Rutile titanium dioxide films deposited with a vacuum arc at different temperatures

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\textbf{Abstract.} Rutile crystalline phase of TiO\textsubscript{2} has been one of the most investigated materials for medical applications. Its implementation as a surface layer on biomedical implants has shown to improve hemocompatibility and biocompatibility. In this work, titanium dioxide coatings were deposited on glass and steel 316L substrates using cathodic arc deposition. The coatings were obtained at different substrate temperatures; varying from room temperature to 600ºC. The crystalline structure of the films was identified by glancing angle X-ray diffraction. Depending on the substrate material and on its temperature during the deposition process, anatase, anatase+rutile and rutile structures were observed. It was determined that rutile films can be obtained below 600 ºC with this deposition method.

1. Introduction

Titanium dioxide has been widely studied due to its outstanding physical and chemical properties. This compound is known to exhibit three main polymorphs: rutile, anatase and brookite. Rutile is the only thermodynamically stable phase at all temperatures, while anatase phase can be retained when it is nanostructured. Since its high refractive index, rutile films are used as optical coating in lenses and optical fibers. In the last few years, the most investigated topic on rutile thin films has been its implementation as a surface layer on biomedical implants; it has been found that these coatings improve hemocompatibility as well as biocompatibility [1,2]. It was demonstrated that when the structure of a TiO\textsubscript{2} layer changes from anatase to rutile, the dissolution rate of metallic ions in a simulated body fluid can be substantially decreased [3]. Rutile has been shown to be more chemically stable than anatase at both low and high pH levels [4].

TiO\textsubscript{2} films have been prepared by a great variety of deposition techniques such as sol-gel [5], chemical vapor deposition [6], evaporation [7], various reactive sputtering techniques [8], ion beam assisted process [9], atomic layer deposition [10], pulsed laser deposition [11] and cathodic arc deposition (CAD) [12]. In cathodic arc discharges, a metallic plasma jet generated from the cathode surface flies away from it, penetrating into the chamber volume, with energies typically in the range 30-100 eV. If a substrate is located facing the plasma jet, its surface is coated with a metallic film; the production of compound films being achieved when a reactive neutral gas flows into the discharge.
chamber. Phase formation during deposition by CAD is mainly determined by the substrate temperature and the ion energy, yielding amorphous TiO$_2$ at low temperature and low ion energy. Therefore, synthesizing crystalline TiO$_2$ by CAD requires either heating or biasing the substrate during deposition. According to Löbl diagram, rutile phase can be achieved when in the process the particle energy is higher than 10 eV at room temperature or beyond 800°C with thermal energies [13]. Crystalline TiO$_2$ coatings can also be attained by annealing amorphous films, requiring an annealing temperature higher than 800°C for rutile transformation. However, this sort of treatment can generate tensions in the film that may cause cracking or even delamination.

The purpose of this work was to obtain rutile TiO$_2$ films crystallized directly in the growth stage, avoiding the subsequent annealing. The crystalline structure of films grown at different temperatures on steel 316L and glass substrates was studied.

2. Experimental details

The vacuum arc device used to synthesize the films, described in detail in a previous work [14], is schematically shown in figure 1. The arc was run with a current of 120 A between a Ti cathode and a grounded vacuum chamber serving as anode. The system was operated in an oxygen atmosphere with a continuous incoming gas flux of 63 sccm and a working pressure in the range of 2–5 Pa. Substrates were located at 30 cm from the cathode surface on a heater, which allowed fixing the temperature with an accuracy of 5%. TiO$_2$ samples were obtained at different temperatures ranging from room temperature to 570°C. The temperature was measured with a thermocouple located on the front surface of the sample that was coated. The heater was electrically isolated of the chamber. Samples were exposed to the discharge during 2 min. Substrates were square pieces of 3×3 cm$^2$ of glass and of stainless steel 316L.

In order to evaluate the deposited mass, the samples were weighed before and after deposition using a Ohaus analytical balance, model AS200. The crystalline structure of the films was identified by X-ray diffraction (XRD) using a Philips PW 3710 diffractometer with a CuK$_\alpha$ radiation source. It was operated with glancing angle geometry by using a Philips thin film attachment, with an incidence angle of 1°.

![Figure 1. Schematic diagram of the employed CAD device.](image)

3. Results and discussion

The deposited mass on the substrates was ~ 1.1 mg. The film thickness was estimated to be ~ 300 nm, assuming a film density of 3.8 g/cm$^3$, this value corresponding to the density reported for amorphous and anatase films [15].

