Tailoring the Ti surface via electropolishing nanopatterning as a route to obtain highly ordered TiO$_2$ nanotubes

A Apolinário$^1$, C T Sousa$^1$, J Ventura$^1$, L Andrade$^2$, A M Mendes$^2$ and J P Araújo$^1$

$^1$IFIMUP and IN—Institute of Nanoscience and Nanotechnology, Departamento de Física e Astronomia, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 678, 4169-007 Porto, Portugal
$^2$LEPAE—Dep. Engenharia Química-Faculdade de Engenharia, R. Dr Roberto Frias, 4200-465 Porto, Portugal

E-mail: jearaujo@fc.up.pt

Received 3 May 2014, revised 29 August 2014
Accepted for publication 11 September 2014
Published 7 November 2014

Abstract

Highly ordered TiO$_2$ nanotubes (NTs) were synthesized by the electrochemical anodization of Ti foils subjected to electropolishing (EP) pre-treatment. We found that the Ti surface roughness plays an important role in the onset of pore nucleation in enhancing the local focusing effect of the electrical field. Additionally, EP induces the formation of dimple structures on the metal surface, which can work as a pre-pattern prior to anodization. These shallow ripples lead to a preferentially ordered pore nucleation, offering an organizational improvement of the anodic oxide NTs. We found that, depending on the EP applied potential, the roughness and the spatial period of the ripple-like structures varies from 8–2 nm and from 122–30 nm, respectively. Such tuning allowed us to focus on the influence of the initial Ti pre-surface topography features on the NTs’ length, organization, and hexagonal arrangement quality, as well as diameter and density. Our results show that an EP under 10 V is the most suitable to obtain a small Ti surface roughness, the largest NT length (40% enhancement), and the effective improvement of the ordered hexagonal NTs’ arrays over larger areas. Furthermore, the NTs’ dimensions (pore diameters and density) were also found to depend on the initial Ti surface topography. The use of optimized EP allows us to obtain highly hexagonal self-ordered samples at a reduced time and cost.

Keywords: TiO$_2$ nanotubes, anodization, electropolishing

(Some figures may appear in colour only in the online journal)

1. Introduction

The electrochemical anodization of Ti to obtain highly ordered nanotube (NT) arrays of TiO$_2$ continues to gain increasing importance for a large number of applications, such as photoelectrochemical cells for H$_2$ production (water splitting) [1, 2] and particularly for dye-sensitized solar cells [2]. TiO$_2$ NTs have received great attention due to their one dimensional structure, which provides a direct and efficient path for electrons [1].

TiO$_2$ NTs can be obtained by the electrochemical anodization of Ti in fluoride-based electrolytes. The addition of ethylene glycol was later found to lead to longer (hundreds of microns) and more ordered arrays of TiO$_2$ NTs [3–9]. In contrast to the well-known case of Al anodization [10], the Ti anodization presents a non-steady state due to the out of equilibrium dissolution and oxidation processes on the NT bottom and to the additional chemical dissolution process mainly at the NT’s top [5, 11–15]. This unbalanced anodization leads to a maximum TiO$_2$ NT length after a given anodizing time. Besides the length, other NT parameters are influenced by factors such as the electrolyte type (e.g., electrolyte concentration and pH), anodization temperature, and applied potential [3–11, 16–19].
Aiming a degree of order comparable to that of anodic alumina oxide (AAO) at 10% porosity [20], intense research has been performed on the organization and final ordering of TiO$_2$ NTs in a closed-packed hexagonal array [21–25, 41]. The organization of TiO$_2$ NTs is mainly influenced by the Ti foil purity, the anodization voltage [22], and the local surface morphology of the Ti substrate [23–26, 41]. Regular or periodic dimples in a valve metal surface can lead to an improvement of the organization degree of NT arrays, inhibiting their random nucleation [26, 27]. In this context, the two-step anodization process was found to be mandatory to improve organization in AAO [10] and has been widely used to improve the structural order of TiO$_2$ NT arrays [21–23, 28]. On the other hand, an electropolishing (EP) pre-treatment of the metal foil prior to the anodization was shown to be highly suitable to induce a high degree of organization in AAO [28]. In the case of TiO$_2$ NT arrays, several pre-treatments (such as EP, mechanical polishing, or chemical etching) were also studied, targeting smoother Ti surfaces. This ensures that a highly homogeneous electric field distribution is obtained over the Ti surface during the initial anodization stages, a crucial condition to reach highly ordered NT arrays [23–25, 29, 41]. In particular, EP pre-treatments were shown to decrease the Ti foil surface roughness, resulting in more uniform NT length and higher NT density [23–25, 29].

