



INVESTIGATION OF CHANGES IN THE COMPOSITION OF ANODIC TiO₂ NANOTUBES AT DIFFERENT STAGES OF FORMATION BY AES AND TOF SIMS METHODS

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About this work

This work presents a complex research of the chemical composition and morphology of nanotubular (NT) anodic TiO₂ 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). Such complex research aimed 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 mechanisms in anodic titanium oxide.

Experimental

TiO₂ 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 HNO₃:HF solution during 120 s, then washed in deionized water (18.2 MΩ) 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 has carried out in ethylene glycol 98 vol.% C₂H₄O₂ with the addition of 0.3 vol.% NH₄F and 2 vol.% H₂O. After anodizing, the samples were washed in ethyl alcohol and dried in a stream of air. Subsequently, ready samples were not subjected to heat treatment and remained in the amorphous state. Morphological characterization of anodized samples was employed by scanning electron microscopy (FEI Quanta 3D FEG). The AES system used for investigations was Physical Electronics PHI-670xi Scanning Auger Nanoprobe. Time of flight secondary ion mass spectrometry investigations was performed on TOF.SIMS-5 instrument (IonTOF GmbH, Germany).

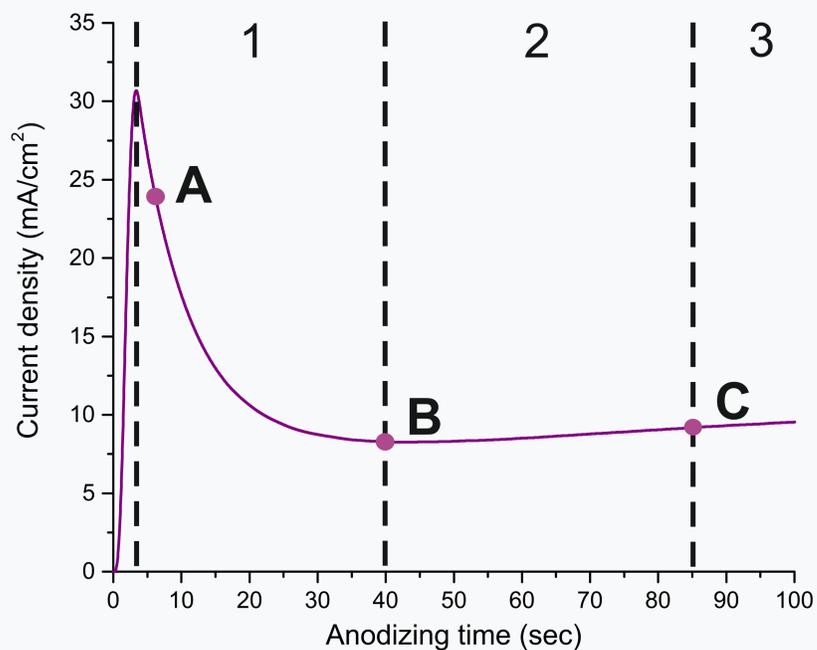


Figure 1 shows a typical chronoamperometric curve of the nanotubes layer growth process with highlighted formation stages (1, 2, 3) and critical current density points - A, B, C. These critical points were chosen to analyze the chemical composition of the samples by the depth.

Stage 1 - the current sharply decreases to a critical value due to the formation of a initial oxide layer with high resistance.

Stage 2 - as the pores develop, the current increases to the maximum value.

Stage 3 - the current begins to stabilize, which is associated with the establishment of equality of the oxide formation rate at the metal/oxide interface and the dissolution rate at the oxide/electrolyte interface.

