Optimized synthesis for improved TiO$_2$ NT array surface

(Otimização do processo de síntese de NT de TiO$_2$ visando a obtenção de uma melhor qualidade de superfície)

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Abstract

Different thicknesses of photoresist layers were deposited on the Ti foil in order to decrease the initial current during the anodization process, avoiding or diminishing in this way the formation of the initial compact TiO$_2$ layer. The studies of the initial synthesis stages were performed in both cases, for the conventional synthesis and for that with photoresist layer on top of the Ti foil. TiO$_2$ nanotube pH electrodes were fabricated to study the effect of this change in the anodization process. The nanostructure morphology was analyzed through scanning electron microscopy technique. Total removal of the undesirable layer and a complete release of the nanotube mouth were obtained. The pH electrodes were characterized utilizing a buffer solution and improved pH sensitivity and absence of hysteresis effects were observed for the devices fabricated with TiO$_2$ nanotubes obtained with the optimized process.

Keywords: TiO$_2$ nanotube arrays, morphology, initial nucleation layer, photoresist layer.

INTRODUCTION

Titanium dioxide (TiO$_2$) is an n-type semiconductor that has attracted great interest due to its wide band gap, photosensitivity, non-toxicity, low-cost and high thermal and chemical stability [1, 2]. Furthermore, it is a promising material for nanotemplating, photocatalytic, photovoltaic, photoelectrolysis and sensing applications [3, 4]. These outstanding properties stimulated the production of different TiO$_2$ morphologies. Several structures have been obtained such as nanoparticles and nanotubes. Among these, nanotubular structures present a larger surface area, higher light-harvesting and less electron recombination than TiO$_2$ nanoparticles [5]. From the fabrication point of view, titanium dioxide nanotubes are obtained through various processes as sol-gel technique, gminated growth, and hydrothermal process. However, Ti foil electrochemical anodization in fluorinated solutions has demonstrated to be one of the best techniques to obtain highly ordered and high aspect ratio structures with a well-defined and controllable diameter, wall thickness and tube length.

The performance of devices based on TiO$_2$ is affected by the shape and size of the TiO$_2$ nanotubes. For example, the TiO$_2$ nanotube electrodes have better sensitivity towards pH than thin film electrodes because of their high surface area and abundant hydroxyl groups on its surface [6]. However, during the anodization process, an initial nanoporous layer often remains as residue, also bundles of clumped remnants could be produced at the nanotube tops [7], as shown in Fig. 1, prejudicing device performance. The characteristics of these remnants depend on the anodization voltage and time since for each applied voltage (keeping the other parameters constant such as pH, agitation, temperature, and electrolyte composition) exists a limit anodization time to avoid disordered top layers [8]. To understand the cause of this limit time for each different applied voltage, an interpretation of the growth mechanism is needed. The anodic oxide growth process has two main reactions: field-assisted oxidation and chemical dissolution. Initially, the applied electric field transports hydroxyl ions (OH$^-$) from the electrolyte to the titanium metallic interface and these
ions react with the metal surface to form a compact oxide layer. At the same time, the chemical dissolution of the oxide occurs when there are fluoride ions in the electrolyte. This late reaction originates the initial porous layer formation and, for increasing process time, the NTs’ self-organized arrangement [9]. The chemical dissolution occurs mainly on the array surface and therefore the dissolution rate remains constant along the process, depending only on the F- ions concentration. On the other hand, the oxide growth occurs at the TiO2/Ti interface and therefore its rate decreases as the oxide (TiO2) thickness increases, being controlled by the diffusion of the OH- ions through the oxide layer. In this way at the initial stage, the titania formation is faster than its chemical dissolution, but when the oxide thickness increases the diffused OH- ions at the oxide/metal interface diminish and so the growth rate. As a consequence, for a given oxide thickness and process time, the dissolution rate dominates the growth rate and thus the TiO2 nanotubes stop growing. As the oxide growth is assisted by an electric field that depends on the applied voltage, this limit time is a function of the applied voltage.

