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### **Investigation of changes in the composition of anodic TiO<sub>2</sub> nanotubes at different stages of formation by AES and TOF SIMS methods**

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**Abstract:** The article presents comprehensive studies of the chemical composition and morphology of nanotubular anodic TiO<sub>2</sub> layers at the first stages of the porous structure nucleation, by scanning electron microscopy (SEM), Auger spectroscopy (AES), time-of-flight secondary ion mass spectrometry (TOF.SIMS). Our goal was to show the profile distribution of chemical elements and reaction products at each of the initial stages of the anodic oxide growth in the ethylene glycol-based electrolyte containing fluoride, which will help expand the understanding of pore formation mechanism.

**Keywords:** TiO<sub>2</sub>, nanotubes, anodization, AES, TOF.SIMS

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Материалы конференции

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### **Исследование изменения состава анодных нанотрубок TiO<sub>2</sub> на разных стадиях формирования методами AES и TOF SIMS**

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**Аннотация.** В статье обсуждаются комплексные исследования химического состава и морфологии нанотрубчатых анодных слоев TiO<sub>2</sub> на первых этапах зарождения пористой структуры методами сканирующей электронной микроскопии (СЭМ), Оже-спектроскопии (ОЭС), времяпролетной вторично-ионной масс-спектрометрии (ВИМС). Цель такого комплексного исследования — показать профильное распределение химических элементов и продуктов реакции на каждой из начальных стадий формирования анодного оксида во фторсодержащих электролитах на основе этиленгликоля, что позволит расширить представления о механизме порообразования в оксиде титана.

**Ключевые слова:** TiO<sub>2</sub>, нанотрубки, анодирование, ОЭС, ВИМС

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### Introduction

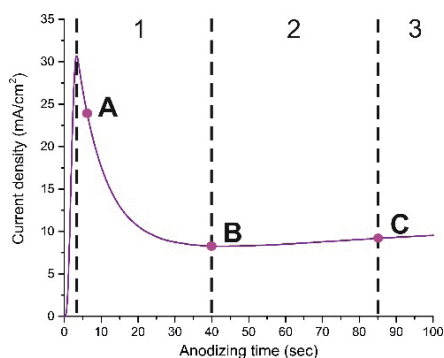
Nanostructured titanium oxide currently represents a major research interest due to its possible application in the storage of energy sources [1], photocatalysis [2], and solar cells [3].

One of the promising nanostructured modifications of titanium oxide is nanotubular anodic titanium oxide ( $\text{TiO}_2$  NTs). The anodic formation process makes it possible to create not only a highly ordered  $\text{TiO}_2$  NTs array on a titanium substrate, which facilitates the formation of electronic structures based on them but also allows very precise control of geometric parameters during growth, in contrast to classical powder nanomaterials based on  $\text{TiO}_2$  [4]. Despite the extensive studies of the structure-properties based on  $\text{TiO}_2$  NTs, the nucleation and growth mechanism of pores is still not fully clear.

In this article, the distributions of chemical elements and ionic fragments of nanotube titanium oxide during the formation stages were demonstrated by Auger spectroscopy and time-of-flight secondary ion mass spectrometry methods.

### Materials and Methods

$\text{TiO}_2$  NTs were formed on titanium foil (0.89 mm thick, 99.7% metal basis, Alfa Aesar). The substrate was pretreatment in acetone in an ultrasonic bath for 15 min. Prior to anodization, substrates were chemically polished in  $\text{HNO}_3$ :HF solution during 120 s, then washed in deionized water (18.2 M $\Omega$ ) and dried in an air stream. The electrochemical growth of titanium oxide was carried out in a potentiostatic mode (60 V) and a temperature of 20 °C. A platinum grid was used as a counter electrode. Anodizing was performed in 98 vol.% ethylene glycol with the addition of 0.3 vol.%  $\text{NH}_4\text{F}$  and 2 vol.%  $\text{H}_2\text{O}$ . After anodizing, the samples were washed in ethyl alcohol and dried in an air stream. Subsequently, ready samples were not subjected to heat treatment and remained in the amorphous state.



