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SURFACE PERSPECTIVE OF A TiO_2 NANOARCHITECTURE

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În cadrul acestei lucrări este prezentat un studiu de suprafață prin AFM, SEM şi EDS a unor electrozi de titan, acoperiți cu TiO_2 sub forma unei nanoarhitecturi autoordonate, subliniindu-se două structuri morfologice: nanopori şi nanotuburi. Aceste două timpuri de structuri se evidențiază printr-un tratament post-anodizare ca urmare a ultrasonării pe termen lung a suprafeței de oxid de titan crescut.

This paper presents a surface study through AFM, SEM and EDS of titanium electrodes covered with a TiO_2 selfordered nanoarchitecture, underlining two morphological structures: nanopores and nanotubes. These two types of structures are highlighted by a post-anodizing treatment, as a result of the long term ultrasonication over the grown titanium oxide surface.

Keywords: anodizing, TiO_2, ultrasonication, AFM, SEM

1. Introduction

The growth of selfordered TiO_2 nanotubes was first reported in 1999 [1] through an anodizing process. Since then the interest started a wide range of studies into this area. Different variation of growth conditions lead to a characterization of these nanostrucutres that presented different conformations with respect to their heights, diameters and lengths [2-5].

The properties of these TiO_2 nanotubes recommends this material for a wide range of applications in biosensors [6,7], gas sensing [8-10], photocatalysis [11] for hydrogen generation [12,13] or organic compounds degradation [14-16], biocompatibility [17,18], self-cleaning [19], solar energy conversion [20].

Usually most of the growths of nanotubes are made through fluoride electrolytes anodizing, as this is the preferred choice for the generation of the selfordered TiO_2 matrix. Also, a glycerol electrolyte was used, due to the added flexibility over the tube diameter that can be adjusted by the increase of water content [21]. In this study relatively low water content of 4% H_2O was used.

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In a previous work [22] a surface variance of the TiO_2 matrix from nanotube towards nanopore was observed by changing the anodizing potential. An ultrasonication (US) treatment was further applied to eliminate the disordered precipitated layer over the nanotube arrays [23].

Many aspects of the nanostructures growth have been intensively studied. In this paper the study is focused on the surface influence of the ultrasonication phenomenon in a water environment over the already grown nanostructures [22].

In US, ultrasound energy is generated by sound frequencies between 20 kHz and 50 MHz. Consequently, an US ultrasonic bubble is formed in a liquid and (over 400µs from the bubble formation) high energies are released generating cavitations [24] at its collapse.

Due to these aspects, important changes of the TiO_2 matrix surface were achieved, generating the shift of nanopore/nanotube surface aspect by the variation of US times. These aspects are emerging due to a long term US treatment applied over the grown titanium oxide surface.

These changes of the grown TiO_2 nanostructures open new perspectives over the versatile properties that already recommend this material for a wide applicability [25].

The results were obtained through AFM statistical data, SEM morphological images and EDS evaluations.

2. Experimental

The anodizing was carried out with a two electrode system: a titanium working electrode of 99.6% purity from Goodfellow Cambridge Ltd UK and a graphite counter electrode connected to high-voltage MATRIX MPS-7163 power source. The working electrode was previously polished with SiC paper of granularity up to 4000 until a mirror surface was achieved. Further, the samples were ultrasonicated for 5 min in distilled water in a Raypa UCI-150 ultrasonic cleaner.

The electrolyte used for anodizing was a glycerol solution with 4% Millipore 18.2 MΩ·cm ultrapure water and 0.36M NH_4F. After the TiO_2 nanostructures were grown at 60V applied potential for 2 hours, the working electrode was rinsed with ultrapure water and dried for 2 hours at 80ºC in a Caloris EG-50 oven.

After the anodizing and rising process, the TiO_2 nanostructures were ultrasonicated at different time intervals from 15 min to 35 min in a distilled water environment.

