INVESTIGATIONS OF THIN TITANIUM OXIDE FILMS GROWN BY REACTIVE PULSED LASER DEPOSITION

Gabriela Dorcioman[1, 2], Oana Fufa[1], Valentin Craciun[1,2], Marimona Miroiu[1], Petronela Garoi[1, 2], Emanuel Axente[1, 2], Felix Sima[1], Doina Craciun[1]

[1]National Institute for Lasers, Plasma and Radiation Physics, Magurele-Ilfov, Romania
[2]DENTIX MILLENNIUM SRL, Sabareni-Ilfov, Romania

e-mail: doina.craciun@inflpr.ro, *tel.* 0731650725

ABSTRACT

Titanium oxide thin films were deposited on Si monocrystalline substrate using the pulsed laser ablation technique in a reactive oxygen atmosphere. The films were obtained starting from Ti and TiO_2 targets which were ablated using a KrF* excimer laser (λ = 248 nm). During the deposition, the Si substrates were heated at 300 °C under various high purity oxygen atmosphere of 1.0, 0.5 and 0.1 mbar. Grazing incidence X-ray diffraction investigations revealed the presence of a nanostructured film consisting of a mixture of several titanium oxides, with crystalline grains size of few nm to 10 nm. Only the film deposited from the Ti target at a pressure of 1.0 mbar exhibited crystalline grains of 30-40 nm. Thin films surface morphology and topography, studied using atomic force and scanning electron microscopy, revealed a relatively smooth surface with the presence of some submicron droplets, typical for laser ablation technique. Films deposited at 0.5 mbar pressure from both targets were significantly rougher than the other deposited films.

Key words: titanium oxide, thin films, pulsed laser deposition

INTRODUCTION

The oxide layer formed naturally in the ambient atmosphere on the Ti surface or Ti-based alloys such as TiAl6V4 is very dense and adherent. It plays a chemical protection role, basically stopping the diffusion of oxygen inside the material, limiting thus the growth of the oxide layer to just a few nm. It was recently shown that the oxide layer also plays a key role for biomedical applications, by significantly reducing the rate of dissolution and degradation in biological fluids and increasing their biocompatibility [1-6]. To this purpose, several studies have been undertaken to increase the thickness of the Ti oxide layer. Thus, one can mention thermal oxidation studies [7, 8], anodic oxidation [9, 10], plasma-assisted oxidation [11, 12], or mechanical-chemical polishing [13].

An attractive method for the synthesis of metal oxide films for research purposes is the pulsed laser deposition (PLD). Due to the versatility of the experimental parameters, this technique allows growing highly adherent thin films on practically any type of substrate. Moreover, it is widely used to probe the role of structure and composition on physical-chemical properties of the coatings. The PLD technique can also be easily used to obtain bioactive doped films and induce localized activation of these oxidized implants [14]. In addition, tailoring the structure and roughness of the oxidized surfaces can generate an improved interface to promote osteointegration [15, 16].

Titanium oxide thin films grown by PLD were typically obtained at higher substrate temperatures [17]. However, the use of high temperatures for medical implant

coatings could be problematic, because they have intricate shapes. This could result in nonuniform heating, local oxidation and dimensional variation. In this study we investigated the deposition at a moderate temperature of only 300 °C of thin titanium oxide films using the PLD technique starting from pure Ti and TiO_2 targets that were laser ablated in an oxygen atmosphere. Results about their structure, morphology and composition are presented below.

MATERIAL AND METHODS

To obtain TiO_x films, a pulsed laser ablation deposition set up with an excimer laser (KrF*, $\lambda = 248$ nm, $\tau = 25$ ns, fluence 2 J/cm^2, frequency 10 Hz) was used. The laser enters through an amorphous SiO_2 window that is transparent at $\lambda = 248$ nm radiation, into the stainless steel deposition chamber, where a vacuum of the order of 2×10^{-7} mbar has been achieved by mechanical and turbomolecular vacuum pumps. The films were deposited under oxygen atmosphere from targets of Ti and TiO_2 on Si substrates placed at a distance of 5 cm and at a temperature of 300 °C. Substrate heating was performed with a rate of 10 °C / min, while cooling was slower, just 5 °C / min in order to avoid thermo-mechanical stresses in the deposited films. Oxygen pressure during deposition, measured with a capacitive vacuum gauge, was 1.0, 0.5 or 0.1 mbar.

