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## Phase Transformation of TiO<sub>2</sub> Thin Films in Function Bias Voltage

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### Abstract

Titanium dioxide thin films have been deposited on silicon (100) and 316L stainless steel substrates by cathodic arc deposition in oxygen atmosphere with a titanium cathode. The process was run at room temperature and at 300 °C, biasing the substrate with pulsed voltage (up to –10 kV) and DC voltage (up to –120 V). The crystalline structure was studied by Raman spectroscopy and X-ray diffraction. At room temperature, the films were obtained with an amorphous base with small isolated crystals of rutile and anatase. At 300 °C, with DC bias, samples grew crystalline with the presence of both anatase and rutile.

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### 1. Introduction

Titanium dioxide is a known material by having excellent chemical stability, non-toxicity and good mechanical properties (U. Diebold 2003), also it has excellent hydrophilicity (Sirghi et al. 2003) and good photocatalytic properties when irradiated with ultraviolet light (Hossain et al. 2008). Also, in recent years, it has been found that titanium oxide coatings improve biocompatibility and hemocompatibility on prosthesis (Huang et al. and Larsson et al. 1994). Onto surface of implants can be generated problems related by contamination with bacterial growing on the surface thereof during surgery, being many of them resistant to antibiotics (Costerton et al. 1994). Hence the

need for biocompatible coatings and antibacterial. Titanium dioxide in anatase phase has a high photocatalytic activity, in an aqueous medium under ultraviolet light, can induce the formation of reactive species such as  $\bullet\text{OH}$  and  $\text{O}_2^-$  (Fujishima et al. 2000) which can decompose various microorganisms, having an antibacterial effect. Furthermore, it has found that the  $\text{TiO}_2$  rutile phase may decrease the rate of dissolution of metal ions in a body fluid and is chemically more stable than the anatase phase even at high or low pH (Forberg et al. 1986). These properties make that  $\text{TiO}_2$  in both phases, a very attractive material for prosthesis coatings.  $\text{TiO}_2$  films were obtained by various growth techniques, including cathodic arc deposition (Kleiman et al. 2009). On these equipment is produces a discharge to low voltage and high current between two electrodes immersed in a vacuum chamber. Metal particles ionized and accelerated are ejected from the cathode, resulting in a jet of plasma which when it is intercepted by a substrate, is deposited on it to form a metallic coating. When the ions arrive at substrate, the energy of arrived can be varied with biasing negatively. In addition, various compounds can be obtained by injecting reactive gas into the discharge chamber during the deposition process. In this work  $\text{TiO}_2$  films were obtained using a cathodic arc employing a titanium cathode operated in an oxygen atmosphere. The purpose of this study was to obtain crystalline films combining the bias voltage with heating the substrate, for a future application on biocompatible surfaces.

## 2. Experimental Procedure

The cathodic arc system used on this synthesis of the films has been described in detail in a previous work (Márquez et al. 2004). System consists of a titanium cathode and a vacuum chamber made of stainless steel which acts as the anode of the discharge. The arc was operated at a current of 130 A in an oxygen atmosphere with a continuous flow of 63 sccm input and a working pressure of 2-5 Pa. The substrates were placed on a heater electrically insulated from the chamber, which can set the temperature with an accuracy of 5 % and is located at distance of 26 cm from the cathode surface. Samples were grown at room temperature by biasing the substrate with DC voltage (between 0 and -120 V) and pulsed biasing voltage (between 0 and -10 kV). The pulse width was 50  $\mu\text{s}$  and the frequency 200 Hz. Also the films were obtained with the DC bias maintaining the substrate at 300 ° C. The samples were exposed to the discharge for 2 min. Substrates of steel 316L and 2.5 cm diameter and silicon substrates (100) of approximately 1.5 x 1.5 cm were used which were previously cleaned with ethanol and acetone. The samples were weighed before and after deposition on an analytical balance Ohaus model AS200, in order to determine the amount of deposited mass and estimate the thickness of the films. The crystalline structure of the films was identified by X-ray diffraction (XRD), and Raman spectroscopy. Were measured XRD geometry Bragg - Brentano with a diffractometer Panalytical Empyrean detector Pixcel 3D and grazing incidence (incidence angle: 1°) on a Philips PW 3710 with copper anode ( $\text{CuK}\alpha$ ) using an accessory Philips for thin films. Raman spectra were obtained with a computer LabRAM Horiba Jobin Yvon. The morphology was observed with an optical microscope.

