

## Investigation on the ordering of titanium oxide nanotubes fabricated by anodization on different substrate surface morphologies

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**Abstract:** In this study, titanium oxide nanotubes anodized on three different surface morphologies of titanium foils, were investigated. AFM images is used to show different surface roughness of these foils. Nanotubes were anodized on titanium foils with 1) no polishing process (A sample), 2) electropolishing process (B sample) and 3) electropolishing process in ethanolic electrolyte (C sample). To study the ordering of titanium oxide nanotubes, the FE-SEM images of nanotubes backside were investigated. It can be seen that by decreasing surface roughness, the distribution of nanotubes diameter size becomes more uniform significantly and thereby highly ordering of nanotubes can be observed.

**Key words:** TiO<sub>2</sub> nanotubes, Electropolish, Order, Anodize, Semiconductor.

### 1. INTRODUCTION

Over the past decades, electrochemical fabrication of TiO<sub>2</sub> nanotubes by anodization method has received considerable attention due to the variety of applications. Sensors [1], photocatalyst [2], biomedicine [3], hydrogen generation [4] and dye-sensitized solar cells [5, 6] can be mentioned as some of the TiO<sub>2</sub> nanotubes applications. The geometry and morphology of the anodic titanium oxide have a significant role in the performance of these devices. In dye-sensitized solar cells, a tube length in the range of 10-20 μm [7] and a small tube

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diameter [8, 9] leads to a high conversion efficiency.

There are many parameters affected on the TiO<sub>2</sub> nanotubes structure. Anodization voltage, water content, kind and pH of the electrolyte and anodization time are some of these important parameters. It is reported that the diameter of nanotubes is controlled linearly by the applied voltage [10, 11]. The tube length was investigated as a function of anodization voltage and fluoride concentration [12]. However, another effective factor in the growth of the tubes is the anodization time [13]. The nanotubes grown in organic electrolyte, such as ethylene glycol [14], glycerol [15], has a significant difference in morphology with respect to the nanotubes grown in aqueous electrolytes [16]. Water content of the electrolyte has a crucial role in the nanotubes diameter [17], tube length [18], the transition between TiO<sub>2</sub> nanopores and nanotubes [19] and the smoothness of tube walls [10].

A key factor to control the characteristics of the TiO<sub>2</sub> nanotubes is initial surface roughness before anodization. There exist a very limited number of reports about the effect of initial surface conditions on the TiO<sub>2</sub> nanotubes structure. Schmuki's group have shown that the existence of an oxide layer which is created by pre-anodizing in F-free electrolyte [20] or mechanical polishing [21] acts as a protective layer to prevent chemical etching of the tube tops. In their other work, they have produced a template including both TiO<sub>2</sub> nanotubes and nanopores by changing the thickness of initial TiO<sub>2</sub> layer at different pre-anodizing voltages [22]. Some scientists have investigated the order of the nanoporous layer produced by two-step anodization [23] and three-step anodization [24] on the electropolished surface. The other group has studied the effect of electropolished surface on the uniformity of length and the order of back side of the tube bottoms [25]. The effect of added ethanol to electropolishing electrolyte on diameter and length of TiO<sub>2</sub> nanotubes are investigated in our previous work [9].

In the present work, two different initial surface roughness of titanium foil by changing the polishing conditions are fabricated [9]. The morphology of the surfaces is investigated by AFM images and also the behavior of the electropolishing current density is studied. The mechanism of electropolishing and the act of ethanol is explained in detail. After that titanium dioxide nanotubes are fabricated on these surfaces by electrochemical anodization. According to FE-SEM images, the morphology of nanotubes backside is investigated. Then the ordering of nanotubes and also distribution of outer nanotubes size are compared to each other and also to as-received sample.

## 2. EXPERIMENTAL

Three different samples are: 1) as-received sample is nominated "A" sample, 2) sample electropolished at 10°C in an electrolyte solution containing perchloric acid (65%, Merk) and glacial acetic acid (100%, Merk) is nominated "B" sample and 3) sample electropolished in above mentioned electrolyte with additional 15 vol.% ethanol at 1°C is nominated "C" sample. The electropolishing voltage was increased from 0 to 50 V with rate of 1 V/s and held at 50 V for 6 min. The anodization was performed at fixed temperature of 20 °C in an ethylene glycol based electrolyte containing 0.3 wt.% NH<sub>4</sub>F and 2 vol.% H<sub>2</sub>O at a constant potential of 60 V and the electrolyte stirring speed of 1100 rpm. Anodization time for all samples was 2 hours. Before anodization, roughness factor of the surfaces (RMS) was measured by an atomic force microscopy (Veeco AFM AutoProbe CP-Research). The field emission scanning electron microscopy images were taken by Hitachi FE-SEM S-4160. The experiment procedure is explained in more detail in our previous work [9].