**Fig. 1.** Chronoamperometry curve for growth of nanotube  $\text{TiO}_2$  layer

Fig. 1 shows a typical chronoamperometric curve of the nanotubes layer growth process with highlighted formation stages (1, 2, 3) and critical current density points A, B, C. These critical points were chosen to analyze the chemical composition of the samples by the depth.

At the beginning of the anodizing process (i.e., when a potential is applied) in stage 1, the current sharply decreases to a critical value due to the formation of an initial oxide layer with high resistance. The current rises as the pores develop to a local maximum (stage 2). Finally, the current reaches a constant value in stage 3, when the equilibrium state of the formation of  $\text{TiO}_2$  is reached, which is achieved by the equality of the oxide formation rate at the metal/oxide interface and the dissolution rate at the oxide/electrolyte interface [5].

### Research methods for titanium oxide

Morphological characterization of anodized samples was employed by scanning electron microscopy (FEI Quanta 3D FEG). No charging effects were observed; therefore, no additional coatings on the samples were required. The accelerating voltage used for imaging was 3 kV and the working distance was 4 mm.

The AES system used for investigations was Physical Electronics PHI-670xi Scanning Auger Nanoprobe. The argon ion gun operated at 2 kV with ion current 0.35 A was used for sample surface sputtering during depth profiling. The etching rate was controlled by a  $1 \times 1.5 \text{ mm}^2$  ion beam raster. Depth profiling over an area was performed at the primary electron beam energy of 10 keV and a current of 20 nA. A profile research of the composition of the  $\text{TiO}_2$  oxide layer was carried out on an area 75–100  $\mu\text{m}$  in diameter by a primary electron beam.

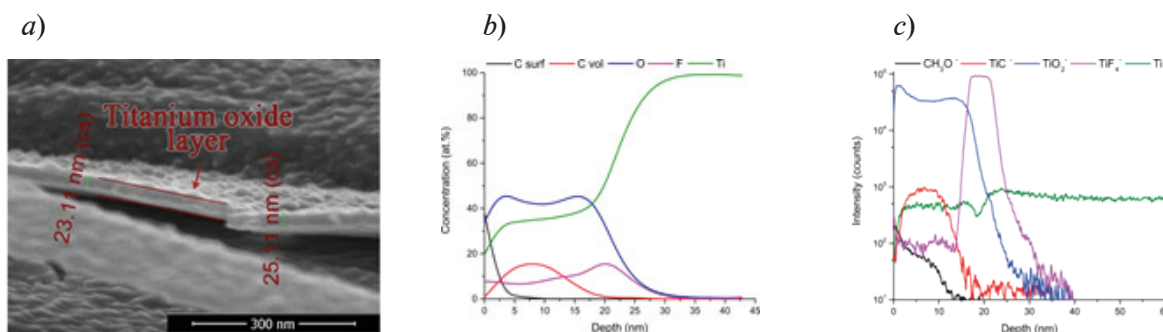
Time of flight secondary ion mass spectrometry investigations was performed on TOF.SIMS-5 instrument (IonTOF GmbH, Germany). For depth profiles acquired in this study, 500V  $\text{Cs}^+$  with 40 nA current was used to create a 300  $\mu\text{m}$  by 300  $\mu\text{m}$  area, and the middle 100  $\mu\text{m}$  by 100  $\mu\text{m}$  area was analyzed using a pulsed 0.6 pA  $\text{Bi}_3^{++}$  primary ion beam at 30 kV accelerating voltage with 14 ns pulse width and 112 ns buncher delay.

## Results and Discussion

### Point A

As can be seen from the SEM image (Fig. 2, *a*), during the first 6 seconds of anodizing, a textured dense titanium oxide layer of about ~23–26 nm thickness is formed on the surface of the titanium foil.