Figure 2 shows XRD patterns obtained from TiO$_2$ films deposited on glass substrates at 25, 360, 400, 450, 500 and 560°C. At room temperature the film grew amorphous. The peak associated to the
(101) plane of the anatase phase was visibly detected in the diffractograms corresponding to samples deposited at 360°C, while those deposited at temperatures in the range from 400°C up to 500°C presented both anatase and rutile phases. As the temperature increased the relative height of anatase peaks respect to rutile peaks diminished. In the case of samples obtained at 560°C only the presence of rutile structure was clearly registered. The broad elevation observed in all patterns for 2θ in the range 20-30 deg corresponds to amorphous glass.

![Figure 2. XRD patterns of TiO₂ films grown on glass substrates at different temperatures.](image)

XRD patterns corresponding to films deposited on steel 316L are plotted in figure 3. In the same figure the diffractogram obtained from a non coated substrate is also shown. The phase transformations as functions of the process temperature observed from the diffractograms were very similar to the behavior described for the glass substrates. At room temperature just the substrate peaks were registered, indicating an amorphous film; at intermediate temperature the presence of both anatase and rutile phases was observed; and for the film grown at 570°C only the presence of rutile phase was evident. However, a difference came out comparing with glass substrate for films grown at 360°C, on steel substrate not only anatase peaks appeared in the diffractogram, but also rutile peaks were visible.

Figure 4 shows the phase diagram proposed by Löbl et al. [13] for the synthesis of different TiO₂ structures depending on growth conditions: ion energy and substrate temperature. The working region corresponding to this work - taking into account the employed temperature range and plausible values for the ion energy - is indicated in the diagram. XRD patterns obtained from samples grown at 360°C revealed different structures for films deposited on different substrates.
Figure 3. XRD patterns of TiO$_2$ films grown on steel 316L substrates at different temperatures.

Figure 4. Phase diagram proposed by Löbl et al. [13]. The working region (temperature and energy ranges) is indicated.
Samples grown on glass presented only anatase phase, while rutile was also detected in films obtained on steel. This is in agreement with Löbl’s diagram considering that the energy range of involved ions is close to – and likely includes – the threshold for obtaining anatase or anatase+rutile. Nonetheless, it seems rutile phase can be obtained at a lower temperature on steel than on glass substrates. This fact suggests that the electrical properties of the substrate affect on the energy of the ions arriving at the surface.

4. Conclusions
The obtained results indicate that cathodic arc deposition is a capable technique to synthesize rutile TiO₂ films on glass and steel substrates. Energetic particles provided by the plasma jet ejected from the cathode allow the growth of this phase without biasing and with in-situ heating at relatively low temperatures. By changing the substrate temperature employed in the process is possible to control the proportion of rutile to anatase in the film. A subsequent annealing that may cause delamination or cracking on the films was avoided.

Acknowledgments
This work was supported by grants from Universidad de Buenos Aires and CONICET.

References
[1] Huang N, Chen Y, Luo J, Yi J, Lu R, Xiao J, Xue Z and Liu X 1994 Biomater. J.Appl. 8 404-12
[2] Larsson C, Thomsen P, Lausmaa J, Rodahl M, Kasemo B and Ericson L 1994 Biomaterials 15 1062-74
[3] Tsyganov I, Maitz M F and Wieser E 2004 Appl. Surf. Sci 235 156-63
[4] Forberg S 1986 Adv. Ceram. 20 321-7
[5] Sabate J, Anderson M A, Kikkawa H, Xu Q, Cervera-March S and Hill Jr C G 1992 J. Catal. 134 36-46
[6] Williams L M and Hess D W 1983 J. Vac. Sci. Technol. A 1 1810
[7] Fujii T, Sakata N, Takada J, Miura Y, Daitoh Y and Takano M 1994 J.Mater. Res. 9 1468-73
[8] Okimura K, Shibata A, Maeda N, Tachibana K, Noguchi Y and Tsuchida K 1995 J. Jpn. Appl. Phys. 34 4950-5
[9] Gilo M and Croitoru N 1996 Thin Solid Films 283 84-9
[10] Aarik J, Aidla A, Kiisler A-A, Uustare T and Sammelselg V 1997 Thin Solid Films 305 270-3
[11] Yoon H S, Kim S K and Im H S 1997 Bull. Kor. Chem. Soc. 18 640-3
[12] Kleiman A, Márquez A and Lamas D G 2007 Surf. Coat. Technol. 201 6358-62
[13] Löbl P, Huppertz M and Mergel D 1994 Thin Solid Films 251 72-9
[14] Márquez A, Blanco G, Fernandez de Rapp M E, Lamas D G and Tarulla R 2004 Surf. Coat. Technol. 187 154-60
[15] Prasai B, Cai B, Kylee Underwood M, Lewis J P and Drabold D A 2012 Properties of amorphous and crystalline titanium dioxide from first principles J. Mater. Sci., DOI 10.1007/s10853-012-6439-6