## 3. RESULTS AND DISSCUSSION

Fig. 1 shows the AFM images of Ti foils with different surface morphologies: A, B and C samples. The corresponding surface roughness is also given in Table 1. As can be seen from Fig. 1a, the A sample has a rough surface with random heights. By electropolishing, the surface smoothness improves considerably. According to table 1, the roughness of the electropolished surfaces (B and C samples) declines significantly. Electropolishing creates flat surfaces with a moderate fluctuation. Moreover the variation of height in C sample is very regular than B, Fig. 1b and Fig. 1c; and only small undulations can be seen on its surface. Also there are some small pits on B surface in all regions, Fig. 1b, without any regularity which can be seen in C sample.

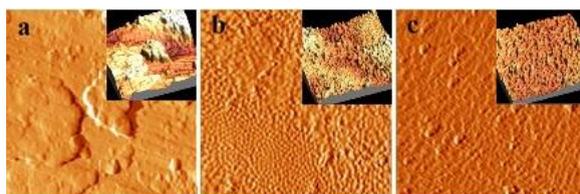


Fig.1. AFM images of Ti samples in different surface conditions: a) A sample, b) B sample and c) C sample.

Table 1. Surface roughness, outer diameter size of TiO<sub>2</sub> nanotubes and maximum value of electropolished current density.

Sample	RMS of Surface Roughness (nm)	Electropolished $I_{MAX}$ (mA/cm <sup>2</sup> )	Outer diameter from nanotubes backside (nm)
A	25.95	-	125±5
B	11.43	122	120±5
C	8.14	222	92±5

Fig. 2 shows the electropolishing curves of current density and voltage versus time for B and C samples. The amount of the current density of C sample is more than the other one at all times, and, the maximum amounts of current density ( $I_{MAX}$ ) of B and C samples are 122 and 222 mA/cm<sup>2</sup>, respectively, Table 1. The reason of this event is due to existence of ethanol in polishing electrolyte which increased the electrolyte conductivity. As it is illustrated in the figure, for both electropolished samples, two current peaks are observed as the voltage is increased. Then the current densities drop sharply as the voltage becomes constant and after a few minutes, they go to a constant value. The reduction rate of current density in B sample is faster than C. Thereby it reaches to a stable value in a shorter time for B sample, about 300 s, whereas this value for the other sample (C) is about 400 s.

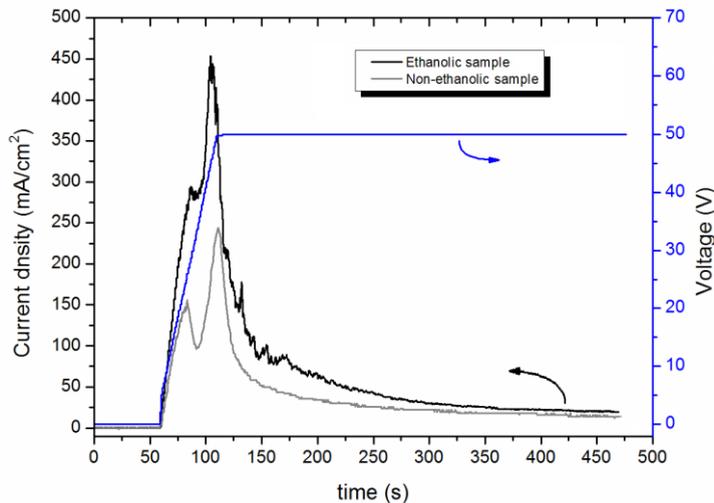


Fig. 2. Electropolishing curves of current density and voltage versus time curves of non-ethanolic (B sample) and ethanolic (C sample) samples.

It is worth to explain the process of electropolishing in more details. Fig. 3 shows the mechanism of electrolyte polishing on the rough surface of titanium. On this surface, a viscous liquid layer are immediately produced by the reaction between the metal and electrolyte. This layer of solution, known as the polishing film, has a greater electric resistance than the rest of the electrolyte and it controls the smoothing action. Because the distance A-B is less than the distance C-D, the resistance at peak A will be lower than at deeper point C. Thereby, the current at A will be much higher than at C, causing metal to dissolve faster at A than at C, and producing a nearly level, gently undulating surface by removing asperities in order size of micrometer to have a smooth surface. More rapid ionic and molecular diffusion through the thinner polishing film at A, as well as differences in anodic polarization phenomena at A and C, may also contribute to the leveling or smoothing action. To have brightened surface, irregularities as small as about  $0.01 \mu\text{m}$  are eliminated due to a thin polishing film [26].