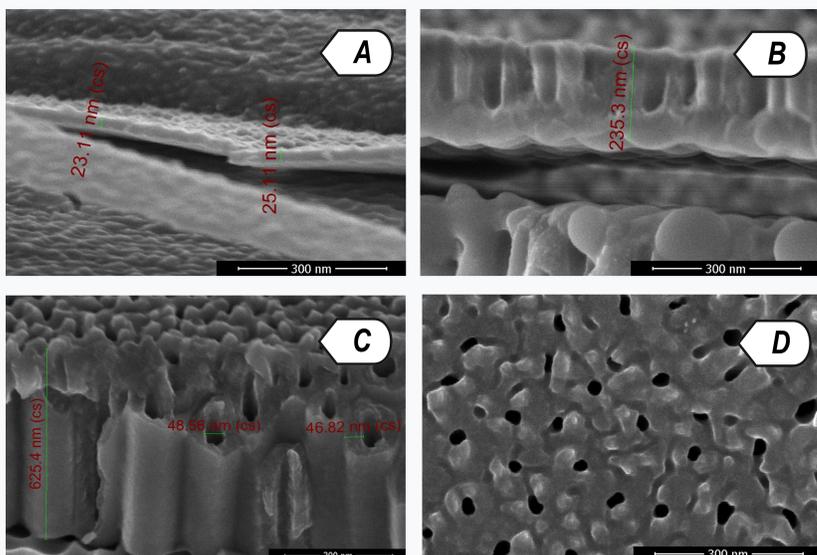


Figure 2. Cross-sectional view SEM images of an array of TiO₂ at point A (A); at point B (B); at point C (C) and top-view of TiO₂ nanotubes at point C (D). SEM images clearly visualize each stage of the anodizing process from the compact oxide layer to the nanotubes array with a worm-like surface.

Point A

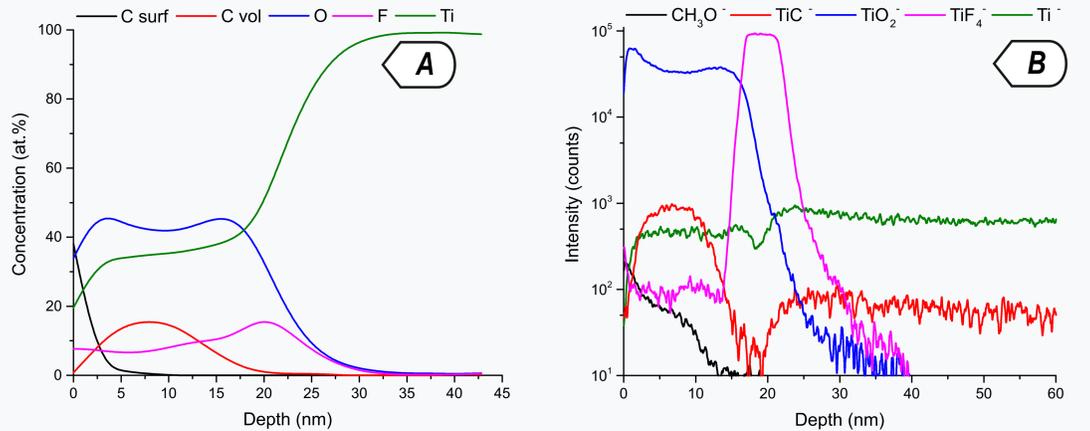


Figure 3. AES depth profiles (A). ToF SIMS depth profile (B) of the sample at point A.

C surf - hydrocarbon contaminants. This contamination is represented as an ionic fragment (CH₃O⁻) related to the residual reaction products from the electrolyte. C vol - corresponds to the carbide peak of carbon in the oxide film volume, in the TOF.SIMS analysis represented by the TIC⁻ ionic fragment. The presence of fluorine atoms in the structure is associated with the use of fluoride electrolytes whose anions are incorporated into the film during growth. The ionic fragment TIF₄⁻ repeats the distribution form from F in the AES method. From the depth distribution profile of TiO₂ it can be said that the oxide layer formed during the first 6 seconds of anodization was about 25 nm, which agrees with the image in the secondary electron SEM.

