. Aarik, A. Aidla, H. Mandar, T. Uustare, M. Schuisky, A. Harst, "Atomic layer growth of epitaxial TiO$_2$ thin films from TiCl$_4$ and H$_2$O on α-Al$_2$O$_3$ substrates", Journal of Crystal Growth, vol. 242, pp. 189-198, 2002.

[20] S. K. Kim, G. W. Hwang, W.-D. Kim, and C. S. Hwang, "Transformation of the Crystalline Structure of an ALD TiO$_2$ Film on a Ru Electrode by O$_3$ Pretreatment", Electrochem. Solid-State Lett., vol. 9, pp. F5, 2006.

[21] M. Popovici, A. Delabie, C. Adelmann, J. Meersschaut, A. Franquet, M. Tallarida, J. van den Berg, O. Richard, J. Swerts, K. Tomida, M.-S. Kim, H. Tielens, H. Bender, T. Conard, "Understanding the Interface Reactions of Rutile TiO$_2$ Grown by Atomic Layer Deposition on Oxidized Ruthenium", ECS Journal of Solid State Science and Technology, vol. 2, No 1, pp. N23-N27, 2013.

[22] M. Mayer, AIP Conf. Proc. vol 475, pp. 541, 1999; SIMNRA (Simulation Program for the Analysis of NRA, RBS and ERDA) developed by M. Mayer; http:// http://home.rzg.mpg.de/~mam/.

[23] L. Aarik, T. Arroval, R. Rammula, H. Mändar, V. Sammelselg, J. Aarik, "Atomic layer deposition of TiO$_2$ from TiCl$_4$ and O$_3$",Thin Solid Films vol. 542, pp. 100-107, 2013.

[24] H. R. Z. Sandim, B. V. Morante, P. A. Suzuki, "Kinetics of thermal decomposition of titanium hydride powder using in situ high-temperature X-ray diffraction (HTXRD)", Materials Research, vol. 8, no.3, pp. 293-297, 2005.

[25] H.-E. Cheng, C.-C. Chen, "Morphological and Photoelectrochemical Properties of ALD TiO$_2$ Films", Journal of The Electrochemical Society, vol. 155, No 9, pp. D604-D607, 2008.

[26] M. E. Mrose, B. Post, S. Weissmann, H. F. McMurdie, M. C. Morris, W. F. McClune (eds.), Powder Diffraction Data, Joint Committee on Powder Diffraction Data Standards, Swarthmore, PA, cards 16-617, 21-1272 and 21-1276, 1976.

[27] M. Bouroushian, T. Kosanovic, "Characterization of thin films by low incidence x-ray diffraction", Crystal structure theory and applications, vol. 1, pp. 35-39, 2012.