Electropolishing is a well-known technique [30] for metal removal at the micrometer level [31–35] and to obtain smooth and highly reflective surfaces. While (mostly) at the industrial level the process is best known for the surface bright polish, at the research level other important benefits, often overlooked, arise. Besides the usual advantages, like microfinishing improvement or size control, the EP surface “waviness” offers great promise to improve the organization of anodic oxide nanopores or NTs. A new overridding application of EP arises to create nanopatterns in the surface of aluminum, titanium, zirconium, tantalum, and tungsten [33, 34], working as a pre-pattern prior to the anodization and ultimately leading to highly ordered oxide nanostructures. In fact, the EP of Al foils was shown to be a simple and efficient method to induce a high degree of organization in AAO templates, since the shallow ripple-like structures it produced favor a preferential ordered pore nucleation [28, 34, 35, 37–41]. In Al, the EP process has been widely studied and optimized, where EP parameters, such as temperature, time, stirring, distance to the electrode, and electrolyte type were found to play an important role in the process [36, 37]. Nevertheless, a parameter of crucial importance is the EP applied voltage, since its variation can result in features like stripes or hexagonally ordered dimples (from 50–150 nm) [34–37, 41]. However, the nanopatterning of a Ti foil by varying the EP potential has been overlooked so far. EP of Ti is usually performed using sulphuric acid-based electrolytes, which results in smooth surfaces [32], although other EP conditions (e.g., H$_2$SO$_4$/HF electrolyte under an applied voltage of 15 V) lead to an organized dimple-pattern structure at the Ti surface [34].

In this work the growth of TiO$_2$ NTs is optimized by tuning the Ti foil surface roughness, using different EP conditions: in particular, adjusting the EP applied potential ($V_{EP}$). An integrated approach, based on previously optimized anodization parameters [3–19, 21–27] and directly focused on the effect of the Ti surface roughness and topographic features on the length and organization of the obtained NT arrays, was followed here. By varying $V_{EP}$ and comparing with an as-rolled (AR) Ti foil, our results show the critical role played by the Ti surface topography and roughness, prior to the anodization on the maximum NT length, and their organization in a regular hexagonal pattern. By tuning $V_{EP}$, adequate EP conditions were found that enable highly ordered hexagonal closed-packed arrays of TiO$_2$ NTs with lengths above 100 μm.

2. Materials and methods

Ti foil (0.127 mm thick, 99.99+% purity from AlfaAesar) pieces (1 cm$^2$) were ultrasonically cleaned in ethanol and deionized water for 10 min. Prior to the anodization, the pieces of the AR Ti foil were pre-treated by an EP in a H$_2$SO$_4$/HF (8:3) solution under applied potentials ($V_{EP}$) between the Ti foil and an inert Pt mesh (at a distance of 2.5 cm) for 4 min. Several samples were fabricated with different $V_{EP}$ of 5, 10, 15, 18, and 20 V; the solution was mechanically stirred (300 rpm) and kept at room temperature [34, 42]. The Ti surfaces of all electropolished samples, as well as an AR Ti sample, were analyzed using a Nanoscope Multimode Atomic Force Microscope (AFM) from Veeco Instruments. Subsequently, the samples were electrochemically anodized in a homemade anodization cell (two electrodes), where the Ti foil acted as the anode, and an inert Pt mesh was used as cathode. The time evolution of the current density $i(t)$ was monitored during the anodization using a Keithley 2004 Sourcemeter remotely controlled by a LabView application. The electrochemical anodization was carried out for all samples at a constant potential of 60 V for 17 h in a freshly prepared ethylene glycol solution containing NH$_4$F (0.3 wt %) and H$_2$O (2 wt %) at room temperature with mechanical stirring [12]. The NTs’ morphology was evaluated by an FEI Quanta 400FEG Field Emission Scanning Electron Microscope (SEM), using surface top and bottom views and cross-sections for the NTs’ length calculation. The bottom views were obtained by natural peeling-off, originating free-standing and non-curving membranes. Using SEM images, a statistical analysis (with the ImageJ image processing software) [43] was performed, enabling an evaluation of the organization pattern and NT structure dimensions (diameters and density).