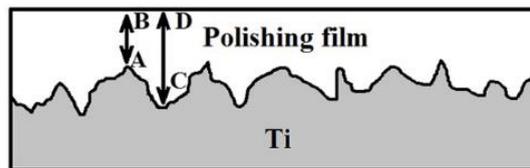


Fig. 3. Mechanism of electrolyte polishing

Here by adding ethanol to the polishing electrolyte, the brightness of the surface is increased. According to Table 1, the surface roughness of C sample is  $8.14 \text{ nm}$  where this is less than  $10 \text{ nm}$  which is necessary to have a bright surface. Actually the added ethanol to the polishing electrolyte increases the disintegration of ions; thereby the resistance of the electrolyte decreases. As a result, the polishing film of this sample will have a less resistivity than the B sample. Therefore, the local current density at the sharp points (ex. point A) of C sample is more than the B sample, then the higher rate of polishing and brightening action occurs and finally a smoother and brighter surface is produced.

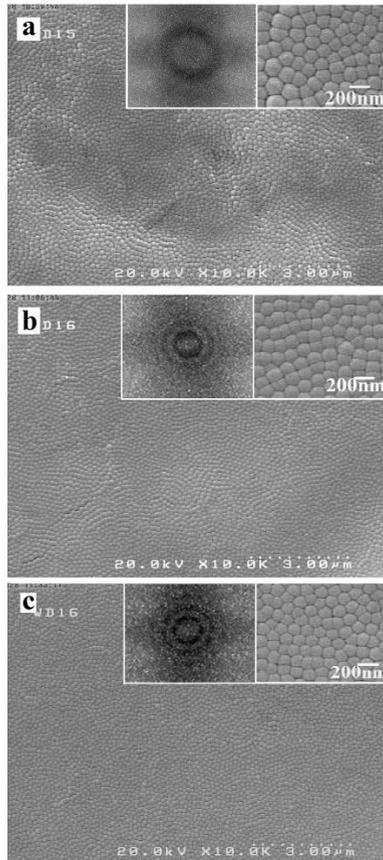


Fig. 4. FE-SEM images of the backside of  $\text{TiO}_2$  nanotubes anodized in different initial surface conditions: a) A, b) B and c) C samples, with their 2D fast Fourier transforms (FFTs).

After anodizing on different initial surfaces, the anodized layers are peeled off from the Ti substrate to investigate the effect of initial surface condition on topography and ordering of the  $\text{TiO}_2$  tube bottom. Fig. 4 shows the FE-SEM images of the  $\text{TiO}_2$  nanotubes backside of anodized A, B and C samples. Also, their corresponding 2D fast Fourier transforms (FFTs) are shown in this figure. The curved shape of backside of  $\text{TiO}_2$  nanotubes layer reflects the initial surface morphology of Ti foil. It is clear from this figure that electropolishing process has a great effect on the smoothness of the template surface. The distinguished darkness difference in image of the anodized A sample indirectly indicates a rougher surface compared to anodized electropolished samples. Also, as it is expected darkness difference in image of anodized C sample is less than B

sample. As shown in insets of FE-SEM images of Fig. 4, by decreasing the surface roughness, the uniformity of the nanotubes outer diameter size distribution is increased. The nanotubes outer diameter of the anodized A sample differs significantly from one tube to the other one, Fig. 4a, whereas the distribution uniformity of the anodized electropolished samples (B and C samples) can be seen clearly. At a closer look, the nanotubes outer diameter of C sample has a more distribution uniformity than the B sample. In addition, the outer diameter of nanotubes backside decreases by decreasing the surface roughness. The outer diameter of anodized A, B and C samples are 125 nm, 120 nm and 92 nm respectively, Table 1. Therefore, by decreasing the surface roughness, the number density of tubes increases, which it affects the efficiency of devices included TiO<sub>2</sub> nanotubes very much.

According to the Fig. 4, the FFT pattern of the A sample shows a ring shape which indicates slightly ordered array of the nanotubes. In contrast, the FFT of the anodized electropolished samples show a more ordering of nanotubes where the order of anodized C sample is more than the anodized B sample. The FFT pattern of the C sample consists of six distinct spots which demonstrate a highly long range hexagonal ordered of nanotubes arrangement of this sample.

#### 4. CONCLUSION

By investigating three initial surface roughness of Ti foils, interesting results are observed for TiO<sub>2</sub> nanotubes structure produced by anodizing on them. By smoothing Ti initial surface, nanotubes diameter size distribution becomes more uniform significantly, also, the number density of tubes increases because of reduction of outer diameter of nanotubes from 125 nm to 92 nm. In addition, ordering of nanotubes increases very much. Actually, highly ordered TiO<sub>2</sub> nanotubes with smaller outer diameter were fabricated on Ti surface electropolished in ethanol electrolyte (C sample), which shows the high effect of initial surface roughness on TiO<sub>2</sub> nanotubes structure.

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