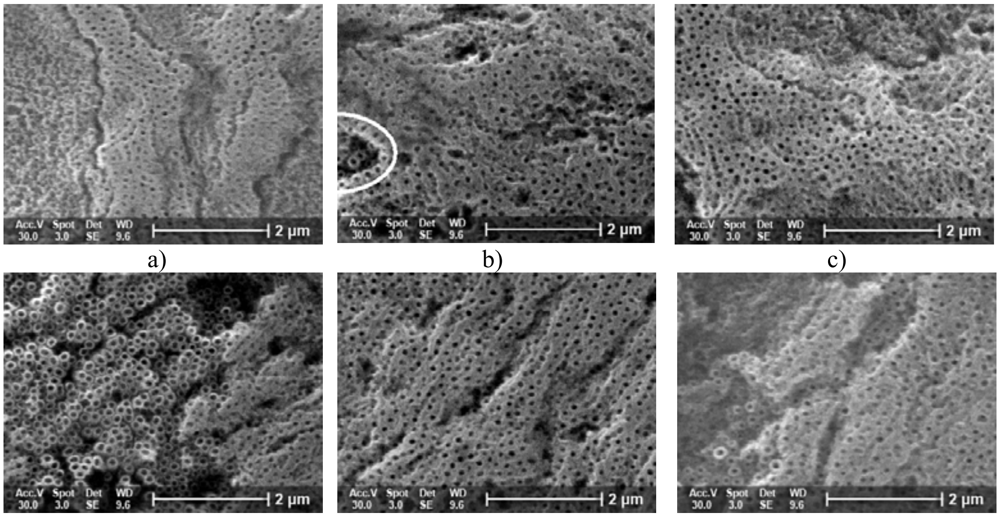
The surface microscopy information was collected with an Atomic Force Microscope (AFM) from APE Research, Italy and Scanning Electron Microscope XL 30 ESEM TMP. XL 30 ESEM TMP was also used for EDS determinations.

3. Results and discussions

3.1 SEM characterization

The US treatment was performed and substantial morphological change was noticed, as presented in SEM images below (Fig. 1).

Where no US treatment was applied, a disordered oxide layer described as a precipitate layer [23] can be observed next to the surfaced nanopore structure. In Fig. 1 b for 15 min US in the highlighted area a nanotube emerges from the nanopore surface. Further a solely nanopore surface is restored (Fig 1 c), followed by a mainly nanotube surface (Fig. 1 d) for 20 and 25 min US times respectively. The same behavior is observed for 30 and 35 min of US treatment (Fig. 1 e and f).



a) b) c)

d) e) f)

Fig. 1–SEM images for the evolution in time of TiO_2 nanostructures:
a) 0 min US, b) 15 min US, c) 20 min US, d) 25 min US, e) 30 min US f) 35 min US

Regarding the pores area, the US treatment has an impact over its dimensions (Fig. 2).

A maximum area of the pores has a value of 8 and 8.5 μm^2 for the 0 and 35 minutes of US, respectively higher values for 15, 20 and 25 minutes of US (around 11.5 μm^2), with an intermediary value of 10.5 μm^2 at 30 minutes US.

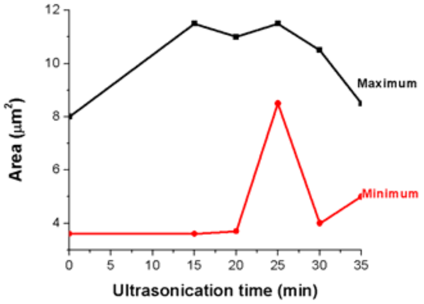
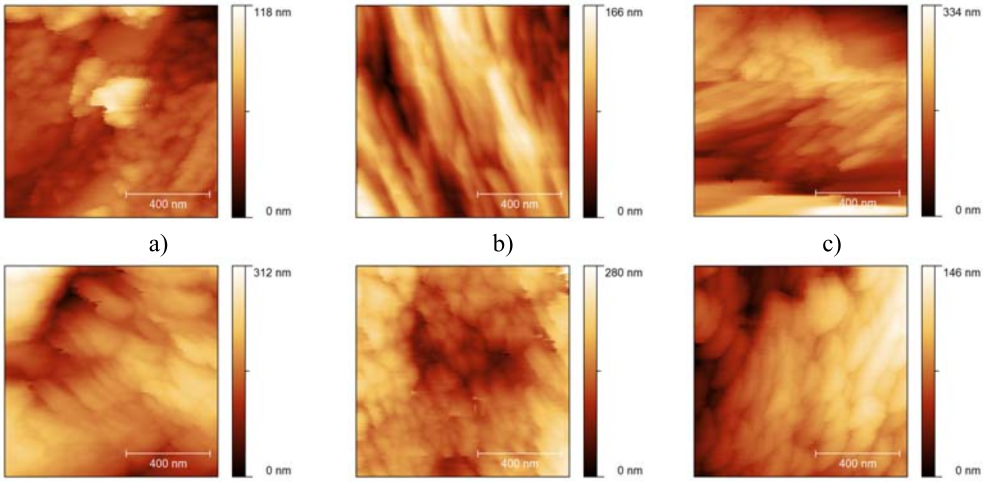


