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Surface and sorption properties of TiO₂ nanotubes, synthesized by electrochemical anodization

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Abstract. Electrochemical anodizing of titanium metal in the fluorine-containing electrolyte was used for production of nanotubes of titanium dioxide. The surface morphology of the films was investigated by scanning electron microscopy. It was found that with increasing anodizing voltage the inner diameter, growth rate and nanotubes interporous distance is increasing. The distribution of pore volume studied by the method of adsorption and desorption of nitrogen. The specific surface area of titanium dioxide films was measured for determine the conditions of anodizing on their changes. The sorption capacity of the films was studied.

1. Introduction

Currently titanium dioxide is a major semiconducting material in the dye sensitized solar cells (DSSC). It has been achieved about 12-13% efficiency at the best lab samples of solar cells manufactured on the basis of TiO₂ nanoparticles [1]. The use of nanotubes instead of nanoparticles can be the one of the ways to increase the efficiency of DSSC-cells. This is due to the 3-dimensional electron transport carried out in the films made of nanoparticles TiO₂. The connection between the nanoparticles, which is formed by thermal annealing, affects the electron transfer ability between the nanoparticles. Unformed chemical bonds lead to a decrease in the efficiency of electron transport. When using nanotubes it is a one-dimensional electron transport along the walls. It reduces the transfer of electrons from the charge generation points to the electrodes, as well as, if electrodes are properly designed the defects hindering electron transport are minimal [2].

The amount of light absorbed by a photovoltaic cell depends on the number of dye molecules adsorbed on the semiconductor surface. Increasing the specific surface area of the semiconductor oxide layer allows adsorb a greater number of the dye molecules and leads to increased absorption of solar light and increases the charge carriers concentration in the semiconductor layer.

There are many different methods, which results structures of different morphology, are used last years for obtaining nanostructures on the basis of titanium oxide [3-9]. They are mainly nanoparticles, nanotubes, nanowires and nanorods. There have been synthesized nanotubes of titanium dioxide [10-14] by various methods, the specific surface area of which exceeds hundreds of meters per unit area.

TiO₂ films with vertically oriented and highly ordered arrays of nanotubes were firstly obtained by electrochemical anodization of titanium foil in the fluorine-containing electrolyte by D. Gong et al. [15]. Since then, many works have been devoted to the study of the growth mechanism and the formation of TiO₂ nanotubes [16-19].

This paper presents the investigation results of electrochemical anodization conditions on a surface area of titanium oxide films, pore volume, sorption properties and geometric characteristics of TiO₂ nanotubes.

2. Experimental part

The titanium foil with a thickness of 60 microns was subjected to chemical polishing in a solution consisting of H₂SO₄ - 60%, HF - 25%, C₃H₅(OH)₃ - 15%. The polishing process occurs at a voltage of 20 V with vigorous stirring for 10 minutes. After polishing the samples were washed with distilled water, dried and then they were excised from the plate the required dimensions. Before anodization the samples were sonicated into 2 M solution of HCl, and then in acetone for 10 minutes to remove impurities and degreasing

As the basis of electrolyte the C₂H₆O₂ was used (content of NH₄F is 0,5 wt%, H₂O is 3 wt%). Anodic oxidation of titanium was carried out in an electrochemical cell in potentiostatic mode at a temperature of 5-7 °C. The platinum foil was as a cathode. The distance between the anode and cathode was 3 cm.

The electrochemical oxidation process consists from two steps. First is anodizing for 2 hours. Separation the formed film at the first step is carried out in an ultrasonic bath of 1 M hydrochloric acid solution. Then the sample was washed with copious amounts of deionized water and dried at a temperature of 80 °C. The duration of the second step of anodizing was 24 hours. Anodizing voltage was varied from 20 V to 70 V.

After the second stage of the anodizing the obtained TiO₂ nanotubes were sonicated to remove the byproducts and the surface oxide layer. Then they were washed with copious amounts of distilled water and dried in a stream of nitrogen. Crystallization of the amorphous phase of TiO₂ was performed by the thermal treatment of samples in a muffle furnace at 450 °C for 3 hours with a temperature increase of 5 °C per minute.

For measurement of the specific surface area the nanotubes film were separated from the titanium foil by H₂O₂ (37%) and placed in the adsorber. Specific surface area was measured by the BET method. Pore size distribution and pore volume dependency on their diameter was obtained from the adsorption isotherm and desorption of nitrogen in measuring complex Sorbi-MS (Russia). Thermal training of samples was carried out at 100 °C for 180 minutes in the preparation block «SorbiPrep».