## 3. Results

The mass deposited on steel substrates was  $\sim 0.5$  mg in all samples, without significant differences between the samples obtained under different conditions of temperature and substrate bias. Assuming a mass density of 3.6  $\text{g}/\text{cm}^3$ , which is the value reported for films of amorphous  $\text{TiO}_2$  (Bendavid et al. 2000), the film thickness was estimated at  $\sim 340$  nm. Figure 1 shows typical images the surface of the films observed with optical microscopes, Figure 1 (a) corresponds to a film grown in steel and Figures 1 (b) and 1 (c) films grown on silicon substrates. It was observed in all cases that the film is compact and it copies the substrate irregularities. The images of the surfaces obtained for samples grown with different bias voltages used were similar. The photograph shown in Figure 1 (c) was obtained with greater increase in Raman spectrometer microscope. In the picture you can see a relatively uniform basis of light color and darker small isolated regions with typical sizes between 1 and 4  $\mu\text{m}$ . From the measurements made by Raman spectroscopy it was found that the observed differences on the morphology were associated to different crystal structures.

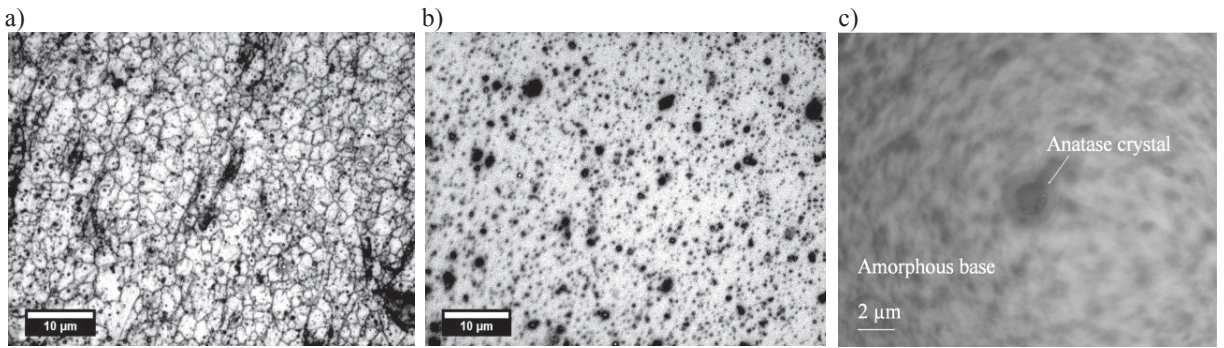


Fig. 1. Images taken with optical microscope of the surface of films grown (a) on steel 316L and (b) and (c) on silicon.