Fig. 2 –Variance of the maximum and minimum values for the internal areas of the nanostructures after different US times

The minimum values for the area of the examined samples are around 3.6 μm^2 for 0, 15 and 20 minutes of US; it rises to 8.5 μm^2 and lowers again to 4 and 5 for 30 and 35 minutes of US respectively. The highest variance between the maximum and minimum areas is of 7.9 μm^2 at 15 minutes and the lowest is of 3 μm^2 at 25 minutes. The measured internal areas of the nanostructures after different US times show that the 25 min of US treatment lead to the smallest area variance of the TiO_2 nanostructures.

3.2 AFM evaluation

The statistical data over the surface topography were obtained from scanned AFM images presented in Fig. 3. The functions are computed after a horizontal stroke correction as normalized histograms of the height, where ρ is the normalization of the densities, presented in Fig. 4 for different US times.



a) b) c)

d) e) f)

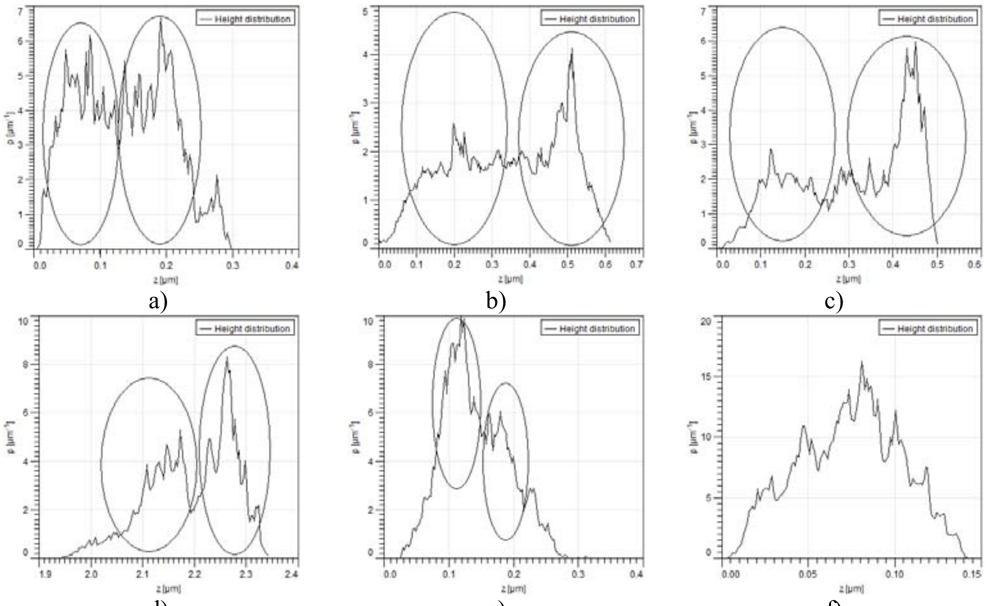
Fig. 3 – AFM micrographs for the evolution in time of TiO_2 nanostructures:

a) 0 min US, b) 15 min US, c) 20 min US, d) 30 min US, f) 35 min US

The initial TiO$_2$ precipitate layer of the sample where no US treatment was applied presents an average roughness value of 59.7 nm, indicating a relatively smooth surface. This is confirmed by the SEM image in Fig. 1 a). As US effect acts over the surface through cavitation, the average roughness increases at 131.6 nm for 15 min US. A longer US leads to a smoothing of the surface from the roughness point of view. Average roughness values of 115.8 nm, 69.6 nm, 41.4 nm and 24.3 nm for the sample subject to 20 min, 25 min, 30 min and respectively 35 min of US were determined.