After deposition, the film structure was investigated using grazing incidence X-ray diffraction (GIXRD) with a Panalytical Empyrean diffractometer. The diffractometer worked using Cu K_α radiation in a parallel beam geometry by means of a mirror in the incident beam side and a beam collimator of 0.27° in front of the detector.

The morphology of the deposited film surface and its chemical composition were investigated by means of a scanning electron microscope (FEI-Inspect S50) provided with an elemental energy dispersion X-ray spectroscopy (EDS) detector.

Also, an atomic force microscope (AFM), model TT-AFM Workshop, was used to obtain surface topography film images on areas of up to 15 x 15 μm^2. In addition to the three-dimensional qualitative assessment of the topography, the AFM was able to determine quantitative parameters of the amplitude of the roughness, an essential component of a surface texturing aspect.

The roughness values were recorded on the profile (line scan), so we obtained values of the arithmetic mean deviation (Ra), representing the arithmetic average of the absolute values recorded and, respectively, the values of the root mean square deviation (RMS) that defines the standard deviation of the profile height distribution.

The chemical composition was studied using X-ray photoelectron spectroscopy (XPS) with an ESCALAB 250Xi instrument equipped with a monochromatic Al anode as the X-ray source. Wide range analyzes (survey scans) were initially performed on the surface of the deposited film and then high resolution scans of the C1s, O 1s, and Ti 2p regions were performed.

RESULTS AND DISCUSSION

To investigate the structure of the deposited films, GIXRD analysis were performed at incidence angles from 2° to 3°, which were optimized to maximize the diffraction peaks intensity of the deposited TiO_x films.

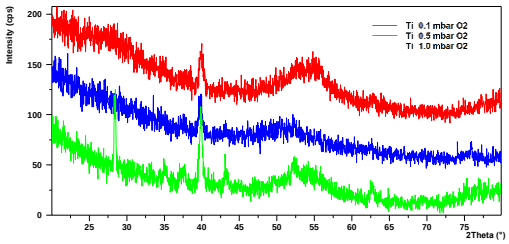


Figure 1. GIXRD patterns acquired from films deposited using the Ti target under different oxygen pressures.

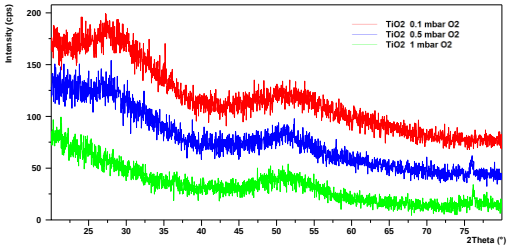


Figure 2. GIXRD patterns acquired from films deposited using the TiO_2 target under different oxygen pressures.

The patterns obtained from films deposited using the Ti and TiO_2 targets are shown in Figs 1 and 2, respectively, while an example of their analysis is shown in Fig. 3. It can be seen from Fig. 1 that the pressure of 1 mbar and the use of Ti target was the combination that led to the appearance of a well-crystallized film. A Williamson Hall analysis of the diffraction peaks for this film indicated the presence of 41 nm crystalline grains and 0.4% micro-strain. According to the results of the analysis presented in Fig. 3 and Table I, the deposited film consisted of a mixture of titanium oxides. The phase identification is far from perfect or unique because the films being thin and nanostructured, the diffraction peaks were rather broad and the intensities were low. Also, there are several hundreds of titanium oxide patterns in the database, from low oxygen content, that exhibit diffraction patterns very similar to metallic Ti, up to stable TiO_2 anatase. Also, the films could be stressed or nonstoichiometric, which further complicates the analysis. When using a TiO_2 target, the deposited film were either amorphous or had very small crystalline grains for all the oxygen pressure values used in this study. The diffraction patterns shown in Fig. 1 clearly indicate that the ablated Ti atoms from the target interacted with the ambient oxygen atoms and resulted in the deposition of a titanium oxide film on the surface of the substrate.

