Scholtz *et al. Applied Adhesion Science* (2015) 3:1
DOI 10.1186/s40563-015-0031-7

Applied Adhesion Science
a SpringerOpen Journal

RESEARCH Open Access

Pulsed bias effect on roughness of TiO_2:Nb films deposited by grid assisted magnetron sputtering

Juliano Sadi Scholtz[1], Joel Stryhalski[1,2], Julio César Sagás[1], Abel André Cândido Recco[1], Marcello Mezaroba[1] and Luís César Fontana[1*]

* Correspondence:
luis.fontana@udesc.br
[1]UDESC Physics Department Centro de Ciências Tecnológicas CCT, Rua Paulo Malschitzki, s/n Campus Universitário Prof. Avelino Marcante, Zona Industrial Norte, zip code: 89.219-710 Joinville, SC, Brazil
Full list of author information is available at the end of the article

Abstract

In this work Nb-doped TiO_2 (TiO_2:Nb) films were deposited by reactive sputtering. The substrate was biased with negative pulses to change the energy of the ions nearby the sample surface during the deposition. As consequence, the film crystalline structure and roughness were changed. It was verified that higher energy favours the rutile growth with a higher roughness, even under low temperature as 300°C, and the material structure can be controlled by setting the duty cycle, voltage and frequency of the switched power supply applied to the substrate.

Keywords: Nb-doped TiO_2 films; Roughness; Reactive deposition; Substrate bias; Switched power supply

Background

TiO_2 films have been investigated because of their wide variety of technological applications. For example, the adhesion of the human oral mucosa soft tissue on TiO_2 microimplants was evaluated in [1], observing some potential clinical benefits, including the possibility of bone resorption. Other examples include the TiO_2 use in photovoltaics and photocatalysis fields [2-5].

Increasing the implant surface roughness enhances its adhesion to the soft tissue, but can also increase the infection risk due to the bacterial accommodation in the space between its valleys and peaks. The photocatalytic property of TiO_2 in the anatase structure to eliminate bacteria was evaluated in [6], identifying its use as an excellent way for sterilizing the implants surfaces and reduce the infection risk. The incorporation of Nb into the TiO_2 favors the nucleation of grains and electrical conductivity, producing nanostructured and transparent films [7-10].

Thin film deposition by magnetron sputtering enables the control of different parameters that can improve physical-chemical properties, microstructure and film adhesion on the substrate. The substrate negative bias is a strategy used for increasing the kinetic energy of the ions striking the film surface during the deposition [11]. In this work, the effects of pulsed bias in the microstructure of TiO_2:Nb films deposited on stainless steel substrate were analysed by X-Ray diffraction (XRD) and Atomic Force Microscopy (AFM).

Methods

Deposition chamber

The deposition chamber is a stainless steel vacuum vessel with 30 cm (diameter) by 30 cm (height). The ultimate pressure inside the chamber is 10^{-5} Torr, done by a vacuum system composed of a mechanical pump and a turbo molecular pump. Inside the chamber there are a magnetron, a grounded grid, a sample holder for 6 samples and an electric heater (controlled by a PID). The temperature is monitored with a thermocouple inserted in the substrate holder and its temperature is maintained at 300°C. The working pressure is measured by a capacitive gauge Adixen ASD 2004 and the base pressure is measured with a Penning gauge Edwards CP 25 EK. The gases flowing into the chamber are controlled by two mass flow meters of 200 sccm.

The base plasma is generated by a direct current power supply (up to 1000 V and 2.0 A). The (Figure 1) shows a schematic drawing of the experimental setup.

The TiO_2:Nb films were deposited on stainless steel using a Grid Assisted Magnetron Sputtering System [12]. The target used was a titanium disc (99.5% purity) with 100 mm in diameter holding 12 inserts of niobium (99.5%) with 3 mm in diameter each one, disposed in the erosion area, producing Ti/Nb films with ratio of 9:1. The working gas used in the sputtering process was a mixture of Ar and O_2 in order to get a TiO_2: Nb film - experimental details are showed in (Table 1).

