Thin TiO₂ films deposited by implantation and sputtering in RF inductively coupled plasmas

R Valencia-Alvarado¹, A de la Piedad-Beneitez², R López-Callejas¹², S R Barocio¹, A Mercado-Cabrera¹, R Peña-Eguiluz¹, A E Muñoz-Castro¹, B G Rodríguez-Méndez¹ and J M de la Rosa-Vázquez³

¹Instituto Nacional de Investigaciones Nucleares, Plasma Physics Laboratory, AP 18-1027, 11801 México DF, Mexico
²Instituto Tecnológico de Toluca, AP 890, Toluca, Estado de México, México
³ESIME-Zacatenco-IPN, AP 07738, México DF, Mexico

Email: raul.valencia@inin.gob.mx

Abstract: The achievement of titanium dioxide (TiO₂) thin films in the rutile crystalline phase is reported. The samples result from the implantation of oxygen ions of Ti in argon/oxygen plasma generated by inductively coupled RF at a commercial 13.56 MHz frequency. Simultaneously, a sputtering process is conducted on the titanium target in order to produce TiO₂ thin films in the anatase phase over silicon and glass substrates. Both implantation and sputtering processes shared the same 500 W plasma with the target, polarized between 0 and -3 kV. The substrates were placed between 2 and 3 cm from the target, this distance being found to be determinant of the TiO₂ deposition rate. The rutile phase in the target was obtained at temperatures in the order of 680 °C and the anatase (unbiased) one at about 300 °C without any auxiliary heating. The crystalline phases were characterized by x ray diffraction and Raman spectroscopy. The morphology and average roughness were established by means of scanning electronic and atomic force microscopy, whereas the reaction products generated during the oxidation process were analyzed by mass spectrometry. Finally, the stoichiometric composition was measured by means of X-ray photoelectron spectroscopy.

1. Introduction

Today, thin titanium dioxide (TiO₂) films attract considerable interest of multiple research groups due to a vast number of useful properties, particularly in photocatalytic applications, water purification, air treatment and the development of biocompatible coatings of human implants [1-4]. In the biomedical sector, TiO₂ films are considered an especially biocompatible material, some of whose effects on the human body have recently been compiled by Ellingsen and Lyngstadaas [5], and a decisive factor in the development of bioengineering materials, as described by Ratner and Oshida [6-7]. The ecological value of these films arises from their photo-catalytic qualities, as described by, e.g., Sakai and Tavares [8-9].

In their investigations, Anpo [10] has found that the photo-catalytic activity of TiO₂ increases when the particle diameter is reduced under 10 nm. Liu [11] has pointed out that an increase in the few nm thickness of a titanium oxidized coat, naturally found over titanium samples, clearly improves the TiO₂ bioactivity. The photo-catalytic properties of TiO₂ in the anatase and rutile phases were initially reported by Fujishima and Honda in 1972 [12]. Among the plasma processing techniques connected...
with film deposition, one finds chemical vapor deposition [13], electron-beam evaporation [14], ion-beam assisted deposition [15], RF reactive magnetron sputtering [16], plasma source ion implantation [17], and inductively coupled plasma-assisted sputtering [18-20].

This work describes the simultaneous growth of anatase and rutile by means of an implantation/diffusion and sputtering process in inductively coupled radio frequency plasma of calibrated argon/oxygen mixtures without post annealing.

2. Setup

The implantation/diffusion and sputtering process has been conducted within a Pyrex-like glass cylindrical vessel, 50 cm long and 20 cm in diameter, around which a 3 mm diameter copper pipe antenna is wound helicoidally. The plasma is generated from calibrated argon/oxygen (80%/20%) gas mixtures by transferring 500 W to the antennae through an automatic coupling network from a 1.2 kW RF generator where induction works as in a transformer with the plasma playing the role of a secondary coil. Figure 1 exhibits this experimental set up, with its substrate holder, reported elsewhere [18-19].

Figure 1. Diagram of the plasma reactor.

The vessel was evacuated at pressures <5×10^{-6} mbar by a turbomolecular pump operating at 500 l/s. After attaining the base pressure, the work argon/oxygen mixture was admitted through a precision leak valve up to 5×10^{-2} mbar pressure at which the highest plasma density is obtained. Commercially pure titanium (CpTi) cylindrical samples, 9 mm in diameter and 5 mm long, were introduced to the vessel and oxidized by the plasma during periods up to 5 hours by means of a sputtering and implantation/diffusion process. The substrate temperature was kept about 250 °C by the action of the plasma alone and when the Ti sample is biased, this temperature was raised to 300 °C by the sputtering action. When the samples were biased at -3000 V DC, the ion bombardment increased the sample temperature to around 680 °C, as measured by a commercial K type thermocouple. Insulation between the biased piece and the thermocouple-reading meter was provided by an isolation amplifier. Electrically floated silicon and glass substrates were placed on the holder 2 and 3 cm away from the CpTi sample, becoming thermalized between 250 °C (by the plasma alone) and 300 °C (during the oxidation process).