Anodizing voltage is a key factor in the growth kinetics of TiO2 nanotubes (NTs) because it determines the electric field intensity [10]. Low potential supplies lower driving force for ionic species (H+, OH- and F-) to move across the barrier layer at the bottom of the nanotubes array, which hampers the ionic mobility of the Ti/TiO2 interface into the Ti metal [11]. On the other hand, the anodization time affects the length of titania nanotubes, which increases with the anodizing time, provided the anodization process did not extrapolate the limit time previously outlined [12]. In previous studies, it was observed that the titania nanotubes growth is not linear [7, 12, 13], even more, the average growth rate decreased for increasing anodization time due to the imbalance between oxide growth and dissolution for long-time experiments [13-15]. The formation of NT bundles was observed for high anodization voltage, above 60 V, or for long process time, for low voltage values, where dissolution rate dominates the growth rate. For samples grown under low applied potential and time process, a porous layer on the NT top is observed [7]. This is a critical issue for many applications, because the nano-remnants affect the infiltration of materials, charge transport and recombination in TiO2 nanotube solar cells and sensors, etc. [16, 17]. In order to avoid the presence of TiO2 porous layer in the top of NTs, consequently to have the compact TiO2 layer initial formation, the idea is to utilize a photosresist thin film layer during the anodization process. To understand better the application of the photosresist layer, first is necessary to understand the different growth stages during the anodization process, each of these stages is characterized by a current density vs. anodization time behavior (Fig. 2), where porous oxide (PO) stands for a growth process in the presence of fluorine ions and compact oxide (CO) stands for just plain oxidation without dissolution agent. In this way, the first anodization step (I), where the Ti dioxide compact layer growth occurs, must be eliminated. For this purpose, it is necessary to diminish significantly the initial current density which can be attained with an appropriated photosresist layer. This insulating layer substitutes the compact Ti dioxide layer, formed in the first step (PO), limiting the current and thus making the anodization process to start from stage II with the pits and nanotubes formation [7]. This optimized process can be utilized for low time processes avoiding the presence of the Ti porous membrane and also for long time processes, because the photosresist film layer protects the nanotube mouth from the dissolution process that occurs for long times, avoiding the NT bundles. When NT formation finishes, the photosresist layer is removed.

Figure 1: SEM images of TiO2 NT arrays covered with: a) initial nucleation layer; and b) nanogras layer.

Figure 2: Schematic of characteristic current density vs. anodization time curves (adapted from [7]).
of materials, charge transport and recombination in TiO₂ nanotube solar cells and sensors, etc. [16, 17]. TiO₂ NT arrays were characterized by scanning electron microscopy (SEM) technique. TiO₂ nanotubes arrays obtained with and without photoresist layer were utilized and characterized as pH sensor electrode.

**EXPERIMENTAL**

Sample preparation: titanium foils (99% purity, Alfa Aesar) were polished using nitric, acetic and hydrofluoric acid solutions in a volume proportion of 3:1:1 for 3 min [18]. In sequence, the foils were immersed in an electrochemical solution consisting basically of a mixture of ethylene glycol+2.56% (volume) of deionized water and 0.146 M of NH₄F solution. The anodization was carried out at controlled temperature (25 °C) and applying a constant voltage of 30 V to obtain TiO₂ NTs, for the study of stages of TiO₂ NT growth, and 60 V for studies to avoid the NT top and disordered layer and its stages of TiO₂ growth. A lower value of voltage was utilized for the study of the different TiO₂ growth stages with 15 and 30 min and washed with conventional cleaning. To study the different TiO₂ growth stages without photoresist in order to permit a more precise observation of the initial NT growth steps that occurred in the few initial seconds. For higher voltages, this step of the growth process occurs very rapidly and thus is difficult to visualize it.

Nanotubes growth process: a positive photoresist (PR) layer (AZ1518) was deposited by spin coating on the Ti surface. The Ti foils were rinsed in isopropyl alcohol and in Table I the parameters utilized to obtain the different insulating layers studied are shown. For a sacrificial layer of 1 μm, the photoresist was diluted in a proportion of 1:4 in a photoresist thinner (1-methoxy-2-propyl acetate 100-65-6). The photoresist softbake was carried out at 100 °C for 30 min. In sequence, the samples were anodized at 60 V for 5, 15 and 30 min and washed with conventional cleaning. To study the different TiO₂ growth stages with 1μm photoresist layer anodization times of 1, 4, 15 and 27 s were utilized.

| Sample | Photoresist | Spin (rpm) | Time (s) | Thickness (μm) |
|--------|-------------|------------|----------|----------------|
| 1      | AZ 1518     | 3000       | 30       | 1              |
| 2      | AZ 1518     | 3000       | 30       | 2              |

Table I - Parameters utilized to prepare the sacrificial layers.