Two types of carbon, one of which is hydrocarbon contamination ( $\text{C}_{\text{surf}}$ ) and the other corresponds to the carbide state of carbon in the oxide film volume ( $\text{C}_{\text{vol}}$ ), can be seen in the depth distribution graph obtained by Auger-electron spectroscopy (Fig. 2, *b*). A more detailed description of the features of the analysis and the rationale for the choice of the analyzed peaks of chemical elements are presented in our previous work [6]. Surface contamination disappears almost completely at about a depth of 10 nm, while the signal of carbide begins to drop noticeably only at a depth of about 20 nm. The carbide form of the carbon Auger peak can be associated with chemical bonds of titanium with organic fragments, i.e. the Ti-C bond [7].



**Fig. 2** Cross-sectional SEM images for an array of  $\text{TiO}_2$  detached from Ti foil (*a*), AES profile analysis (*b*) and TOF.SIMS profile (*c*) at point A

The presence of fluorine atoms in the structure is associated with the use of fluoride electrolytes, the anions of which are incorporated into the film during growth. In addition, as was shown in [8],  $\text{F}^-$  ions have a higher migration rate through the titanium oxide film as compared to oxygen ions  $\text{O}^{2-}$ . This speed difference results in the formation of a fluorine-rich layer at the interface between the oxide and the titanium substrate.

Secondary ion time-of-flight mass spectrometry (TOF.SIMS) was used to establish the chemical bonds of fluorine and carbon with other elements in the oxide. The possible chemical bonds and their variations of fluorine and carbon in the  $\text{TiO}_2$  oxide layer can be determined by analyzing the depth distribution of ionic fragments.

From the results of TOF.SIMS profile analysis (Fig. 2, *c*) we can see that on the surface of the oxide (about 5 nm) there is an increased intensity of organic contamination, represented by the ionic fragment  $\text{CH}_3\text{O}^-$ , which gradually decreases and is probably associated with the residual reaction products from the electrolyte.

The ionic fragment of  $\text{TiF}_4^-$  repeats the shape of the distribution from fluorine in the AES method. The intensity of the  $\text{TiF}_4^-$  fragment is at the upper limit of sensitivity of the device ( $10^5$ ).

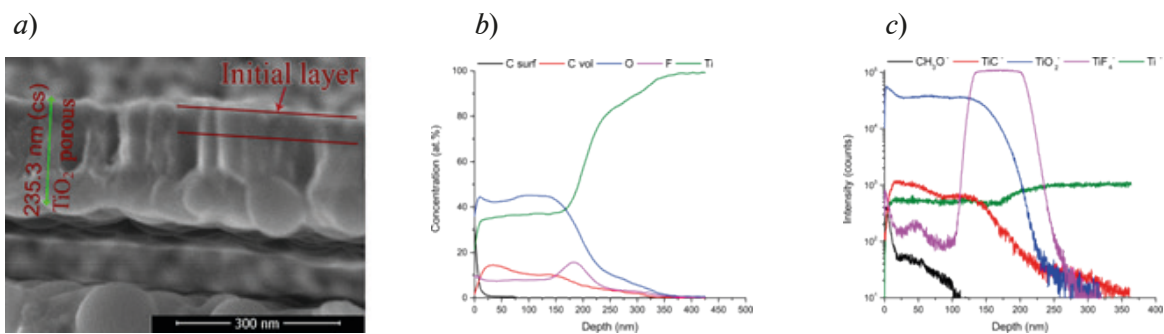
The shape of the distribution of the  $\text{TiC}^-$  ion fragment also repeats the shape of the distribution of  $\text{C}_{\text{vol}}$  by AES.



From the depth distribution profile of  $\text{TiO}_2$ , it can be said that the oxide layer formed during the first 6 seconds of anodizing was about 25 nm, which agrees with the SEM image and the AES profile analysis. It is known that hydrocarbon contamination as well as matrix modification during ion sputtering changes the yield of secondary ions. This effect can influence the decrease of signal intensity from  $\text{TiF}_4^-$  and  $\text{TiC}^-$  ion fragments after removal of hydrocarbon-contaminated layer by ion sputtering.