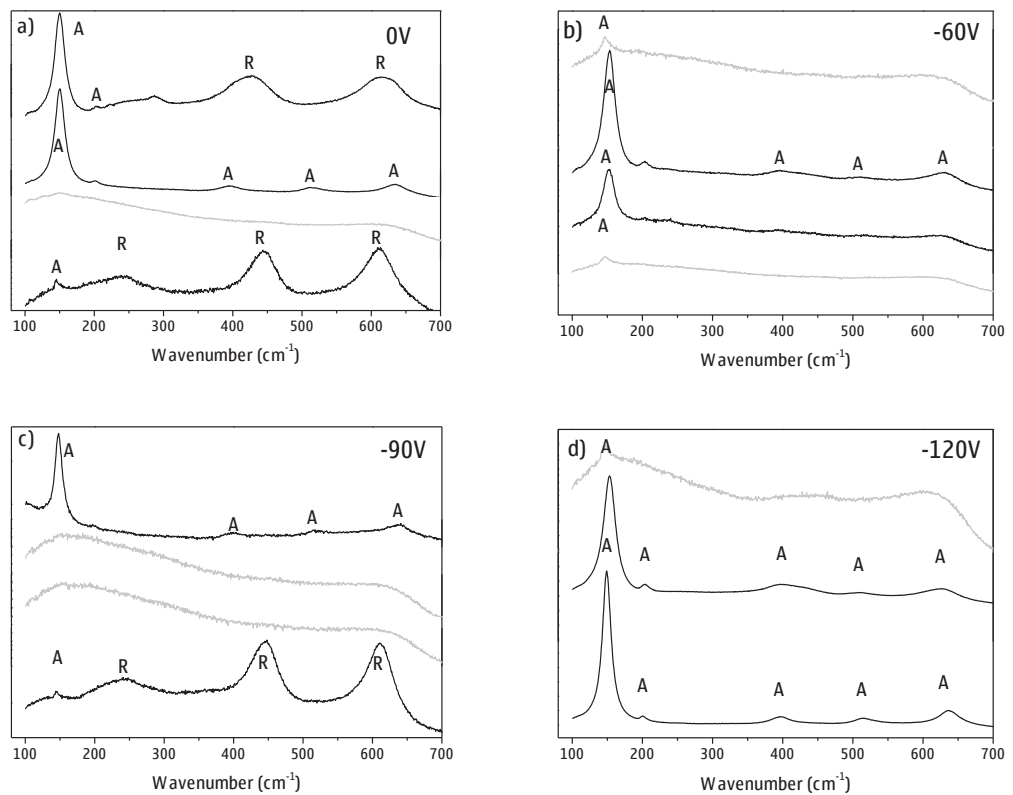


Fig. 2. Raman spectra of  $\text{TiO}_2$  films grown on 316L steel substrates with DC bias. Each graph shows spectra obtained at different points on the sample. The dark lines correspond to spectra taken on the crystals and clear lines spectra taken on the base.

In Figure 2 can be observed corresponding to the Raman spectra steel films grown on DC bias of 0 (ground), -60 V, -90 V and -120V. Each case shows spectra taken in different parts of the sample and it can be observed on the same film were found regions different crystal structures (Figure 2 (a and c)). For all bias voltages employed, the samples showed few crystals isolated anatase and / or rutile on amorphous base, with very small quantity and size of these crystals. Figure 3 shows the Raman spectra obtained for samples grown on steel at room temperature with