Point B

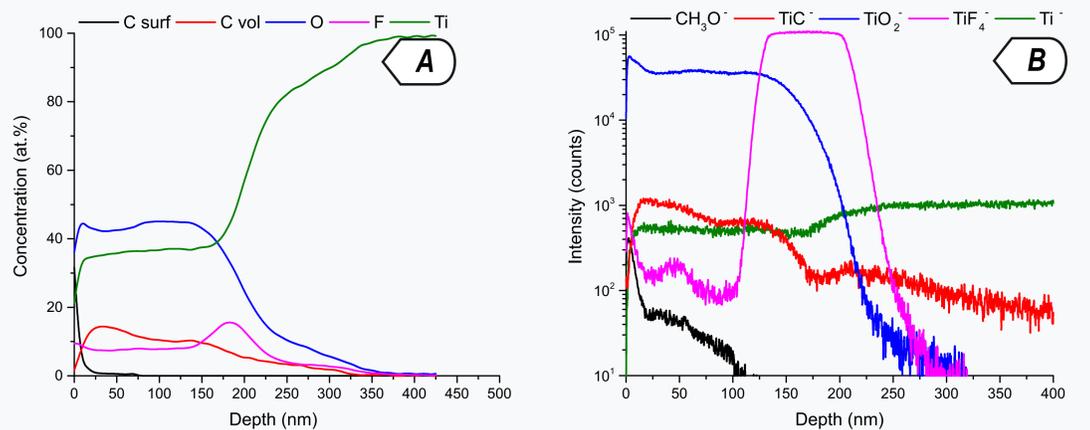


Figure 4. AES depth profiles (A). ToF SIMS depth profile (B) of the sample at point B.

At point B, pores continue to develop. The thickness of the initiating layer is already 150nm. As can be seen from the results of AES analysis of the profile, at point B changes markedly carbon carbide distribution at the oxide / substrate. At point B, it is seen that the concentration of Cvol decreases from 10 to 5 at.% in the volume of this layer. It should be noted that the highest carbon concentration (Cvol) is within the first 20-150 nm and, probably, this is the thickness of the initial initiating layer, which forms a kind of porous crust on top of the nanotube array, which correlates with the SEM. image results. This is also confirmed by the results of the profile analysis of TOF.SIMS.

Point C

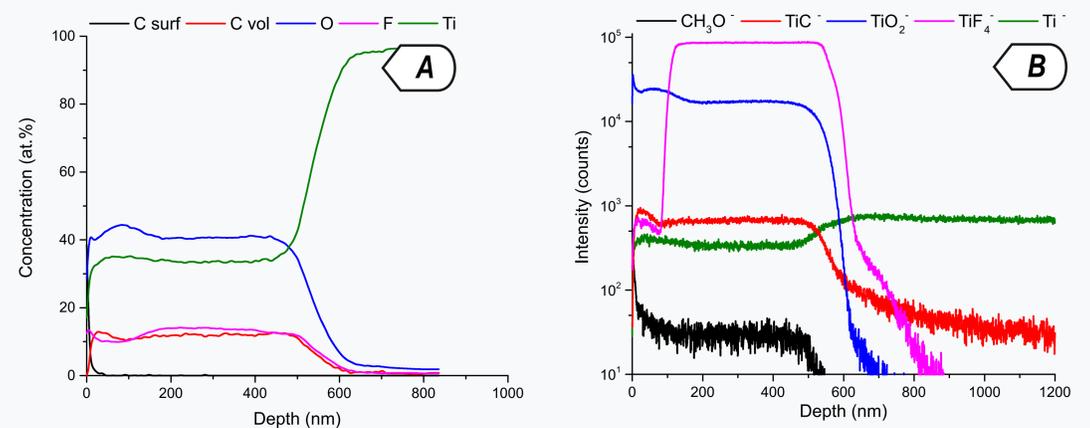


Figure 5. AES depth profiles (A). ToF SIMS depth profile (B) of the sample at point C.

At point C, the pores already develop deep into the titanium foil and the process of further growth becomes equilibrium. According to the results of AES analysis at point C (85 sec of anodizing), the distribution of Cvol and F in the volume (from 150-500 nm) is uniform and amounts to about 15 at.%. At the same time, up to 100 nm, a similar layer of the initiating dense oxide is observed, as at point B. In the profile analysis of TOF.SIMS it can be seen that the ionic fragments CH₃O⁻ have a stable intensity from 100 to 500 nm, which indicates the presence of reaction products from the electrolyte in the array of tubes. The AES data confirm this, but because of the low sensitivity, the hydrocarbon signal does not exceed 1-0.5 at.%. The profile distribution of the remaining ion fragments confirms the results described above AES.

Conclusion

In the present study, it was found that during the anodic oxidation process not only oxidized forms of titanium are formed, but also the incorporation of carbon-containing impurities occurred into the nanotube structure, because of the interactions with an ethylene glycol-based electrolyte. It is also shown that the composition of the near-surface layer differs from that of the underlying nanotube layer, which presumably formed during the initial stage of anodic oxidation at high electric field strengths.