### Point B

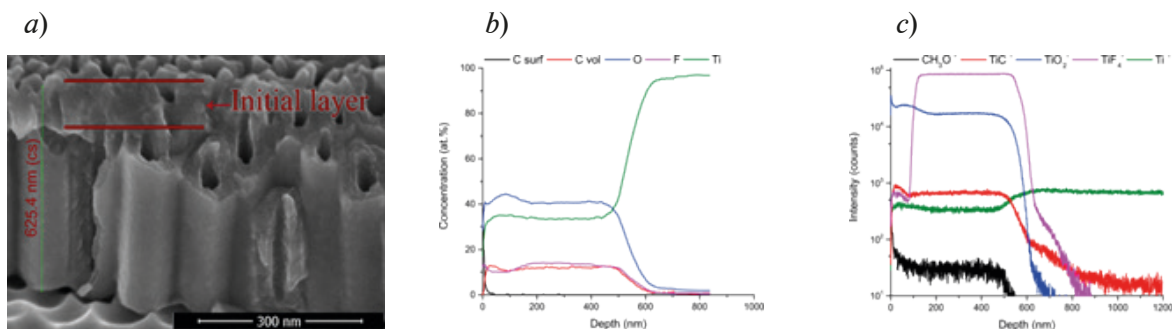
At point B, the pores continue to grow (Fig. 3, *a*). At the previous anodization point,  $C_{\text{vol}}$  was practically not observed in the fluorine-enriched area. At point B, the  $C_{\text{vol}}$  concentration decreases from 10 to 5 at.% in the fluorine-enriched layer volume (Fig. 3, *b*). It should be noted that the highest carbon concentration is within the first 20–100 nm and is probably the thickness of the initial layer, which forms a porous crust over the nanotube array, which correlates with the results of SEM image. This is also confirmed by the results of the TOF.SIMS profile analysis (Fig. 3, *c*).



**Fig. 3** Cross-sectional SEM images for an array of  $\text{TiO}_2$  detached from Ti foil (*a*), AES profile analysis (*b*) and SIMS profile (*c*) at point B

### Point C

At point C, the pores become titanium oxide nanotubes (Fig. 4, *a*). According to the AES analysis at point C (85 s of anodization) (Fig. 4, *b*), the distribution of  $C_{\text{vol}}$  and F in the titanium oxide volume is uniform and is about 15 at.%. In previous work [6], we showed that a single  $\text{TiO}_2$  nanotube has a three-layer structure, where  $C_{\text{vol}}$  is only in the inner layer of the tube, and fluorine is only contained on the outer part of the nanotube. The analysis of the TOF.SIMS depth profile (Fig. 4, *c*) shows that the  $\text{CH}_3\text{O}^-$  ion fragments have a stable intensity from 100 to 500 nm, which indicates the presence of reaction products from the electrolyte in the tube array. The AES data confirm this, but due to the low sensitivity the hydrocarbon signal does not exceed 1–0.5 at.%. The distribution of the profile of the remaining ionic fragments confirms the results of the AES depth analysis.



**Fig. 4** Cross-sectional SEM images for an array of  $\text{TiO}_2$  (*a*), AES profile analysis (*b*) and SIMS profile (*c*) at point C

### Conclusions

It can be concluded that a compact initial layer of titanium oxide is formed on the titanium surface at the first stage of anodizing. Then, fluorine and oxygen ions diffuse through it, under the influence of an electric field, to form a fluorine-enriched layer at the oxide/metal interface. Over time, the surface of the initiating oxide layer becomes more textured and the thickness increases. The fluorine-enriched layer also becomes thicker and eventually forms a porous/tubular structure underneath the compact oxide layer.

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