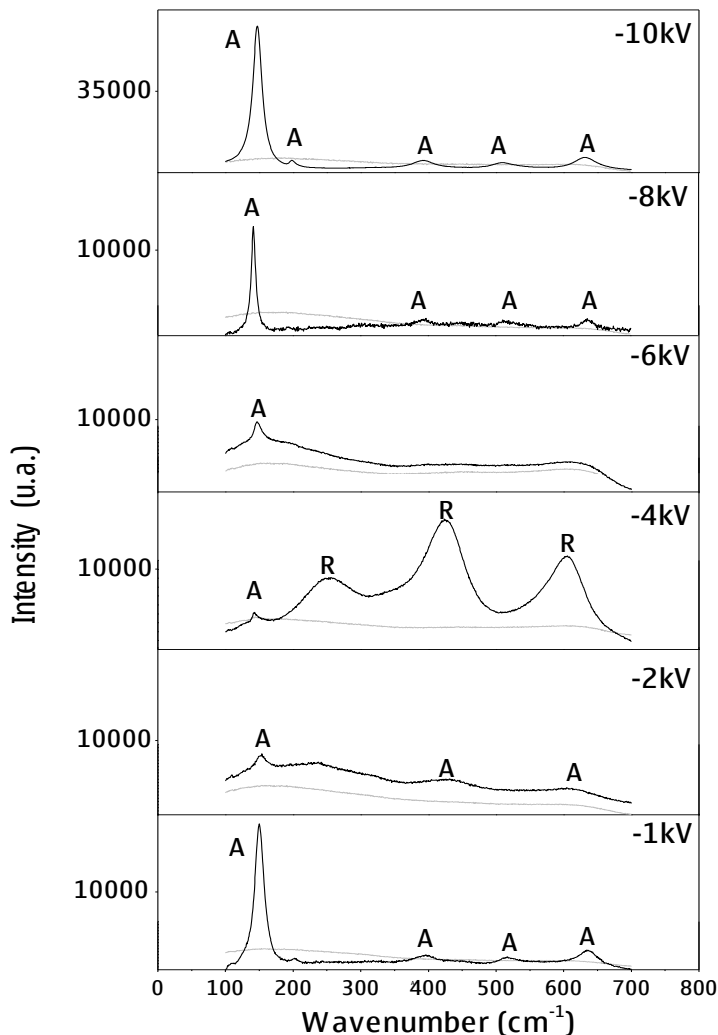


Fig. 3. Raman spectra of TiO<sub>2</sub> films deposited on 316L steel substrate pulsed-bias. The dark lines correspond to spectra taken on the crystals and clear lines spectra taken on the base.

pulsed biasing voltage (-1 kV -2 kV, -4 kV, -6 kV, -8 kV and 10 kV). Each case, signals are obtained in different regions of the sample. Similarly to happened with the films grown with DC bias, it was found that these samples had a base amorphous with few isolated crystals, being the majority of them anatase phase. Among the various voltages used, the only case where it was observed a significant difference compared to the rest of the samples was to -10 kV, where the spectra of the anatase crystals showed greater intensity, indicating to high degree crystallization. All samples deposited on steel at room temperature, either with pulsed or DC biasing, was studied by XRD at grazing incidence. In none case was detected diffraction peaks corresponding to the deposited material. These results are consistent with that observed in the Raman spectra suggesting that the film is constituted by an amorphous base with the presence of some crystals.

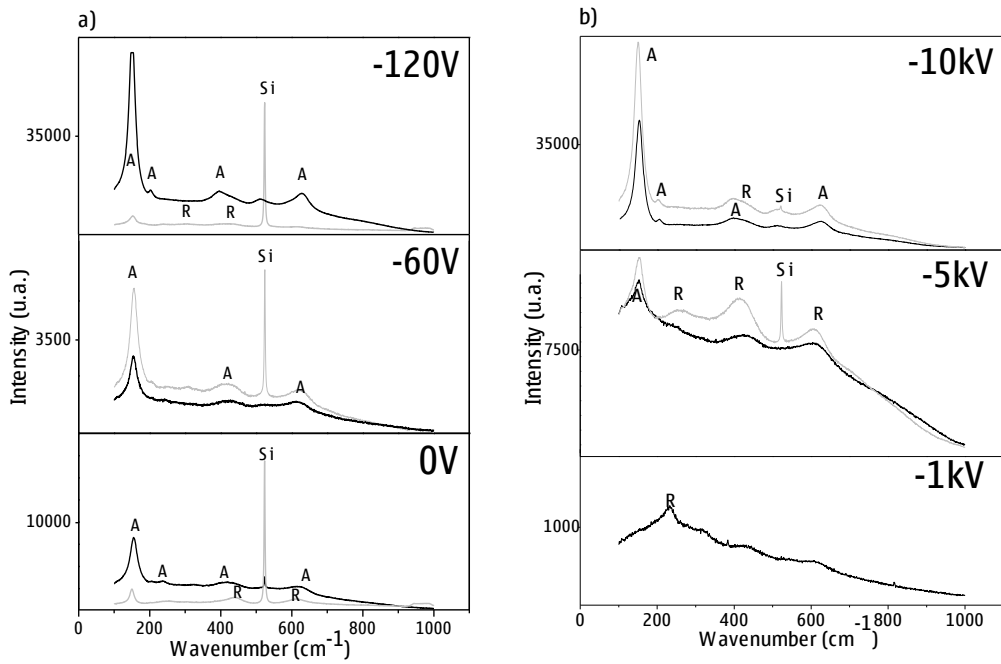


Fig. 4. Raman spectra of TiO<sub>2</sub> films deposited on silicon (100) with (a) DC and (b) pulsed biasing. The dark lines correspond to spectra taken on the crystals and clear lines spectra taken on the basis