The waveform of substrate bias was acquired using an oscilloscope Tektronix TDS 2024B. The (Figure 2) shows an example of the substrate voltage and current signals during the film deposition. The time "on" divided by the period is called "duty cycle" (t/T as showed in (Figure 2)). It means the percentage of time, during one period, on which the substrate is biased. The pulsed power supply is a homemade device specially developed for this work.

The duty cycle was varied from 30% up to 70%. The peak substrate bias was -100 V.

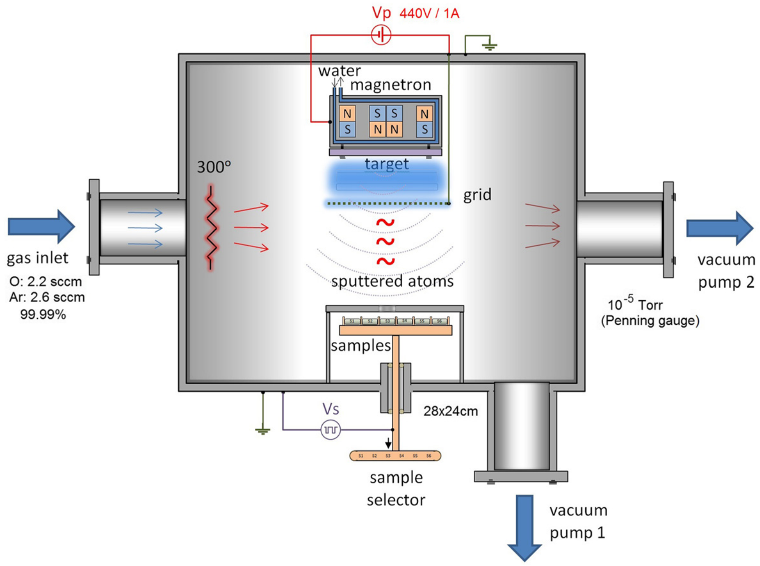

Figure 1 Schematic of the grid assisted magnetron sputtering system.

Table 1 Summary of the experimental parameters

Variable	Value
Deposition time	30 min.
Substrate temperature	300°C
Substrate bias	-100 V
Target voltage	-400 V
Target current	1.0 A
Oxygen mass flow rate	2.2 sccm
Argon mass flow rate	2.6 sccm
Base pressure	10^{-5} Torr
Working pressure	3 mTorr

The (Table 1) shows the summary of the experimental parameters set to the experiment.

The crystalline planes were identified by the SHIMADZU XRD-6000 equipment, using 2θ diffraction angle, with radiation Cu K_α 1,5406 Å.

The chemical composition and also the film thickness were measured by energy dispersive X-ray fluorescence spectrometer (EDX), SHIMADZU EDX-720 model, adjusted in the fp thin films mode to get the signal from a solid state X-ray detector, which was in good agreement with confocal measurements. Follow below the procedure used:

1. Measure the raw substrate in order to identify its own composition;
2. Insert the composition data about the raw material for thickness identification using the fp thin films mode and measure some samples to verify the accuracy, comparing the results with the preview confocal measures;

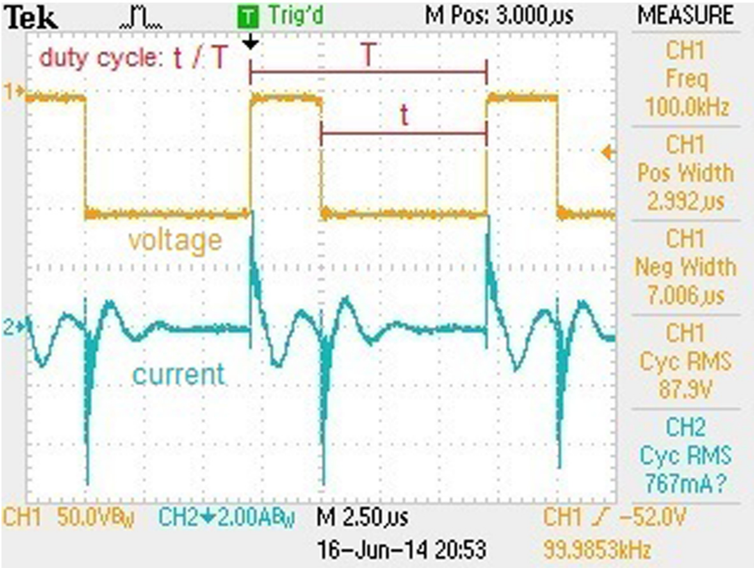

Figure 2 Voltage applied and current measured. The green curve shows the voltage bias pulses and the blue one shows the respectively current trough the substrate (example for 70% duty cycle; 50 V/div; 2A/div).