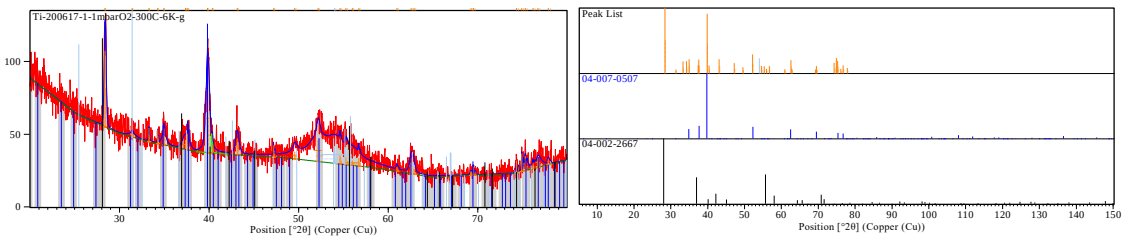


Figure 3. Identification of the XRD peaks present in the diffraction pattern acquired from the film deposited at 1 mbar O_2 from the Ti target

Table I. Results of the identification of crystalline compounds present in the film deposited at 1 mbar O_2 from the Ti target

No.	Ref. Code	Compound name	Chemical formula	Score	Color
1	04-007-0507	Titanium Oxide	Ti_3O	37	Blue
2	04-002-2667	Titanium Oxide	TiO_2	31	Black

Reference code 04-007-0507 corresponds to a low oxygen content titanium oxide with a hexagonal structure (P312, a=5.1418 Å, c= 14.3080 Å), which has XRD patterns very similar to those of metallic Ti. Reference code 04-002-2667 corresponds to rutile, TiO_2, which has a tetragonal structure (P42/mnm, a=4.4920 Å, c= 2.8930 Å). Other oxides could also be present, at lower concentration.

Images of the morphology of the deposited film surfaces obtained using scanning electron microscopy are shown in Figures 4 to 7. It can be noticed that, generally, the surface of the films deposited from the TiO_2 target (see Figs 4 and 5) was rather smooth with some droplets, a typical drawback of the PLD grown films at macroscale. A higher density of droplets or residue was observed on the surface of the films grown at a pressure of 0.1 mbar. At a much larger magnification scale, the surface of the deposited films appears nanostructured, with grains about 20 nm and 40 nm for pressures of 1.0 and 0.5 mbar, respectively, while for the pressure of 0.1 mbar the surface appears smooth, without many details. The nanostructuring was much stronger for the sample deposited at a pressure of 0.5 mbar O_2, the surface having a rougher appearance than the other studied surfaces

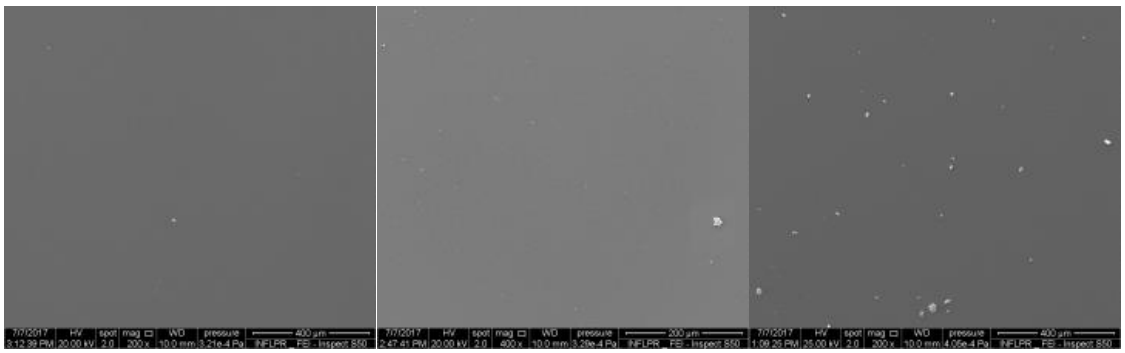


Figure 4. General SEM images of the films deposited from the TiO_2 target at pressures of 1.0, 0.5 and 0.1 mbar O_2, from left to right.