*pH sensor working electrode fabrication*: intending to demonstrate the effect of the photoresist layer in the TiO₂ NT array surface, pH sensors utilizing these NT arrays as working electrode were fabricated and characterized. The measurements were performed using the TiO₂ nanotubes arrays as the working electrode on a bench pH meter (HI 221, Hanna Instr.). Buffer solutions of pH 4, 5.5, 7, 8.5 and 10.0 (Hanna Instr.); buffer solutions of 5.5 and 8.5 obtained through the mixture of 4 and 7 and 7 and 10, respectively) were used as test solutions and the sensor’s electrical response (voltage between the nanotube working electrode and the Ag/AgCl reference electrode) was obtained. A linear fitting was utilized in pH response curves to obtain the pH sensor sensitivity and, to observe the hysteresis effect, a response curve measurement in a buffer solution with pH from 4 to 10 and in a sequence of 10 to 4 was done.

**RESULTS AND DISCUSSION**

Different TiO₂ NT growth stages: in Fig. 3 the TiO₂ NT anodization current density vs. time curve obtained for anodization voltage of 30 V for the first 100 s is shown. The three characteristic different stages are distinguished: I) in the initial anodization stage the curve presented a standard behavior where a TiO₂ compact layer grew, represented by an abrupt decrease in the current [7, 9]. Actually, the compact layer formed during the initial stage can be seen in the SEM images for anodization process times of 3.5 s (Fig. 4a) and 4.0 s (Fig. 4b). In stage II, the current density reached its minimum value and returned to increase due to the TiO₂ compact layer electrochemical dissolution by the fluorine ions [7, 9]. In this stage, it was possible to notice the nanopores (pits) formation in the TiO₂ compact layer (Figs. 4c and 4d). Finally, in stage III the current density returned to decrease slowly due to diminishing ion diffusion rate through the TiO₂ nanotubular structure [7], which in this stage was already well defined, as observed in Fig. 5.

![Anodization (J x t) curve for TiO₂ nanotubes obtained with 30 V, for the first 100 s.](image)

For higher anodization times, the TiO₂ top nanoporous layer was totally consumed and the nanotube mouth started to be attacked by the fluorine ions making the top of the nanotubes a "nanograss" appearance. This nanograss was related with the TiO₂ compact layer that during the dissolution process became a very porous layer and remained as microflakes deposited on the nanotube mouth after the anodization process [7]. This effect occurred for any voltage...
value, since it was correlated with the initial TiO<sub>2</sub> compact layer. So, for the voltage of 30 V and anodization time of 10 min, the nanopore TiO<sub>2</sub> layer was observed while for 30 min nanograss prevailed at the nanotube top as shown in Fig. 6.

Summarizing, the initial nanoporous layer was present while the oxidation process was dominant with respect to the chemical dissolution process. At the moment where the oxidation and the chemical dissolution reached equilibrium, the NT surface was free and the NTs reached their maximum length value; this time was defined as process limit time. After this limit time, the chemical dissolution process was dominant and the nanotube mouth walls were attacked by the fluorine ions and as a consequence nanograss was formed in the NT mouth. In this way, to obtain nanotube mouth free of a compact nanoporous or nanograss layer, it is necessary to obtain nanotubes with a processing time close to the limit time, recalling that this parameter changes with anodization process parameters.

**Method to avoid the formation of the initial compact/nanoporous TiO<sub>2</sub> layer:** as mentioned before, to avoid the formation of the initial compact layer is necessary to reduce the initial current, which can be accomplished by the deposition of an insulating layer on the Ti foil surface. Positive photoresist (AZ1518) layers were chosen as an insulator. In order to investigate the effects of the photoresist layers on the morphology of TiO<sub>2</sub> NT arrays, anodization processes were carried out without and with two different photoresist thicknesses, with 60 V and 5, 15 and 30 min anodization times. Fig. 7 shows the correspondent SEM images of the TiO<sub>2</sub> NT top and side views. It is possible to observe the presence of the initial compact oxide layer in all samples obtained without the insulating layers process. On the other hand, completely open NT array tops were obtained for 1 and 2 μm thick layers and 15 and 30 min anodization times. The thin layer of photoresist acted as an artificial and sacrificial initial layer blocking the high initial current and sustaining most part of the applied voltage, avoiding in this way the formation of the initial compact oxide layer. As part of the applied voltage dropped on this photoresist sacrificial layer, higher process times was needed to form well defined nanotubes as observed in Fig. 7, where nanotubes wall thinning occurred slower than for NT grown without photoresist.