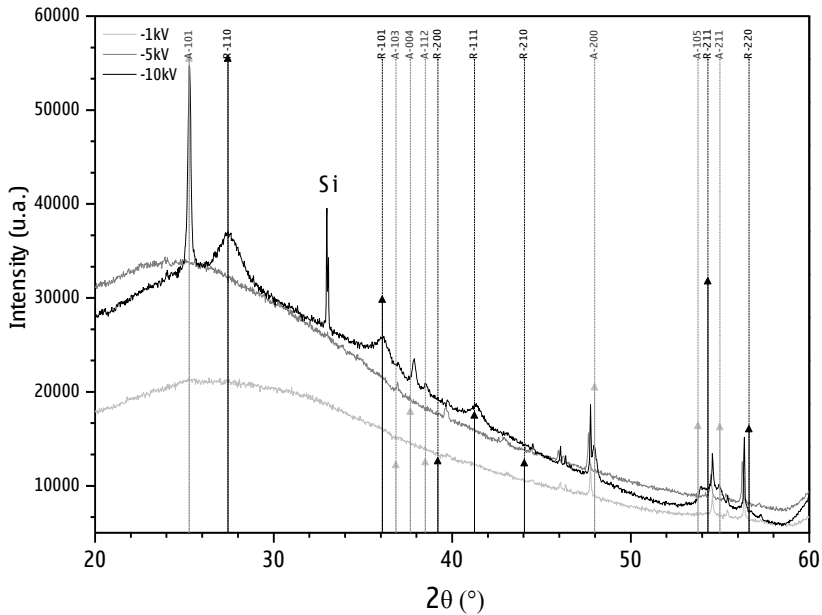


Fig. 5. X-ray diffraction pattern of TiO<sub>2</sub> films grown on silicon with different pulsed biasing voltages.

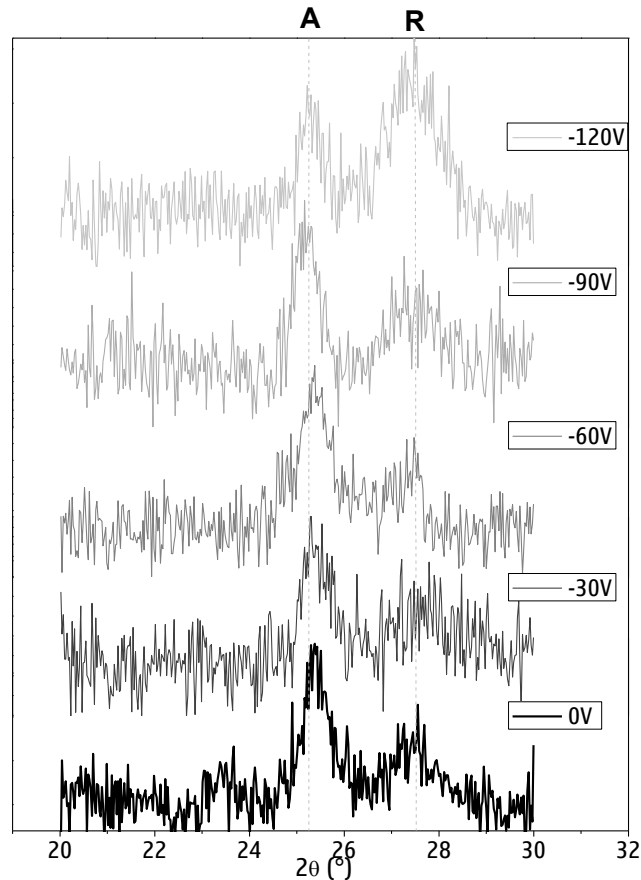


Fig. 6. XRD diffractograms of  $\text{TiO}_2$  films grown at  $300^\circ\text{C}$  on steel substrates 316L DC bias between 0 and -120 V.