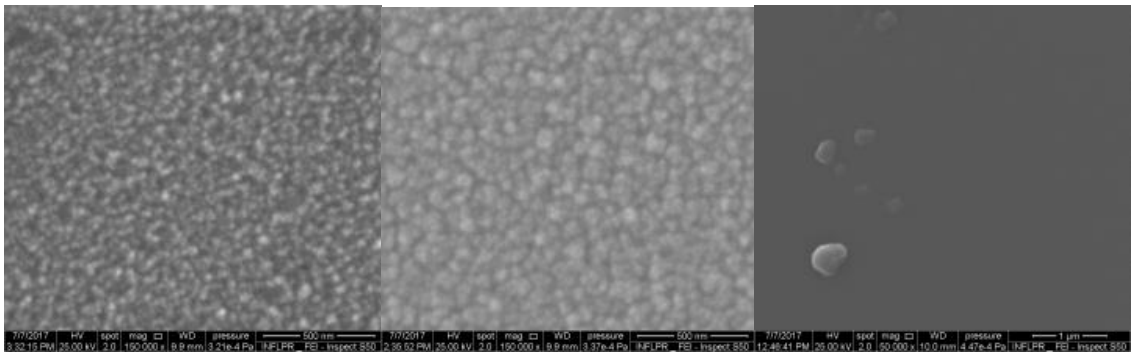


Figure 5. High-resolution SEM images on the surfaces of the thin films deposited from the TiO_2 target at pressures of 1.0, 0.5 and 0.1 mbar O_2, from left to right.

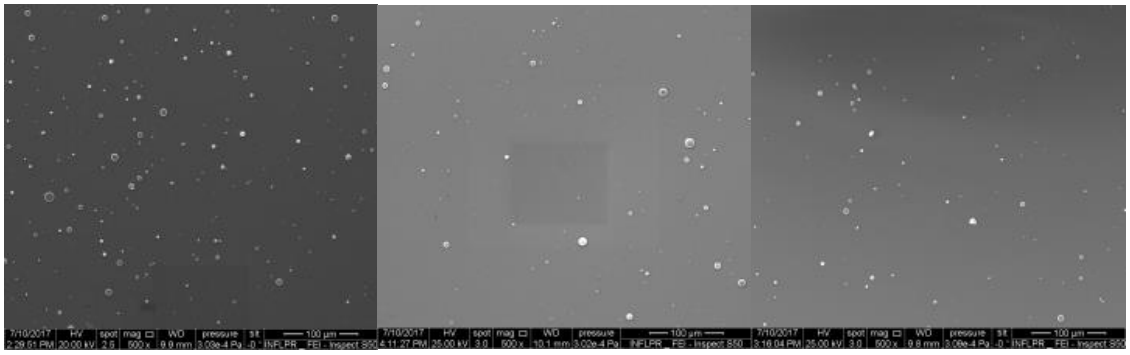


Figure 6. General SEM images of the films deposited from the Ti target at pressures of 1.0, 0.5 and 0.1 mbar O_2, from left to right.

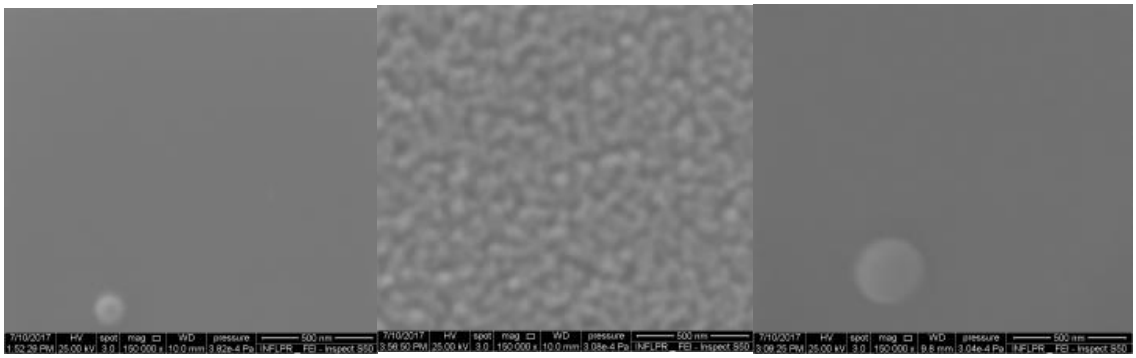
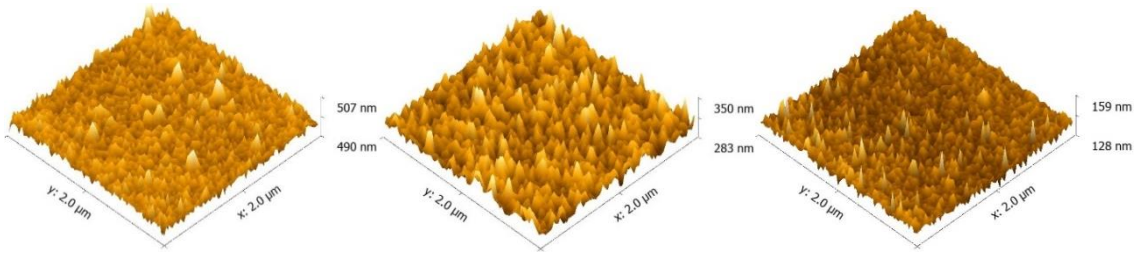


Figure 7. High resolution SEM images on the surfaces of the thin films deposited from the Ti target at 1.0, 0.5 and 0.1 mbar O_2 from left to right.

