Available online at www.sciencedirect.com

ScienceDirect

Physics Procedia 86 (2017) 37 – 43

Physics Procedia

International Conference on Photonics of Nano- and Bio-Structures, PNBS-2015, 19-20 June 2015, Vladivostok, Russia and the International Conference on Photonics of Nano- and Micro-Structures, PNMS-2015, 7-11 September 2015, Tomsk, Russia

Influence of formation conditions on the level of arrays ordering of anodic titanium oxide nanotubes

N. B. Kondrikov*, P. L. Titov, S. A. Schegoleva, M. A. Khorin

Far Eastern Federal University, Sukhanova str. 8, Vladivostok, 690950, Russia

Abstract

Nanotubular titanium oxide coatings with different morphology and dimensional parameters are formed by anodic oxidation under different voltage and time modes in fluorine aqueous-nonaqueous electrolytes containing glycerin as well as several surface-active agents (SAA). Their morphological peculiarities are examined and qualitative and quantitative analysis of obtained types of ordering is carried out, geometric configuration entropy are calculated on the base of analysis SEM images and theory of self-organization.

Peer-review under responsibility of the organizing committee of PNBS-2015 and PNMS-2015.

Keywords: titanium dioxide; nanotubes; anodic oxidation; morphology; self-organization; configuration entropy

1. Introduction

Oxide coatings containing nano-sized structural elements fall into an extensively studied group of nanostructured materials (Petukhof et. al. (2007), Chaplygin (2013), Belov, Gavrilin, Gavrilov et. al. (2011), Fang et. al. (2011)). Nanotubular anodic titanium oxide is for the utmost interest due to its unique self-organized structure and dimensional parameters (Belov (2011), Macak et. al. (2005), Macak et. al. (2007), Macak (2008)). It provides a wide range of its application in gas sensors, solar cells, hydrogen energetics, as catalyst carriers as well as in photocatalytic systems and biocompatible coatings.

* Corresponding author. Tel.: +7-908-974-80-19..
E-mail address: kondrikov.nb@dvfu.ru

Peer-review under responsibility of the organizing committee of PNBS-2015 and PNMS-2015.
doi:10.1016/j.phpro.2017.01.015

Synthesis and analysis of new low-dimensional oxide materials with the structure of nanotubes, nanorolls, nanorods, nanowires, nanoribbons is a surging modern research trend connected with perspectives for application of such materials in microelectronics (Chaplygin (2013), Macak et. al. (2005), Macak et. al. (2007), Macak (2008)). Oxide titanium-based systems are of interest as the electrodes for electrolysis and for electroanalytical purposes due to chemical inertness, electrocorrosion resistance (Fujishima and Honda (1972)).

The challenges of the work were in the examination of influences of conditions for obtaining of nanotubular TiO_2 structures on morphological peculiarities of their combination as well as in carrying out of qualitative and quantitative analysis of obtained types of their ordering.

2. Experimental part

Anode oxidation of titanium was carried out in two-electrode electrochemical cell with application of DC Power Supply HY5003. Pt plate acted as an auxiliary electrode, and Ti plate acted as a main electrode. Electrolyte temperature during anodizing was hold constant and equal to 25°C.

The samples under investigation were obtained in aqueous-nonaqueous and aqueous electrolytes by the method of anodic oxidation on the source of stabilized direct current voltage (Dronov (2009), Lozovaya (2011), Jasin (2007)). Platinum grid was used as the cathode; the samples were obtained during stirring with a magnetic agitator at the speed of 350 revolutions per minute. 99.9% purity, 1.5 cm^2 titanium foil was used as the electrode material. Titanium foil samples were preliminary chemically polished in acid compound $HF/HNO_3/H_2O$ (1:4:5), then flushed by distilled water, and dried out in the air. Table 1 with oxidation modes is represented below.

0.5 g NH_4F and 0.5 g SAA were added to 100 ml distilled water, then 100 ml glycerin were added to prepare electrolyte solution for the sample No. 1 (Glycerin +SAA+NH_4F). Quantity of ammonium fluoride ranged from 0.25 g to 0.5 g, quantity of glycerin – from 50 ml to 100 ml, quantity of water – from 10 ml to 100 ml. 0.5 ml HF and 7.5 ml H_2SO_4 were added to 100 ml distilled water to prepare electrolyte solution for the sample No. 3 (H_2SO_4+HF).

Table 1. Samples oxidation modes.

Sample name	Experiment duration, hour	E, B	I, mA	Electrolyte composition
Sample 1	1.5	20	35	(Glycerin+SAA+0.5%NH_4F) 1:1
Sample 2	1.5	20	35	(SAA+0.5%NH_4F) 1.25:1
Sample 3	4	30	40	H_2SO_4+0.15%HF

Morphological characteristics of the samples were examined on scanning electron microscope “Hitachi S-5500” (Japan). Elemental composition was determined by the use of attachment to the microscope for energy dispersive spectroscopy “Thermo scientific” (USA).

3. Results and discussion

Micrographs of the samples are represented at fig. 1-3. Conditions of obtaining of relevant structures and image scales are indicated in captions. Clusters reflecting dominating type of nanotubes array structure ordering are marked as well.

After visual analysis of the images of the samples 1-3 one may say that sample 1 significantly possesses tetragonal ordering as is clear from fig. 4a. Such fact of tetragonal ordering of nanotubes array may be explained by the fact that under relatively low oxidation potentials (20 V) dispersion of mean pore radius is rather high (Petukhof et. al. (2007)). At the same time nanotubes themselves are outlined rather coarsely in the cross-section, their contours are far from smooth, almost right angles are often observed. As a result, hexagonal close pack is implemented with more difficulty and tetragonal pore pack, that is in the case of the same rounded pores is less close, becomes more preferable, but in this case appears to be optimal.