3. Results and discussion

3.1. AFM imaging analyses: surface topography and roughness characterization

The surface topography of the Ti samples with EP pre-treatments at different $V_{EP}$ and one AR were investigated by AFM
imaging. $1 \times 1 \mu m^2$ topographic images of Ti surfaces were obtained for each sample and then analyzed in terms of surface roughness ($R_q$), defined as the root-mean-square value of the images’ pixel height. Figure 1 shows illustrative AFM images of the Ti surfaces of each sample as well as the $R_q$ values extracted from the measured topography. For the unpolished sample (AR), we observe an irregular surface with a roughness of 8.3 nm that is slightly increased upon a 5 V EP (figures 1(a) and (b)). Nonetheless, the latter shows broad random topographic features (hills), whereas the former shows steeper hills. In contrast, a significantly smoother surface was obtained in other EP samples, particularly the 10 V sample with an $R_q$ of 2.4 nm (figure 1(c)). By increasing $V_{EP}$, the Ti foil surface became slightly rougher: $R_q = 3.4, 4.7,$ and $3.1$ nm measured for samples 15, 18, and 20 V, respectively. Additionally, the Ti surface after EP revealed a periodic dimple-pattern structure whenever $V_{EP}$ was no smaller than 10 V. This shallow ripple-like structure is an EP characteristic of metals [34, 42] and can be used as a pre-pattern prior to anodization to obtain highly ordered oxide nanostructures, as profusely shown in the case of Al [28, 34–37, 41]. In fact, studies in Al foils demonstrated that, by combining adequate EP voltage and time, dimple-patterns from striped to hexagonal arrangements can be obtained [28, 34–37, 41]. However, EP of Ti is usually performed in sulphuric acid-based electrolytes that lead to smooth and plane surfaces [31]. Nonetheless, EP with hydrofluoric acid-based electrolytes can also result in organized dimple patterns under certain conditions (time, temperature, voltage) [34, 42].

Our results clearly demonstrate that the EP voltage also determines the ripple-like structures of the Ti surface, particularly the inter-ripple spatial period ($SP$). Figure 1(e) shows AFM images’ profiles of each $V_{EP}$ sample, giving the mean inter-ripple spatial periods: $SP_{5V} = 122$ nm, $SP_{10V} = 97$ nm, $SP_{15V} = 194$ nm, $SP_{18V} = 30$ nm, and $SP_{20V} = 73$ nm. The variation of the Ti surface waviness with $V_{EP}$ allows its adequate tuning for particular purposes; in our case, we will demonstrate that it makes possible the creation of self-organized hexagonal and long TiO$_2$ NTs. The Ti pre-pattern can be the vehicle to achieve, in an easy way, ordered hexagonally arranged NTs and to enhance the NTs’ growth rate, avoiding the later chemical effects that limit the NTs’ growth.
3.2. Anodization curves

3.2.1. Typical growth mechanism. The evaluation of the mechanisms that lead to the formation and growth of the NTs can be studied using current density (j) curves [42]. For the samples AR, 5 V, and 10 V, these curves present the typical behaviour for Ti anodization and the successful formation of TiO₂ nanotubes (figure 2) [3, 4, 12, 21, 24]. After applying the anodization potential (60 V), a continuous TiO₂ layer is rapidly formed, increasing the resistance (rapid j decrease). The following slight j-decrease marks the onset of NT nucleation, likely on the surface valley-type irregularities where the higher electric field enhances oxide dissolution and hole formation (dissolution promoted by F⁻ ions in favourable spots of the TiO₂ surface) [42]. Consequently, the TiO₂ layer thickness starts to decrease while the pores’ (tubes’) formation accelerates. This is evidenced by the increase of j until a maximum is reached (jmax), forming a barrier layer at the NTs’ bottoms. Afterwards, the emerging NTs will adjust and compete with each other in a self-organization process.

As the anodization proceeds, the formed NTs grow at a constant rate, and the barrier layer thickness (δb) would remain constant if the Ti oxidation balanced the oxide dissolution [3, 4, 8, 11]. However, at this stage, the oxidation/dissolution processes are not in equilibrium, with the TiO₂ dissolution lower than its formation, resulting in a slow decay of j(t) during the anodization. This is associated with the progressive depletion of F⁻ ions (which are crucial to the electrolyte/oxide interface dissolution process) at the NT bottoms during the anodization. Given the high viscosity of the electrolyte and increasing length of the NTs (diffusion limited process), such ions are difficult to replace by new ones at the NT bottom. As a result, the oxidation process is faster than dissolution (j slowly decrease with time), leading to a progressive increase of the oxide δb at the NTs’ bottoms.

