Titanium oxidation by rf inductively coupled plasma

R Valencia-Alvarado¹, A de la Piedad-Beneitez², R López-Callejas³, R Barocio¹, A Mercado-Cabrera¹, R Peña-Eguiluz³, A E Muñoz-Castro³, B G Rodríguez-Méndez¹, and J M de la Rosa-Vázquez³

¹ Instituto Nacional de Investigaciones Nucleares, Plasma Physics Laboratory, AP 18-1027, 11801, México, D.F., Mexico
² Instituto Tecnológico de Toluca, AP 890, Toluca, Mexico, Mexico
³ ESIME-ZACATENCO-IPN, 07738, Mexico, D.F., Mexico

E-mail: raul.valencia@inin.gob.mx

Abstract. The development of titanium dioxide (TiO₂) films in the rutile and anatase phases is reported. The films have been obtained from an implantation/diffusion and sputtering process of commercially pure titanium targets, carried out in up to 500 W plasmas. The experimental outcome is of particular interest, in the case of anatase, for atmospheric pollution degradation by photocatalysis and, as to the rutile phase, for the production of biomaterials required by prosthesis and implants. The reactor employed consists in a cylindrical pyrex-like glass vessel inductively coupled to a 13.56 MHz RF source. The process takes place at a 5×10⁻² mbar pressure with the target samples being biased from 0 to -3000 V DC. The anatase phase films were obtained from sputtering the titanium targets over glass and silicon electrically floated substrates placed 2 cm away from the target. The rutile phase was obtained by implantation/diffusion on targets at about 700 °C. The plasma was developed from a 4:1 argon/oxygen mixture for ~5 hour processing periods. The target temperature was controlled by means of the bias voltage and the plasma source power. The obtained anatase phases did not require annealing after the plasma oxidation process. The characterization of the film samples was conducted by means of x-ray diffraction, scanning electron microscopy, x-ray photoelectron spectroscopy and Raman spectroscopy.

1. Introduction

Titanium dioxide (TiO₂) thin films are of considerable interest because of their outstanding chemical inertness, thermal stability, corrosion resistance, mechanical, optical, electrical, and electronic properties, as well as excellent photocatalytic applications in water purification, the treatment of air and the development of biocompatible coatings in human implants [1-7]. Titanium dioxide structured thin films have been processed using a wide range of deposition and implantation methods such as sputtering [8], chemical vapor deposition [1,5], sol-gel [4], laser ablation [9], plasma immersion ion implantation [10], inductively coupled plasma [2, 11], or atmospheric pressure plasma spraying [6] among other techniques.

The reactive direct current magnetron sputtering may well be the most employed method to obtain TiO₂ structures as it allows the control of the composition and properties of the TiO₂ films through the deposition conditions [12-13]. This control leads to get high quality films with thickness uniformity and controlled stoichiometry. TiO₂ biocompatibility properties, widely used in orthopedic and dentistry surgical implants, depend on the treated layer being thick enough. The photocatalytic property of titanium dioxide takes place when it is illuminated by photons with energies higher than the TiO₂ band gap one. This process generates electron-hole pairs required for the photocatalytic action.

In this paper we describe the simultaneous growth of thin films in the anatase and rutile phases through an implantation/diffusion and sputtering process in an inductively coupled radio frequency plasma of calibrated argon/oxygen gases mixtures without post annealing. The influence of both the deposition time, and bias on the film morphology, composition and structure have been analyzed using different techniques such as x-ray diffraction (XRD), scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The aim of the experiment is studying the
feasibility of obtaining anatase and rutile TiO$_2$ films as a function of target and substrates temperatures.

2. Experimental procedures

The implantation and sputtering process was conducted within a pyrex-like glass cylindrical vessel 50 cm long and 20 cm in diameter around which a 3 mm diameter copper pipe antennae is wound helicoidally. The plasma is developed 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. Fig. 1 exhibits this experimental set up, with its substrate holder, reported elsewhere [14-15].

![Fig. 1. Diagramme of the plasma reactor](image)

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. Titanium commercially pure (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 samples were biased up to -3000 V DC. In the unbiased case, the sample temperature was kept about 250 °C by the action of the plasma alone and no significant evidence of either sputtering or oxidation was found. In the opposite -3000 V DC case, the ion bombardment raises the sample temperature around 700 °C, as measured by a commercial K type thermocouple. Insulation between the biased piece and the thermocouple-reading meter is provided by an isolation amplifier. The electrically floated silicon and glass substrates were placed on the holder 2 cm away from the CpTi sample, becoming thermalised between 250 °C (by the plasma alone) and 290 °C, during the oxidation process. Both the titanium samples target and the glass/silicon substrates were finally cut in cross sections in order to measure their TiO$_2$ film depth. XRD and Raman spectroscopy techniques, used to characterize the oxidised 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 SEM and XPS give ratio for purely TiO$_2$ stoichiometry.