The mechanism for the anodization process utilizing a photoresist layer was very similar to described for TiO<sub>2</sub> nanotube conventional anodization. In Fig. 8 the anodization current density as a function of anodization time curves for samples obtained without photoresist layer and with 1 and 2 μm photoresist layers are shown. For samples obtained without photoresist, the Ti layer surface was directly in contact with the anodization solution and a compact
Figure 7: SEM images of TiO$_2$ NTs obtained for 1 and 2 µm photoresist layer thicknesses, with 60 V and anodization time of 5, 15 and 30 min.

[Figura 7: Imagens de MEV dos nanotubos de TiO$_2$, obtidos utilizando uma camada de fotorresist de 1 e 2 µm de espessura, com 60 V por 5, 15 e 30 min.]
oxide formed by the reaction of the Ti⁺ ions, produced by the anodization voltage, with the O²⁻ originated from 
H₂O molecules present in the anodization solution [7, 9]. Depending on the migration rate of the Ti⁴⁺ and O²⁻ ionic species the growth of the new oxide occurred at the metal-oxide interface and/or at the oxide-electrolyte interface. In the case of a constant anodization voltage (V), the field E=V·d⁻¹ dropped constantly and decreased with the increase of the compact TiO₂ layer thickness (d), in this way an exponential decrease of the initial current with anodization time occurred. A finite thickness was reached that depended on the anodization voltage value. The Ti⁴⁺ injection at the oxide-electrolyte interface reacted with the fluorine ions and produced TiF₆²⁻ water-soluble species. These species were also generated by the chemical corrosion of the TiO₂ compact layer, in this way, a porous oxide and nanotube formation were observed. In this stage, an increase in anodization current was observed and increased as the reactive area increased. The ion migration rate was controlled by the oxide layer thickness; the chemical etching process provided by fluorine ions and oxidation by oxygen ions occurred leading to nanotube formation. When a photoresist layer was utilized, the Ti surface was not exposed to the electrolyte solution avoiding, in this way, the initial compact oxide (TiO₂) layer formation on the Ti surface. In this case, the electric field E had also a constant value and thus the initial current was practically constant. An important fact was that as fluorine ions are very small, they competed with O²⁻ migration through the photoresist layer. With a higher migration rate of fluorine ions than oxygen ones, a fluorine-rich layer in the metal/photoresist interface occurred, so Ti pits formation and consequent oxidation took place, beginning the nanotube formation. In this stage, with a higher reactive area, an increase in the anodization current occurred (Fig. 8).

In order to analyze the initial anodization stages of nanotube formation with the photoresist layers, samples were obtained utilizing the photoresist layer of 1 µm and times of 4, 15 and 27 s. In Fig. 9 SEM images of these samples are shown. Energy dispersive X-ray spectroscopy (EDS) measurements were also performed on the surface of these samples, in order to detect the presence of TiO₂. As observed in Fig. 9a for the sample obtained at 4 s, it was not observed the presence of nanotubes and the EDS measurements for this sample also did not detect oxygen presence, indicating the absence of a titanium oxide compact layer formation. On the other hand, SEM images of samples obtained at 15 and 27 s showed that nanotubes were formed and did not present the TiO₂ compact layer; also, EDS results for the sample obtained with 15 s indicated a surface composition of 33% of Ti and 66% of oxygen. These points, 15 and 27 s, corresponded to the beginning of the current growth, the transition from stage II to stage III and, different to the case without photoresist layer, the titania formation occurred at the photoresist/Ti surface with pits of Ti surface dissolution and consequent oxidation. So, the dissolution process probably did not occur preferentially in the nanotube surface; in this case, the current growth caused the balance with the nanotube growth and the internal nanotube dissolution process. This hypothesis was reinforced as a function of nanotube mouth internal diameter and length. For nanotubes obtained with 15 s, 27 s, and 15

![Figure 8: Current density as function of anodization time for TiO₂ NTs obtained without (30 min) and with 1 and 2 µm photoresist layer.](image)

![Figure 9: SEM images of samples obtained with 60 V for corresponding anodization times of 4 s (a), 15 s (b) and 27 s (c) with 1 µm photoresist layer.](image)
min, diameters of $41\pm8$, $45\pm7$ and $37\pm11$ nm were found and the values can be considered the same under the uncertainty of diameter measurement, and the length values were $586\pm31$, $1000\pm28$ and $2790\pm14$ nm, respectively.