Thus, the ionic migration path along the oxide barrier [8] significantly extends, inhibiting the transport of F⁻, Ti⁴⁺, and O²⁻ ions across δb (Ti⁴⁺ and O²⁻ for oxidation, F⁻ for dissolution), which subsequently limits further NT growth.

3.2.2. Dependence of the anodization curves on different electropolishing voltages. According to the j(t) behaviours shown in figure 2, we can divide the produced samples into two groups: the AR sample and samples with lower VEP (5 V and 10 V) that present lower j-values and the initial transient regime typical of valve metals’ anodization; and samples with VEP ≥ 15 V that have higher j-values and an absence of initial j-transients.

For the first group of samples the j(t) curves show the typical behaviour [3, 4, 12, 21, 24] of mild-anodizations (anodizations under low potentials, <60 V) [21, 44, 45]. Within this group, samples with higher Rq (5 V, 9.13 nm, and AR 8.3 nm), have lower j-values, indicating lower ionic current during the anodization. Thus, high Rq hinders F⁻ from reaching the surface and causes an inhomogeneous electric field over the sample’s area, which is a crucial parameter for a proper oxide dissolution. At this point, the oxidation/dissolution processes are not in equilibrium (non-steady-state anodization), with the TiO₂ dissolution lower than its formation, which limits further NT growth. The AR and 5 V samples present similar Rq (although the Rq of the 5 V sample is slightly higher, since HF works as a chemical etcher of the Ti surface) [42, 46] but different topographic features that cause the differences in the j values and initial transient period. As shown in the AFM results, the 5 V sample presents higher and broader random topographic features than the AR sample which, in turn, shows much steeper hills. This allows the formation of a thicker initial oxide layer (lower j) and a longer transient period (nucleation, oxide dissolution, tube-formation stages). On the other hand, the AR sample presents steep nucleation spots that allow a faster nucleation and oxide dissolution and thus a more rapid formation of the NTs.

The 10 V sample shows the lowest surface Rq (2.4 nm), a reduction of 70% when compared to that of AR. Its anodization curve reveals a more stable j(t), which is fundamental for a longer balance of the oxidation/dissolution processes and indicates higher NT growth rates and thus longer NTs. Besides, this sample reveals unique periodical rippled structures (figure 1(c)) that are a key characteristic for pore formation, since they act as nucleation points (valleys), making the overall nucleation time short. This allows rapid oxide dissolution, leading to a pronounced jmax (inset of figure 2), a shoulder-like trend which is usually ascribed to an optimized hexagonal arrangement of the network. Thus, the ripples of the 10 V sample lead to earlier and more rapidly organized NT nucleation than the random valleys of the AR and 5 V samples, explaining the shorter nucleation and dissolution stages.

For the second group of samples (15, 18, and 20 V), the j(t) curves show a different behaviour from those previously discussed, due to topography effects. The main differences in
focus on two critical aspects: (i) a stronger monotonic decrease of \( j(t) \) along the whole anodization period, and (ii) the absence of the typical \( j(t) \) transient related with the initial growth mechanisms of the TiO\(_2\) NTs.

Regarding the first point, the almost exponential \( j(t) \) decay is typical of hard-anodization (HA) curves (anodizations under high potentials, \( >60 \) V) and indicates a predominance of oxidation over dissolution \([21, 44, 45]\). This HA behaviour can be ascribed to local burning defects on the Ti surface caused by the high EP potentials (15–20 V; figure 3) \([47]\). Under these conditions, the current will flow predominantly through the local features, resulting in a rapid growth of the oxide layer. The migration path of the ionic species along the barrier is then significantly extended, and a non-steady-state anodization occurs from the very beginning. Therefore, the stronger oxidation ionic current seen in the \( j(t) \) curve decay of these samples encourages this type of HA behaviour.