Between 0 and 30 min US bimodal mixtures of two normals can be observed. This corresponds to two different height plateaus of extreme values that keep a significant statistical contribution indicated by the bimodal functions highlighted in Fig. 4.

At 30 min of US treatment, the bimodal function is not so clearly shaped. This is an indication that the two height planes are leveled, fact that is revealed and confirmed by the roughness. This is finally shown by the clear representation of a unimodal statistical height distribution for 35 min US sample.



a) b) c)

d) e) f)

Fig. 4 – AFM statistical data for TiO$_2$ nanostructures:
a) 0 min US, b) 15 min US, c) 20 min US, d) 30 min US, f) 35 min US

The bimodal function may be an expression of a surface with cavitations that after different US times tends to a planar surface close to the nanostructures bottom.

4. Surface overview

The titanium substrate was subjected to two separate processes. One is the anodizing as method for the nanostructures growth [22,26] and other is the ultrasonication as means of surface modification.

The anodizing process essentially comprises two main phenomena: one is TiO_2 oxidation and the other is TiO_2 dissolution [27]. The oxide layer growths over the Ti surface according to the formula:

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+$$

In the presence of the aggressive fluoride, the TiO_2 grown layer is dissolved in accordance with the formula:

$$TiO_2 + 6HF \rightarrow [TiF_6]^{2-} + 2H_2O + 2H^+$$

During this process, a precipitate layer is continuously formed on the surface [23].

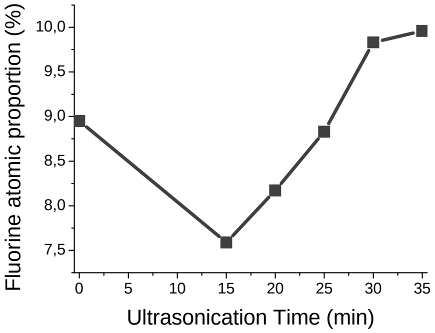


Fig. 5 – EDS atomic proportion of fluorine after different US times

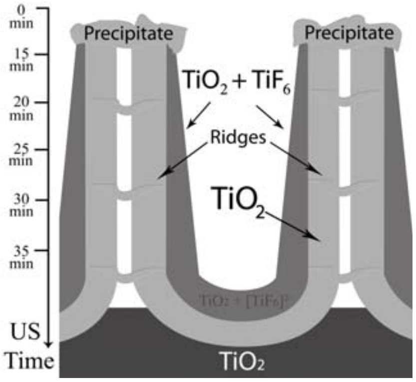


Fig. 6 – Schematic overview of the nanostructures as US acts over time

The US acts over the surface generating cavitations. After ultrasonication continous layered exposure of the grown nanostructures to the US phenomenon was achieved. The EDS measurements (Fig. 5) present a high fluorine proportion of 9%. This is likely due to the presence of an initial fluorine rich precipitate layer at the nanostructures surface after the drying treatment. A significant drop of fluorine of 7.6% is recorded for 15 min US and then it steady increases until 10%. This is likely due to the exposure of the fluoride-containing surface after the layered US action in time (Fig. 6). These EDS measurements correlated with the increase in tube walls (observed in the SEM images from Fig 1 a, d and f) leads us to the conclusion that it exists a TiO_2 area rich with a fluorine complex lining at the interior of the nanostructures. As we reach towards the bottom this lining increases with respect to the increase of the tube wall diameter. This evolution is sketched in Fig. 6.

After 35 minutes of US we can conclude that close to the TiO_2 nanostructures bottom an increased amount of the fluoride compounds can be detected.

5. Conclusions

During the US treatment substantial morphological change of the TiO_2 surface were noticed. We obtained a variation from nanopore to nanotube aspect over the same surface. The AFM statistical data indicates initially two height planes, afterwards reaching a final one plane distribution.

EDS and SEM images after different US times indicates the formation of a fluorine-rich complex that increases with respect to the increase of the tube wall diameter.

The US phenomenon allowed us to obtain a view that reflects the growth mechanism and estimate the nanoarchitecture structural atomic constitution.

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