3. Results

The depth and surface morphology of implantation and deposited films, so much in the titanium target just as on glass and silicon substrates were analyzed by SEM. Figs. 2.(a) and 2.(b) shows images of
cross sections of titanium dioxide thin films resulting from 5 hours processing. Fig. 2.a represents the case of implantation/diffusion when the titanium target was biased around -3000 V DC for 5 hour; the layer depth is between 14 and 20 µm with an atomic concentration rate of 73 % at of oxygen and 27 % at titanium. Fig. 2.(b) corresponds to silicon coating by sputtering. The layer is in the order of 2.5 µm and the deposition rate ~6 nm/min. Fig. 2.(c) shows the anatase phase microstructure on the silicon substrate.

![Layer depth: (a) implantation/diffusion, (b) silicon coating by sputtering and (c) anatase phase microstructure.](image)

The coating was analysed using the technique electron dispersive spectroscopy (EDS) in conjunction with the SEM. The atomic percentages found in average in silicon were ~55 % at. of oxygen and 35 at. % of titanium. The other hand, different percentages were identified in the glass (SiO$_2$+CaO+Na$_2$O) samples (70 at. % oxygen and 23 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 surface and substrates change in colour during the oxidation process according to the temperature and the bias voltage of the treatment. It is observed that the colours are directly related to the composition of the oxide formed as well as to the thickness of the oxide layer. As the bias voltage varies along the 0 to -3000 V DC range, the titanium sample surface typically acquires a dark blue shade which turns silvery and, by the end of the process, into opaque lead grey. This evolution indicates, in an empirical way, the achievement of oxidation in the rutile phase.

Figure 3 shows the relative atomic composition of the anatase phase on a silicon substrate which was analysed with EDS. The spectrum point out the presence of stainless steel (Fe, Ni, Cr) attributable to sputtering from the sample holder.

![Fig. 3 EDS analysis of film anatase deposited on silicon substrate](image)

The case of the glass and silicon substrates involves the appearance of a multicoloured circular pattern, ranging from purple red to olive green, pointing to the existence of crystalline phases acting as prisms.
Furthermore, the multiplication of such concentric strips suggests an increase of the crystalline deposited film depth as the processing time goes by. Finally, the temperature level of the treatment excludes most other phases than the anatase one.

The new crystalline phases of the titanium sample surface modified by implantation and diffusion have been analysed by XRD using Cu Kα radiation within a 2θ=20° to 90° scan range. Fig. 4 displays the XRD patterns of the 5×10⁻² mbar mixture pressure sample at -3 kV of target bias. This spectrum reveals that the rutile phase is present at R(110)=27.7°, R(101)=36.2°, R(111)=41.5°, R(211)=54.6°, R(301)=70° and, for the titanium target Ti(100)=35.1, Ti(002)=38.4, Ti(101)=40.3, Ti(102)=52.6, Ti(110)=62.8, Ti(200)=74.3, Ti(112)=76.2 and Ti(201)=77.4. Given the Scherrer equation, the grain size of the TiO₂ film in the rutile phase implanted with the preferential crystalline orientation (110) was 44 nm.

![Figure 4. X-ray diffraction patterns at 5×10⁻² mbar from de oxidized target.](image)

The deposited films on the glass/silicon substrates were characterized by Raman spectroscopy. The spectrum from glass showed in Fig. 5.(a), confirms the presence of the anatase phase grown at temperatures below 300 °C it is agree with Löbl [16] and Mändl [17]. The Raman amplitudes at wavelengths 150.3, 400.6, 523.5 and 643.2 cm⁻¹ correspond to the anatase phase. The resulting ~6 nm/min deposition rate is considered acceptable in this kind of oxidation process. Fig. 5.(b) describes a similar growth on silicon. The differences at wave lengths between Figs 5.(a) and 5.(b), are due to the microstructural from the grain size. Similar results have been reported by de Vicente and Oja [18-19]. A Thermo Scientific* K-Alpha spectrometer was applied to the characterization of TiO₂ films deposited on glass/silicon substrates. The high resolution XPS spectrum (not shown) corresponding to the silicon surface was revealed by a main doublet composed of two symmetric peaks situated at 458 eV and 464 eV corresponding to Ti2p₁/₂ and Ti2p₃/₂ respectively, and 529 eV for O1s.

![Figure 5. Raman spectra of anatase phase on substrates: a) glass, b) silicon.](image)

4 Conclusions
An inductively coupled plasma source supplied by a specifically designed and built RF generator has allowed obtaining TiO₂ 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. Colour 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 can be related with the deposited film depth. The deposited anatase phase did not require any additional annealing after the oxidation.

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