Both the titanium targets and the glass/silicon substrates were finally taken out and cut in cross sections in order to measure their TiO2 film depth. XRD and Raman spectroscopy techniques, used to characterize the oxidized samples, indicate the growth of the anatase and rutile phases. XRD spectra were used to estimate the mean crystallite size from the Scherrer equation. The surface morphologies and titanium/oxygen atomic percentage on sample and silicon sputtering films were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The stoichiometric
composition was measured thanks to X-ray photoelectron spectroscopy (XPS) and the reaction products during the oxidation process by means of a residual gas analyzer (RGA).

3. Results and discussion

Figure 2 presents SEM images of the cross section of titanium and the growth dioxide (TiO₂) film resulting from 5 h processing. Figure 2(a) corresponds to silicon substrate coating with TiO₂ by sputtering. The layer is in the order of 2 μm and the rate lies between 5 and 7 nm/min. Figure 2(b) shows the growth of the crystalline anatase phase on the silicon substrate.

![SEM Images](image)

Figure 2. Layer depth: (a) implantation/diffusion, (b) growth of the anatase phase.

Looking for an estimate of its chemical composition, the coating was analyzed using 15 kV electron dispersive spectroscopy (EDS) in conjunction with the SEM. In a typical silicon substrate, the atomic percentages found were 75 at % of oxygen, 23 at % of titanium and 2 at % silicon; similar percentages were identified in the sample (73 at % oxygen and 27 at % titanium), indicating the chemical composition of the film albeit not the stoichiometric ratio of two parts of oxygen per one of titanium. The sample surfaces and substrates changed in color during the oxidation process according to the temperature, gas pressure and bias voltage of the treatment. The colors appear to be directly related to the composition of the oxide formed as well as to the thickness of the oxide layer. Initially, the titanium sample surface acquires a dark blue shade which turns silvery and, by the end of the process, goes into lead grayish. This evolution suggests oxidation in the rutile phase. The case of the glass and silicon substrates involves the appearance of a two color circular pattern ranging from purple red to olive green, pointing to the existence of the anatase phase. The multiplication of these concentric strips can be related to the increase of the deposited film depth as the processing time goes by.

The new crystalline phases of the titanium sample surface modified by implantation and diffusion have been analyzed by X-ray diffraction using CuKα radiation within a 2θ = 20-90° scan range. Figure 3(a) displays the X-ray diffraction patterns of the 5×10⁻² mbar sample, this spectrum reveals that the rutile phase is present at 2θ = 27.8°, 36.5°, 41.6°, 44.4°, 54.8°, 56.9°, 62.9°, 69.3° and 70.0°. Given the Scherrer equation, the grain size of the TiO₂ film in the rutile phase implanted with the preferential crystalline orientation (110) was 58 nm. Figure 3(b) shows the Raman spectrum from the same titanium implanted and diffused displaying the rutile peaks.

The thin films grown on the glass/silicon substrates have been characterized by Raman spectroscopy. The spectrum from glass (figure 4(a)) reveals the presence of the anatase phase, interestingly enough, grown at temperatures below 350 °C. The Raman amplitudes at wavelengths 149 and 399 cm⁻¹ enabled to calculate the relative amount of anatase in the TiO₂ films. The resulting ~5
nm/min deposition rates are considered acceptable in this kind of oxidation process. Figure 4(b) describes a similar growth on silicon.

![Figure 3](image1.png)  ![Figure 4](image2.png)

**Figure 3.** (a) X-ray diffraction patterns at $5 \times 10^{-2}$ mbar and (b) the Raman spectrum from oxidized sample.

**Figure 4.** Raman spectra from the films deposited on glass (a) and silicon (b).

Figure 5 displays the XRD spectrum from the film deposited on a silicon substrate, showing the anatase phase peaks, which validates the Raman spectrum in figure 4.

Figure 6 displays the AFM image of TiO$_2$ film deposited on the silicon substrate corresponding to the anatase phase. This film presents root mean squared (RMS) values of 1.6 nm indicating the existence of a smooth surface.

Figure 7(a) show typical resolution XPS spectra of Ti$_2$p and O$_{1s}$, respectively, from the anatase TiO$_2$ film. The Ti$_2$p region is split in 2p$_{3/2}$ and 2p$_{1/2}$ doublet peaks located at 458 and 464 eV binding energy values. This doublet corresponds to Ti(IV). The figure 7(b) shows the spectra from the O$_{1s}$ region taken from the anatase TiO$_2$ film surface. The XPS spectrum binding energy of the main O$_{1s}$ peak appeared at 530 eV. This peak can be associated to the typical stoichiometric oxide of TiO$_2$.

The analysis of the reaction products generated by the oxidation process has been carried out by means of a mass spectrometer coupled to a CUADREX 200 Leybold quadrupole gas analyzer sensor and a turbomolecular vacuum system, resulting in a mass resolution of 1 atomic mass unit. The array was connected through an adaptor to the discharge reactor outlet. The atomic masses of the reaction products...
products generated by the plasma implantation and sputtering were detected as: Ti$^{+}$ with mass 48, TiO$_2$$^+$ with mass 80, Ar with mass 40, as well as masses 16 and 32 corresponding to atomic (O$^+$) and molecular (O$_2$$^+$) oxygen.