It was recently reported \([42]\) that a chemical etching pretreatment also gives rise to anodization curves without the initial typical transient (NTs’ nucleation and growth). The severe chemical etching effects observed in that case damaged the surface, creating areas of different heights and NT growth rates (higher at the valleys). The obtained macroscopic \( j(t) \) curve is then the sum of the microscopic \( j \) contributions from the different anodization zones. In this way, we may realize that the 15, 18, and 20 V samples (presenting lower \( R_q \) and ripples) have a non-homogeneous surface topography over the total area. In particular, the lower \( R_q \) and ripples that promote rapid nucleation (as in the 10 V case) are masked by the anodization areas, where the Ti surface was damaged by the high EP potentials.

### 3.3. NTs’ length and organization

#### 3.3.1. Length

Figure 4 shows an SEM cross-section and top view images of the NT templates for all samples after 17 h of anodization. The resulting template thicknesses (\( L \)) are shown in Table 1. The AR sample has a mean NT template thickness of 89 \( \mu \)m, while the 5 V sample has a slightly smaller thickness, \( L = 83 \) \( \mu \)m. On the other hand, for \( V_{EP} = 10 \) and 15 V, a rapid NT growth occurs, leading to a length increase of more than 40\% (\( L = 125 \) and 101 \( \mu \)m, respectively) when compared with the AR or 5 V samples. Nonetheless, by further increasing \( V_{EP}, L \) decreases to 88.7 and 76.4 \( \mu \)m for 18 and 20 V, respectively.

Comparing \( L \) with the \( R_q \) results, one can infer that the NTs’ growth and template thickness is directly correlated with the surface topography (figure 5). By decreasing \( R_q \), as for the 10 and 15 V samples, we achieved an enhancement of the growth rate (and \( L \)). In fact, the pre-anodization surface conditions with the lowest \( R_q \) of 2.4 nm and the presence of small nucleation sites are crucial to reach higher growth rates and thicker NTs (125 \( \mu \)m). For samples with a lower \( R_q \), we obtain a more homogeneous electric field distribution over the whole sample surface, causing a slower \( \delta_b \) increase during the anodization. Such thinner \( \delta_b \) then promotes an easier ionic electromigration (\( F^- \) and \( O_2^- \)) through the oxide layer, fundamental for the existence of balanced dissolution/oxidation processes and thus of steady state anodization. Also, a smoother surface favours the mobility of the ions involved in the dominant anodization processes, promoting the availability of \( F^- \) at the Ti surface (thus favouring dissolution). On the other hand, the additional chemical effects occurring later in the anodization (namely the

![Figure 3. Top view SEM image of the Ti surfaces of the (a) AR Ti foil and electropolishing samples under (b) 5 V, (c) 10 V, (d) 15 V, (e) 18 V, and (f) 20 V. The images of samples with \( V_{EP} > 10 \) V show representative areas of the whole sample surface.](image-url)
pH decrease) are delayed, since the anodization growth limit caused by the too-thick $\delta_b$ is also belated.

As discussed before, further increasing $V_{EP}$ to 18 V and 20 V, besides decreasing the $Rq$ values and causing topographic ripple-like structures, also leads to areas with defects (burning) and cracks (figure 3). These defects relentlessly influence the anodization rate, decreasing the NT’s growth rate and lowering the final $L$ compared to the AR sample. The anodizing current is, in this case, preferentially directed toward those defective and cracked areas, discouraging the NT’s growth on the rest of the surface sample. The current is thus not homogeneous in the whole sample, resulting in a slower NT growth rate with final thinner and inhomogeneous [increase of standard deviation (SD) in the 20 V sample] thicknesses.

After 17 h of anodization, the oxide nucleation layer of the 10 V sample remains almost intact, while those with a larger $V_{EP}$ have been partially dissolved (see top view SEM images shown in figure 4) [42]. As the anodization proceeds, a local pH decrease occurs at the NTs’ bottom [12], with the electric field driving the $H^+$ ions towards the NTs’ top (V-shaped NTs) [12, 22, 46], resulting in the oxide nucleation layer dissolution [42]. Consequently, the $F^-$ ions can again easily reach the bottom of the tubes, being more readily available to increase the NTs’ growth rate. This is clearly seen in the 15 and 20 V $j(t)$ curves presented in the inset of figure 2, where a $j$-increase is observed at instants 820 min and 940 min, respectively, indicating an upsurge in the NTs’ template thickness. Note that the smaller $SP$ of the 18 V sample led to a rather homogeneous template. Nevertheless, top-view images revealed that the NT’s top in this sample was also dissolved after 17 h.