In Fig. 10 the nanotube length as a function of anodization process time is shown and it is possible to observe an increase of nanotube length as a function of anodization time. This result indicated that it is possible to obtain large length nanotubes without nanograss presence, which is not possible with the conventional method as was shown in Fig. 6b. This was a consequence of the absence of compact layer formation, which would remain as microflakes after the anodization process [7, 9, 19, 20], and due to the decrease of corrosion rate of nanotube mouths given by the protective effect of the photoresist layer. It was also observed that nanotubes obtained with 2 μm photoresist layer had longer lengths than those obtained with 1 μm of photoresist, probably due to a lower attack in nanotube surface and thus higher field-assisted oxidation in relation to the dissolution process. This can be justified observing Fig. 8 where a higher current density value was obtained for 2 μm than for 1 μm photoresist layer.

**pH sensor working electrode response:** pH measurements were performed in buffer solutions with pH values of 4, 5.5, 7, 8.5 and 10. In Fig. 11 the pH sensor response (for pH values of 4 to 10 and 10 to 4) for working electrodes fabricated with nanotubes obtained with 60 V for 10 and 15 min and with and without a photoresist layer is shown. As can be seen, the electrodes fabricated with the TiO$_2$ NTs presented a linear response with pH variation (Fig. 11). It was possible to observe that electrode fabricated with TiO$_2$ NT grown with a thin layer of photoresist presented better results in respect to the hysteresis effect of the electrodes fabricated with TiO$_2$ NTs obtained by the standard process. Analyzing the results, it was observed that electrodes obtained with a photoresist layer of 2 μm presented less hysteresis effect and a more linear behavior than those obtained with 1 μm photoresist layer. This result was attributed to the lower TiO$_2$ length that avoided solution trapping inside the tubes diminishing hysteresis results and improving pH sensitivity values up to approximately 52 mV/pH (Table II). It is important to observe that the worst results were obtained for a working electrode fabricated with TiO$_2$ NTs obtained with the standard synthesis process. As can be seen in Fig. 7, these
NTs presented a TiO$_2$ initial compact layer that difficulted the penetration and trapped the solution inside the tubes, increasing hysteresis effect, and decreasing the pH sensitivity.

**CONCLUSIONS**

Anodic TiO$_2$ nanotube (NT) arrays frequently exhibit a compact, nanoporous oxide layer on the top of the arrays, attributed to the initial TiO$_2$ nucleation layer formed during the initial stage of the anodization process, and for long anodization process time exhibit a nanograss presence due to the dissolution of the nanotube top. This is a critical issue for many applications, because this layer affects the infiltration of materials, charge transport and recombination in the TiO$_2$ NTs. In this way, a modified synthesis method to avoid the formation of this layer was proposed. Prior to anodization, a thin photoresist layer was deposited on the surface of the Ti foil. Two thicknesses were investigated for anodization process carried at 60 V. This layer acted as an artificial initial layer blocking the high initial current, since most part of the applied voltage dropped on it, avoiding the nucleation of the compact TiO$_2$ initial layer formation. It was shown that with this technique it is possible to obtain a totally free TiO$_2$ NT array top surface. The optimized arrays obtained were tested as pH electrodes leading to improved sensitivity (52 mV/pH) and removal of hysteresis effects.

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| Anodization time | 1 µm photoresist layer | 2 µm photoresist layer | Without photoresist layer |
|------------------|------------------------|------------------------|---------------------------|
| 10               | 44.8±1.8               | 50.0±1.4               | 36.4±2.1                  |
| 15               | 40.8±1.8               | 46.8±2.0               | 47.1±4.1                  |

Table II - pH sensibility (mV/pH) of the TiO$_2$ NT electrodes.

[Tabela II - Sensibilidade dos sensores de pH (mV/pH) fabricados com nanotubos de TiO$_2$]