Table 2 Summary of the experimental results for films deposited with $V_{bias} = -100$ V pulsed at 100 kHz

–Duty cycle	Av. grain size	Av. surface roughness (Sa)	Nb/Ti (%wt)
(a) raw substrate	-	1.35 nm	-
(b) 30%;	90 nm	1.58 nm	
(c) 50%;	100 nm	2.13 nm	0.12±0.01
(d) 70%;	145 nm	4.17 nm	

3. Measure the samples using the bulk fp method for wavelength-dispersive spectrometers.

It is important to clarify that the equipment used does not measure small atoms like oxygen.

For the characterization of the surface morphology and roughness in nanometer scale was used a NANOSURF AFM NANITE B S200 equipment, adjusted in the dynamic force mode (constant height).

The average films thickness measured by EDX was (0.28 ± 0.05) μm and its chemical composition is showed in Table 2.

Results and discussion

The (Figure 3) shows the XRD pattern for films deposited at different duty cycles. It is observed that the rutile peak (110) has a strong increase in intensity with increasing

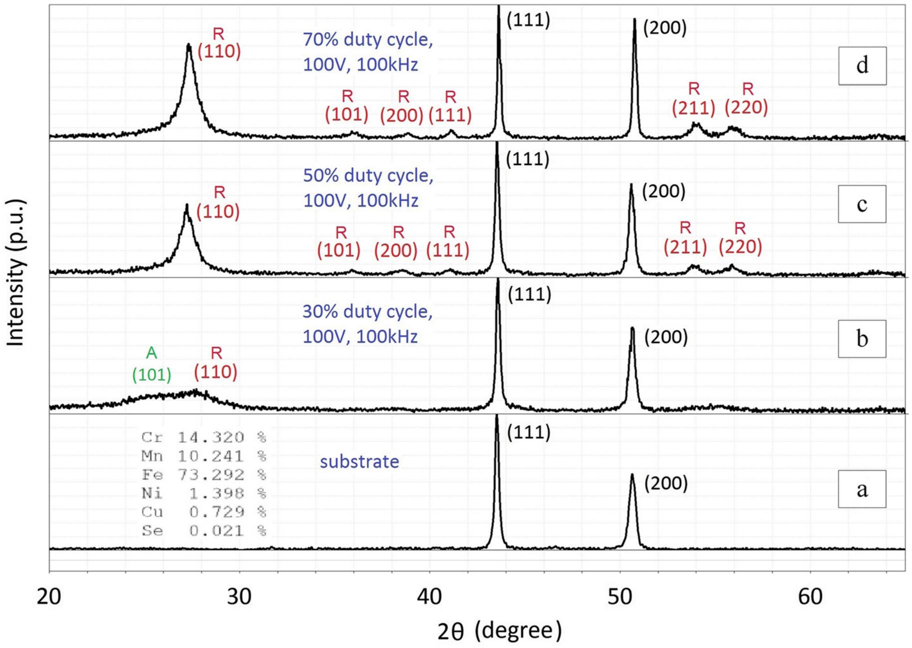

Figure 3 X-ray diffraction pattern of TiO2:Nb films on stainless steel substrate as a function of duty cycle, for -100 V and 100 kHz: Rutile peaks (red) and substrate peaks (black). The plane (101) (green) indicates the presence of anatase. Letters (a), (b), (c) and (d) are index for relating with (Figure 4) and (Table 2). The substrate composition indicated in (a) represents the percentage of each element in mass (in relation to 100%).

duty cycle from 30% up to 70%. Besides that, others rutile peaks of very low intensity (101), (200), (111), (211) and (220) are also identified. The (111) and (200) peaks correspond to the iron alpha phase (α-Fe) of the stainless steel substrate. For 30% duty cycle there is also a shoulder indicating the presence of (101) anatase (25°) in green.