### Table 1. TiO$_2$ NTs’ template thickness results: mean $\langle L \rangle$, maximum $L_{max}$ length, and $SD$.

|        | AR  | 5 V | 10 V | 15 V | 18 V | 20 V |
|--------|-----|-----|------|------|------|------|
| $\langle L \rangle$ (μm) | 88.93 | 82.50 | 124.2 | 101.6 | 85.70 | 76.40 |
| $L_{max}$ (μm) | 91.50 | 89.84 | 125.0 | 114.5 | 88.70 | 82.75 |
| $SD$ (μm) | 4.012 | 8.772 | 1.217 | 4.865 | 2.372 | 15.24 |

**Figure 4.** Top view and cross-section (insets) of the TiO$_2$ NT templates from the different samples after 17 h of anodization: (a) AR Ti foil, (b) 5 V, (c) 10 V, (d) 15 V, (e) 18 V, and (f) 20 V.

**Figure 5.** TiO$_2$ NT template thickness average ($\langle L \rangle$) and Ti surface roughness ($Rq$) as a function of $V_{EP}$.
3.3.2. NTs' organization, diameter, and density. The degree of organization of the obtained NT arrays can be evaluated by the study of the NTs’ bottoms. Since top analysis shows the first oxide nucleation pore distribution (that follows the initial non-optimized topography), the bottom analysis arises as the best method to evaluate organization [21, 24, 42]. The order-degree was evaluated as a function of the NTs’ hexagonal arrangement [ideal Hexagonal Closed-Packed Array (HCPA) structure] and their individual shapes [22, 42]. The NTs’ organization increases as they pack themselves in a closed-packed hexagonal arrangement, leading to tubes with a hexagonal section. The deviations from this shape due to Ti defects and grain boundaries result in pentagons, heptagons, or circular shapes [22, 42].

Our results show that only the 10 and 18 V samples present both the HCPA structure and NT of hexagonal shape (figure 6). Therefore, the samples with the highest $R_q$ (AR, 5 V) and the 15 and 20 V samples present a smaller degree of organization since, although having some HCPA domains (areas with HCPA), the NTs’ shape is not a perfect hexagon.

The NTs’ organization is also related to the surface parameters. The combination of the $R_q$ and topographic periodic ripples leads to an almost perfect organization. The 10 V sample presents the lowest $R_q$ (2.4 nm) with an $SP$ of 97 nm, while the 18 V sample has an $R_q \sim 5$ nm, and $SP = 30$ nm. These small topographic features lead to a more uniform electric field distribution, causing a much easier NT nucleation and inducing an ideal NT array distribution from the beginning of the anodization. Thus, the smallest $SP$ could be considered as an important advantage in terms of the NTs’ organization.

The 20 V sample, although having a similar $SP$ to that of the 10 V and a lower $R_q$ than that of the 18 V, shows worse organization (and smaller $L$), since these factors are shadowed by the EP potential-induced catastrophic defects. This leads to a non-efficient anodization due to the focusing of the electric field on these defects.

Based on the bottom NTs’ analysis, the NTs’ diameter ($D$) and density (number of NTs per unit area) were also quantified (figure 7). The average diameter was estimated from the size-histogram, which was then fitted to a log-normal distribution. (The inset of figure 7 presents an example for the 10 V sample.) The NTs’ density was calculated by counting the NTs in the same single domain area where $D$ was estimated.

A correlation between $R_q$ and $D$ (and consequently with the density) could then be determined: by decreasing the surface $R_q$, the NTs’ diameter increases, and the corresponding density decreases. The lowest $R_q$ achieved under 10 V leads to the highest and more uniform ($SD$ of 0.2 nm) diameter obtained after the anodization. Accordingly, the slight $R_q$ increase (for the 15 and 18 V samples) was also reflected in a slight decrease of the NTs’ diameter. The same correlation is followed by the 20 V sample, in which an $R_q$ decrease leads to a $D$ increase.