SEM investigations of film surfaces deposited from the Ti target (Figs 6 and 7) revealed a much higher density of droplets for all three O_2 pressures used. High resolution images showed that in between droplets, the surface was very smooth for films deposited at 1.0 and 0.1 mbar of O_2 while a nanostructured surface was observed for the film grown under 0.5 mbar pressure, similar in size and shape to those obtained at the same pressure when using the TiO_2 target.

The results of EDS analyzes revealed the presence of Ti and O in the films. Due to very low thickness of these films, the EDS spectra were dominated by the Si signal from substrate and C (external contamination) and it was not possible to accurately quantify their composition



a) **b)** **c)**

Figure 8. AFM images of the films deposited from the Ti target at 1.0 mbar (a), 0.5 mbar (b) and 0.1 mbar O_2 (c)

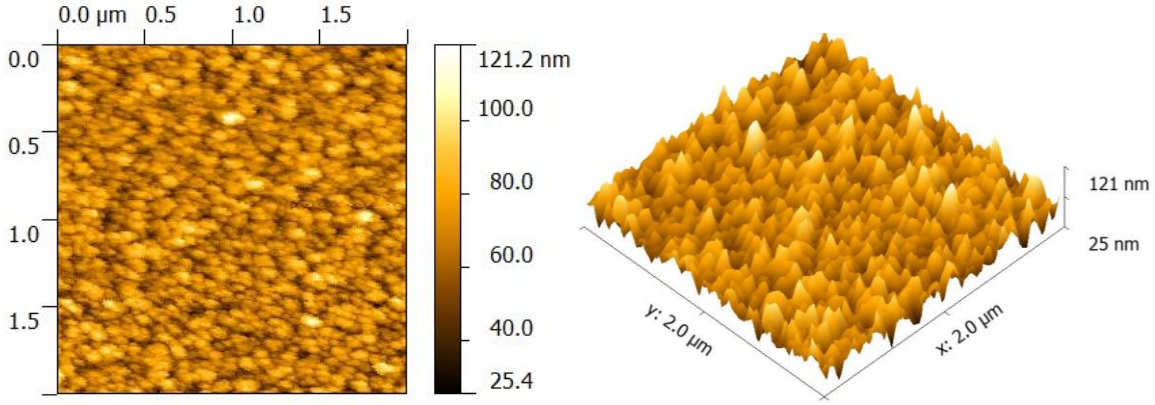


Figure 9. Two-dimensional (a) and three-dimensional (b) AFM images of the titanium oxide film surface deposited from the TiO_2 target at 0.5 mbar O_2.

AFM investigations of the deposited thin film topography revealed relatively smooth, textured and nanostructured surfaces for both targets, Ti (Figs 8a-8c) and TiO_2 (Fig. 9). In addition, higher values of roughness parameters were confirmed for film surfaces deposited in O_2 at pressures of 0.5 mbar versus 1.0 or 0.1 mbar. The parameters were evaluated by processing the images shown in Figures 8 and 9 and gave values of Ra of the order of several nanometers, 6-7 nm for the films grown under 0.5 mbar O_2 from the Ti target and 7.5-8.5 nm respectively for the TiO_2 target, significantly higher than the values between 1.5-2.0 nm for films grown using both targets under 1.0 or 0.1 mbar O_2. Similarly, higher Rms values (11-12 nm) were found for films grown at 0.5 mbar pressures than only a few nanometers in all other cases.