According to (Figure 3), depending on the duty cycle adjustment, the TiO_2 nucleation can favor the rutile crystalline structures.

The (Figure 4) shows the AFM images for the films deposited at different duty cycles. The grain size increases with increased duty cycle, as well the average surface roughness.

The (Table 2) shows a summary of roughness and grain size measurements. The grain size was calculated by CTR AFM software, using the surface profile (dark for valleys and bright for peaks and vice-versa), and the average value was calculated for each condition (b), (c) and (d). Similarly, the average surface roughness "Sa" was calculated using (eq. 1) taking as reference the AFM NANITE B S200 manual.

$$S_a = \frac{1}{MN}\sum_{k=0}^{M-1}\ \sum_{l=0}^{N-1} \left|Z(X_{k,}X_l)\right| \qquad (1)$$

where, z (x_k,x_l) is the peak intensity for each (k,l) point.

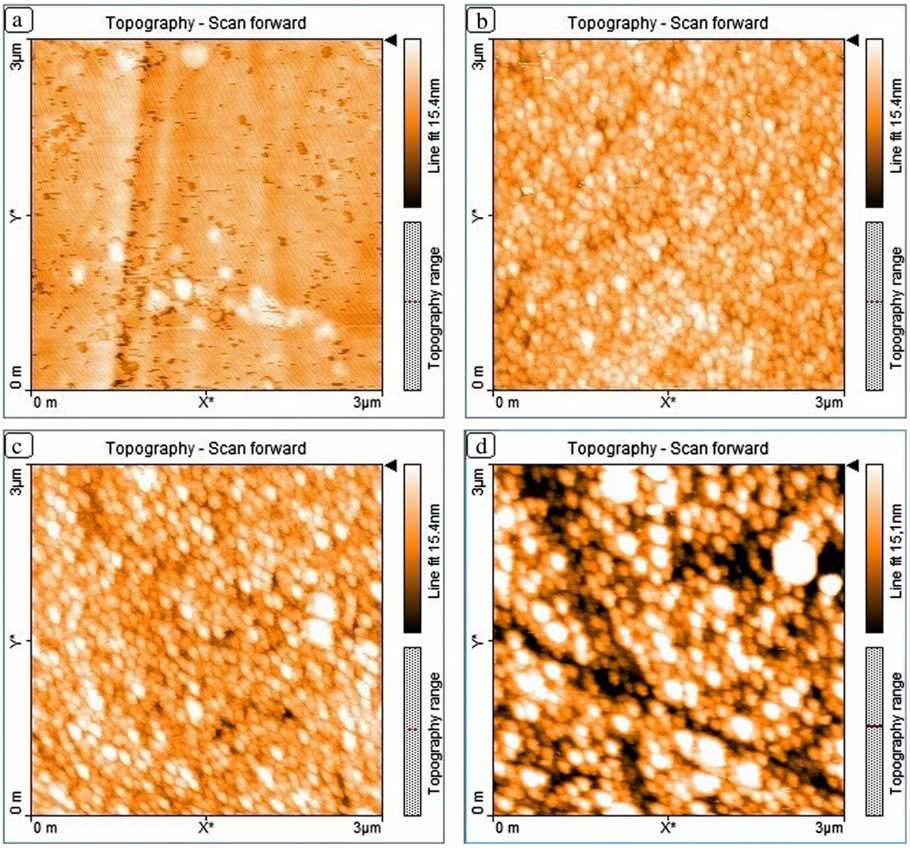

Figure 4 Non Contact AFM images for different duty cycles. a) raw substrate; **b)** 30% duty cycle; **c)** 50 duty cycle and **d)** 70% duty cycle. Scan size 3.0 × 3.0 μm^2.

By comparing the AFM and XRD results it is possible to correlate the crystallinity and roughness: both increased with the duty cycle. The increased duty cycle means a larger bombardment time and as consequence promotes higher energy delivered to the film.