The same parameters were also determined for the AR sample ($D = 144.7$ nm, and density $= 55.03$ NTs $\mu\text{m}^2$). According to these relations, the NTs’ $D$ and density are determined by the Ti $R_q$ prior to the anodization. However, no direct relation between $SP$ and the NTs’ diameter was obtained (figure 7). The 10 V sample has periodic ripple–like structures with an $SP$ of 97 nm that causes a final diameter of 157 nm. Both doubling the ripples’ $SP$ (15 V sample) and decreasing the $SP$ to 30 nm (18 V sample) lead to a $D$ decrease. However, notice that both 15 and 18 V samples...
present higher $R_q$ than the 10 V sample, which leads us to conclude that an accurate balance between these two features ($R_q$ and $SP$) affects $D$ and the NTs’ organization. Such balance results in a higher and more uniform $D$ and more organized NT distribution for $V_{EP} = 10$ V. As discussed before, the patterned Ti with small ripple-like structures, which act as nucleation points, forces nucleation to occur on those topographic minima. Since this periodical structure for 10 V has $SP = 97$ nm, each valley behaves as a single nucleation site, forcing the NTs’ nucleation to occur simultaneously in an organized manner (see figure 4(c); the 10 V sample shows more ordered pore distribution in the initial nucleation layer) and leading to NTs with diameters of the same order ($D \sim 157$ nm). The NTs are then more packed and with slightly higher diameters due to an increase of the current flowing through these sites and almost no competition exists between the NTs.

Notice that increasing the $SP$ (15 V sample) leads to a less optimized electric field on the resulting large valleys and thus in the NTs’ competition during the anodization. This in turn decreases the degree of organization (NTs with no hexagonal shape) and the NTs’ diameter. On the other hand, by just decreasing $SP$ but increasing $R_q$ (18 V sample), we obtain highly organized NTs but with much lower $D$.

A direct correlation between $R_q$ and $D$ was determined, refining the usually stated linear relation between the anodization potential and $D$ [44, 48, 49]. Using the same anodization potential of 60 V, we can obtain different diameters just by tuning $R_q$ and $SP$, using different electropolishing potentials.

4. Conclusions

The influence of the Ti surface topography on the anodization quality and organization was evaluated. We found that by optimizing the EP potential, the Ti surface roughness can be decreased by about 70%. The combination of a lower roughness and the ripple-like structures patterned by the EP leads to the enhancement of both the degree of order and NT length. An EP under 10 V led to thick TiO₂ NT templates and to NTs’ bottoms with a highly hexagonal array distribution.

The analysis of the anodization curves revealed the importance of the surface roughness and topography (such as $SP$ ripple-like structures), where the valleys promote effective nucleation spots and thus the earlier emergence of NT nucleation. It was shown that Ti surfaces with a lower $R_q$ and adequate $SP$ ($V_{EP} = 10$ V) lead to a more homogeneous electric field over the sample surface. This causes a thinner $δ_b$ that facilitates ionic electromigration, leading to an optimized steady state anodization. In fact, the use of adequate electropolishing electrochemical conditions allows a larger potential window for NT optimized formation and enhances the rate of migration of the metal/oxide interface into the substrate. Electropolishing under a potential of 10 V is the pre-determined parameter best suited for 60 V anodization, since, besides decreasing $R_q$, it leads to the appropriated ripples’ $SP$. Higher EP voltages (above 10 V) cause local burning of the Ti surface, originating areas with defects.

Additionally, one of the main achievements of this study is the experimental demonstration that the NTs’ diameter is not only associated with the anodization potential but also with the Ti surface conditions. This work revealed new overriding anodization parameters, the Ti surface roughness and the $SP$ dimples’ topography, that can be tuned to accomplish a higher growth rate, longer NT length, and improved self-organization.

Acknowledgments

A. Apolinário acknowledges financial support under project PTDC/CTM-MET/118236/2010. C T Sousa is also grateful to FCT for the Post-Doc fellow (reference: SFRH/BPD/82010/2011). J Ventura acknowledges financial support through FSE/POPH. L Andrade acknowledges the European Research Council for funding within project BI-DSC—Building Integrated Dye sensitized Solar Cells (Contract number: 321315). The authors acknowledge funding from FCT through the project H2 Solar (PTDC/EQU-EQU/104217/2008) and the Associated Laboratory—IN.

References

[1] van de Krol R, Liang Y and Schoonman J 2008 J. Mater. Chem. 18 2311
[2] O’Regan B and Gratzel M 1991 Nature 353 737
Gratzel M 2001 Nature 414 338
[3] Paulose M, Prakasam H E, Varghese O K, Peng L, Papat K C, Mor G K, Desai T A and Grimes C A 2007 J. Phys. Chem. C 111 14992
Paulose M, Shankar K, Yoriya S, Prakasam H E, Varghese O K, Mor G K, Latempa T A, Fitzgerald A and Grimes C A 2006 J. Phys. Chem. B 110 16179