Raman spectra samples grown on silicon substrates with pulsed and DC biasing are shown in Figure 4. Compared with samples grown in steel, the base was more crystalline and a higher amount of crystals. In spectra taken at the base, silicon peak predominates ( $524\text{ cm}^{-1}$ ), and it being focused on the crystals this peak intensity is very low or not observed. Films grown with DC bias (Figure 4 (a) ) show, at 0 V silicon base , anatase and rutile, with few anatase crystals, to -60 V silicon base and anatase with greater amount of anatase crystals, and at -120 V more anatase crystals with stronger signals. For the films obtained with pulsed bias (Figure 4 (b)), for -1 kV to -5 kV the base of the samples were mainly amorphous, although there was increased presence of the rutile phase than in the DC biasing voltage. However, for the higher voltage used, -10 kV, the base exhibited a higher degree of crystallization with rutile and anatase combination phases and was observed an increase in the number of single crystals of both phases. Figure 5 shows X-ray diffractograms taken in Bragg -Brentano geometry for the samples obtained on silicon with pulsed bias. Only peaks were observed corresponding to the crystalline phases of  $\text{TiO}_2$  when the polarization was -10 kV, and this result is consistent with obtained by Raman. In this spectrum can be observed intense and narrow peaks for anatase and wider peaks for rutile , a fact indicating that the rutile phase was deposited nanostructured way.

Figure 6 shows the XRD (obtained in Bragg -Brentano geometry) of the samples deposited on steel at  $300^\circ\text{C}$  with DC bias between 0 and -120V. It was observed in all samples rutile and anatase small peaks. By increasing the bias voltage, the peak corresponding to the rutile phase is most intense with respect to the peak of the anatase, indicating transformation of the deposited material to rutile phase. According to the phase diagram for growing  $\text{TiO}_2$  proposed by Löbl, based on the energy particles involved in the process and the temperature of substrate (Löbl

et al. 1994), when the growth is carried out with temperature, the ions which have a average energy greater than 40 eV the rutile film grows, as for a substrate at 300°C with ions having a mean energy greater than excess of 10 eV. The results suggest that although the substrate is biasing energy of the particles is not increased enough to crystallize the film just on rutile phase. When metal ions leave the cathode, they lose energy due to elastic collisions braking. Furthermore, due to the high oxygen pressure, many ions are neutralized by collision with gas particles. These neutral metal particles arrive at the substrate but can be accelerated by the electric field generated by the substrate bias. Therefore, the energy average of metal particles that arrive at the substrate is reduced. The fact that films grown at room temperature with biasing have resulted amorphous indicates that the average energy attained by the metal particles is less than 3 eV. This is also consistent with that at 300 ° C the films grow partially crystallized in the two phases. Moreover the results found in the sample on silicon indicate that the crystal structure of the substrate promotes the formation to crystalline structure on the film.

#### 4. Conclusions

By the technique of cathodic arc deposition, the TiO<sub>2</sub> thin films were obtained at different conditions of temperature and substrate bias. With steel substrates at room temperature, mostly amorphous films were obtained containing small single crystals of anatase and rutile in all bias conditions employed. This indicates that the energy provided to the particles by the bias voltage was not sufficient to achieve complete crystallization of the deposited material, possibly due to a high proportion of neutral metal particles arriving at the substrate. Samples collected on silicon substrates at room temperature similar results were observed, except for the cases of higher pulsed bias voltage, wherein was obtained a significantly higher degree crystallization. This shows an influence of the substrate structure on the crystal structure of the film deposited. Furthermore, by keeping the steel substrates at 300 °C during the growth process were obtained films with presence of both phases, anatase and rutile, for all values of DC bias used; increased the proportion of the rutile phase with increasing biasing voltage. This could be seen how the increase in the bias voltage, and the consequent increase in the energy of the ions, promotes the formation of rutile phase. From these results, it is expected that with an increase in the biasing voltage or a small increase in temperature can be achieved films rutile at temperatures below 800 °C required when the heat treatment is performed subsequent to growth (Löbl et al. 1994). It is also expected that the threshold biasing voltage / temperature to achieve films of rutile is lower when using silicon substrates than to use steel.

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