Conclusions

The results showed that the pulsed bias can produce significantly changes on the roughness and the growth of crystalline phases in the film: the rutile phase and roughness are favoured when the substrate is subjected to a higher energy bombardment. For the conditions described in this work, the TiO_2:Nb film formed is rather rutile with preferencial growth (110).

It is observed that increasing the duty cycle from 30% up to 70% (for peak $V_{bias} = -100$ V and 100 kHz) increases the intensity of the rutile (110) as well the nanometric grain size of the film deposited. It is also verified that the average surface roughness increases almost three times by increasing the duty cycle from 30% up to 70%.

Finally, based on the results observed, it is possible to conclude that by setting the duty cycle of the pulsed voltage applied to the substrate allows the control of the film roughness and grain size that can be used, for example, for potential benefits at adhesion clinical applications.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

AR was responsible for the AFM measurements. JSS was responsible for the homemade switching power supply and experiments. JS was responsible for the films deposition. JCS and LCF were responsible for the results discussions. MM was responsible for supervising. All authors read and approved the final manuscript.

Author details

[1]UDESC Physics Department Centro de Ciências Tecnológicas CCT, Rua Paulo Malschitzki, s/n Campus Universitário Prof. Avelino Marcante, Zona Industrial Norte, zip code: 89.219-710 Joinville, SC, Brazil. [2]Department of Physics, Federal Institute of Santa Catarina (IFSC), Jaraguá do Sul, Santa Catarina, Brazil.

Received: 20 November 2014 Accepted: 8 January 2015

References

1. Wennerberg A, Fröjd V, Olsson M, Nannmark U, Emanuelsson L, Johansson P, et al. (2011) Nanoporous TiO_2 thin film on titanium oral implants for enhanced human soft tissue adhesion: a light and electron microscopy study. Clin Implant Dent Relat Res 13(3):184–196
2. Diebold U (2002) The surface science of titanium dioxide. Surf Sci Rep 48:53–229
3. Patil PS, Mujawar SH, Sadale SB (2005) Properties of spray deposited niobium oxide thin films. J Mater Sci Mater Electron 16:38–41
4. Zhang SX, Kundaliya DC, Dhar S (2007) Niobium doped TiO_2: Intrinsic transparent metallic anatase versus highly resistive rutile phase. J Appl Phys 102:013701–013704
5. Aleixo GT (2006) Stability and metastability of phases in Ti-Nb alloys. Dissertação de Mestrado. Unicamp, Campinas
6. Suketa N, Sawase T, Kitaura H, Naito M, Baba K, Nakayama K, et al. (2005) An antibacterial surface on dental implants, based on the photocatalytic bactericidal effect. Clin Implant Dent Relat Res 7(2):105–116
7. Lee H-Y, Robertson J (2013) Doping and compensation in Nb-doped anatase and rutile TiO_2. J Appl Phys 113(6):213706
8. Castro MV, Rebouta L, Alpuim P, Cerqueira MF, Benelmekki M, Garcia CB, et al. (2014) Optimization of surface treatments of TiO_2:Nb transparent conductive coatings by a post-hot-wire annealing in a reducing H_2 atmosphere. Thin Solid Films 550:404–412
9. Tavares CJ, Castro MV, Marins ES, Samantilleke AP, Ferdov S, Rebouta L, et al. (2012) Effect of hot-filament annealing in a hydrogen atmosphere on the electrical and structural properties of Nb-doped TiO_2 sputtered thin films. Thin Solid Films 520:2514–2519
10. Wang C, LI J, Dho J (2014) Post-deposition annealing effects on the transparent conducting properties of anatase Nb:TiO_2 films on glass substrates. Mater Sci Eng B 182:1–5
11. Kelly PJ, Hall R, O'Brien J, Bradley JW, Roche G, Arnell RD, et al. (2001) Substrate effects during mid-frequency pulsed DC biasing. Surf Coat Technol 142–144:635–641
12. Fontana LC, Muzart JLR (1998) Characteristics of triode magnetron sputtering: the morphology of deposited titanium films. Surf Coat Technol 107(1):24–30