The XPS wide range spectra acquired from the surface of the films deposited at a pressure of 0.1 mbar O_2 from the two targets are shown in Fig. 10. The observed peaks were identified as belonging to Ti and O. The C 1s peak, located at 284.6 eV, was caused by surface contamination in the environment and used to calibrate the observed binding energies. It can be seen that although the targets were different, the chemical composition of the film surfaces, corresponding to a titanium oxide, was very similar even for the lowest oxygen pressure used in this study

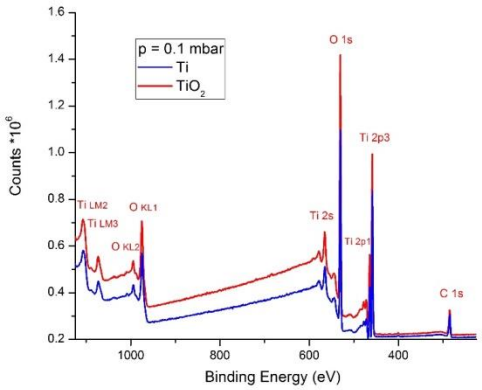


Figure 10. Survey XPS spectra acquired from films deposited at a pressure of 0.1 mbar O_2 from Ti and TiO_2 target.

From the high resolution XPS spectra acquired for Ti 2p (Fig 11a) and O 1s (Fig 11b) regions on films deposited from both targets, it was found that the shape and position of the peaks were almost identical, which implied the presence of the same chemical compound. According to literature [16-18], the Ti $2p_{3/2}$ and O 1s measured binding energies of 458.7 eV and 530.0 eV, respectively, correspond to a TiO_2 compound. If there were differences in the chemical composition of the deposited films, it would have been expected to firstly appear for the lowest oxygen pressure used during deposition, where the role of the ablated target chemical composition in determining the chemical composition of the film is most important

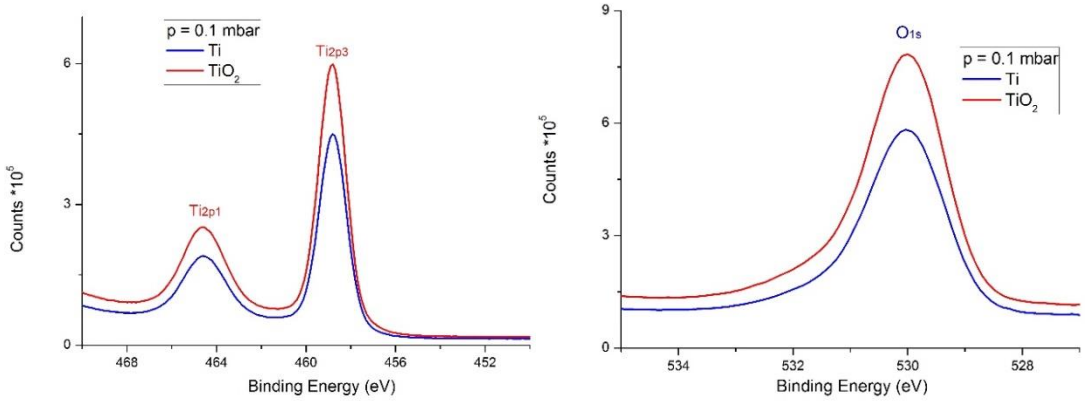


Figure 11. High-resolution Ti 2p and O 1s XPS spectra acquired from samples deposited at a pressure of 0.1 mbar O_2 from both targets (Ti and TiO_2).

CONCLUSIONS

The pulsed laser ablation technique in a reactive atmosphere of O_2 has been used for the deposition of titanium oxides thin films from Ti or TiO_2 targets at 300 ^oC. Grazing incidence X-ray diffraction studies have indicated that films are generally amorphous or nanocrystalline, with nanometric size grains. The film deposited from the Ti target at a pressure of 0.1 mbar, where the bombardment of the substrate with high energetic atoms and ions was the most intense, was the only well-crystallized film. The analysis of diffraction patterns indicated the presence of a mixture of titanium oxides, with Ti_3O and rutile TiO_2 being clearly identified. Scanning electron microscopy and atomic force microscopy studies showed that the morphology and topography of the deposited film surfaces can be controlled by the choice of target and variation of O_2 pressure during deposition. The amount of sub-micrometric droplets strongly depends on the nature of the target, being much higher for the films deposited from the Ti metallic target than from the TiO_2 target. The surface of the films in the droplets-free areas appeared very smooth for pressures of 1 mbar or 0.1 mbar O_2, while at a pressure of 0.5 mbar O_2 a nanostructure effect resulting in the growth of grains up to 40 nm was observed. XPS investigations showed a similar chemical composition of the films surfaces deposited for both targets and all O_2 pressures used in this study. In conclusion, the PLD technique is useful for obtaining titanium oxide films with a controlled surface morphology, with potential for application to oxidized films doped with bioactive ions for localized activation.

Acknowledgments

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