**Figure 5.** XRD-Spectrum from the film grown on silicon revealing the anatase phase film deposited on the silicon substrate.

**Figure 6.** AFM-image of the surface of TiO$_2$.

**Figure 7.** (a) Ti2p from the anatase phase deposited on silicon substrate, (b) O1s from the anatase phase deposited on silicon substrate.

4. Conclusions
An inductively coupled plasma source supplied by a specifically designed and built RF generator has allowed obtaining TiO$_2$ films in the rutile phase by means of the implantation/diffusion of oxygen atoms into a titanium target while, at the same time, films in the anatase phase were developed by titanium sputtering with argon ions. Atomic concentration rates above 2 are due to the presence of TiO-like oxides in addition to the TiO$_2$ An oxygen atomic percentage of 55 at %, versus a 35 at % of titanium leads to a stoichiometry well below to 2. By contrast, percentages on the glass are 70 at % vs 23 at %, respectively, which can be attributed to the silicon oxide composition of the glass itself. Color changes of the samples during their implantation/diffusion processing suggest the evolution of their composition and structure. Thus, a transition from deep blue to silvery white is typically achieved by the end of the process, frequently accompanied by iridescent concentric circular patterns whose number could be related with the deposited film depth. The deposited anatase phase did not require
any additional annealing after the oxidation. The RGA technique can be considered as an efficient methodology in the optimization of crystalline growth of TiO₂ films on both titanium samples and silicon or glass substrates.

Acknowledgements
This project has been partially funded by CONACyT, México. The authors are grateful to Dr. Manuel Espinoza and Mr. Jorge Pérez, for their technical support in the XRD, EDS, AFM diagnostics; and XPS diagnostic to Cuauhtémoc Gutiérrez Rivera and Ma Eugenia Camacho López. The technical assistance received from Pedro Ángeles Espinoza, María Teresa Torres M. and Isaias Contreras Villa is much appreciated.

References
[1] Baroch P, Musil J, Vlcek J, Nam K H and Han J G 2005 Surf. & Coat. Tech. 193 107-11
[2] Li Z G, Wu Y X and Miyake S 2009 Surf. & Coat. Tech. 203 3661-8
[3] Chu P K 2007 IEEE Trans. on Plasma Sci. 35-2 181-7
[4] Lee S H, Kim H W, Lee E J, Hi L H and Kim H E 2006 J. of Biomaterials Applications 20 195-208
[5] Ellingsen J E and Lyngstadaas S P (editors) 2003 Bio-Implant Interface (Boca Raton: CRC Press LLC)
[6] Ratner B D, Hoffman A S, Schoen F J and Lemons J E (editors) 2004 Biomaterials Science, An Introduction to Materials in Medicine 2nd Edition (Elsevier Academic Press)
[7] Oshida Y 2007 Bioscience and Bioengineering of Titanium Materials (Oxford: Elsevier)
[8] Sakai T, Kuniyoshi Y, Aoki W, Ezone S, Endo T and Hoshi Y 2008 Jpn. J. Appl. Phys. 47 6548
[9] Tavares C J, Vieira J, Rebouta L, Hungerford G, Coutinho P, Teixeira V, Carneiro J O and Fernandes A J 2007 Mater. Sci. Eng. B 138 139
[10] Anpo M, Shima T, Kodama S and Kubokaa T 1987 J. Phys. Chem. 91 4305
[11] Liu X, Chu P K, and Ding C 2004 Mater. Sci. Eng. R47 49
[12] Fujishima A and Honda K 1972 Nature 238 37
[13] Sun H, Wang C, Pang S, Li X, Tao Y, Tang H and Liu M 2008 J. Non-Cryst. Solids 354 1440
[14] Habibi M H, Talebian N and Choi J H 2007 Dyes and Pigments 73 103
[15] Yang C, Fan H, Xi Y, Chen J and Li Z 2008 Appl. Surf. Sci. 254 2685
[16] da Silva L L G, Ueda M, da Silva M M and Codaro E N 2006 IEEE Trans. on Plasma Sci. 34-4/1 1141
[17] Okimura K and Furumi T 2004 Jap. J. Appl. Phys. 43-5B L655
[18] Valencia-Alvarado R, de la Piedad-Beneitez A, López-Callejas R, Barocio S R, Mercado-Cabrera A, Peña-Eguiluz R, Muñoz-Castro A E and de la Rosaq-Vázquez J 2009 Vacuum 83 264
[19] Valencia-Alvarado R, de la Piedad-Beneitez A, de la Rosaq-Vázquez J, López-Callejas R, Barocio S R, Mercado-Cabrera A, Peña-Eguiluz R and Muñoz-Castro A E 2010 Int. J. Nanomanufacturing 5 62-8