The images of samples surface were obtained on the scanning electron microscope MIRA 3LMU (Tescan, Czech Republic).

3. Results and discussion

Surface morphology of porous titanium dioxide films, obtained by scanning electron microscope, is showed on figure 1. All samples were anodized in the electrolyte: ethyleneglycol + NH₄F 0.5 wt.% + H₂O 3 wt. % at a variation of the anodization voltage from 20 V to 70 V.

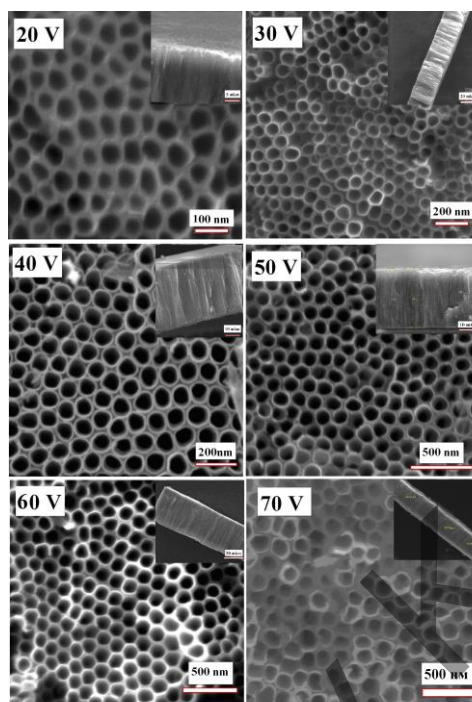


Figure 1. SEM images of the surface and cross-cleavage of titanium dioxide films

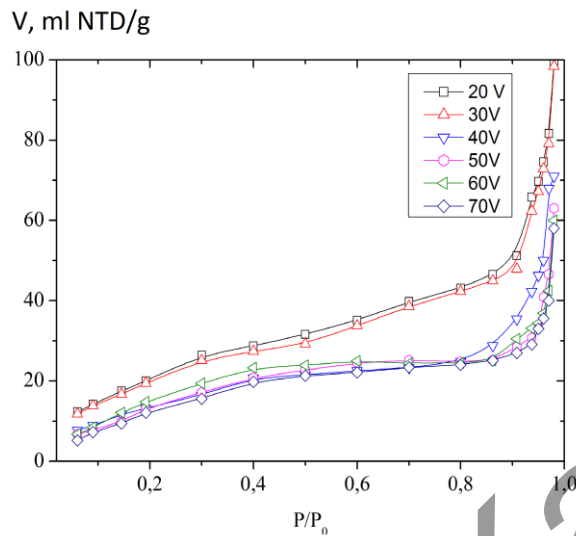
It can be seen that there are highly ordered titanium dioxide nanotubes, perpendicular to the plane of the titanium foil, on its surface. Table 1 shows the characteristics of nanotubes obtained by 24 hours anodizing. There are results of measurements of the specific surface area of the films and the total pore volume of titanium dioxide nanotubes. The total pore volume and pore volume distribution were obtained from the adsorption isotherm and desorption of nitrogen

Table 1. Geometric characteristics and specific surface area, total pore volume of TiO₂ films

Voltage, V	The length of the nanotubes, μm	The average inner diameter of the nanotubes, nm	The average interporous distance, nm	Specific surface area S_{BET} , m^2/g	Specific surface per $1 \mu\text{m}$ S_{BET} , m^2/g	The total pore volume V_p , cm^3/g
20	17,1	55	60	$71,3 \pm 0,8$	4,20	0,200
30	22,0	70	75	$67,84 \pm 1,0$	3,08	0.155
40	27,0	90	86	$61,3 \pm 0,9$	2,30	0.128
50	36,0	110	139	$65,4 \pm 0,8$	1,80	0.112
60	37,0	140	150	$62,45 \pm 0,8$	1,70	0.106
70	40,0	150	170	$59,3 \pm 0,9$	1,50	0.102

The data shows that while increasing the anodizing voltage the average interporous distance, inner diameter and growth rate of the nanotubes length are increasing too. When the anodization voltage is increased the specific surface area and pore volume of the films decreased. This is due to the fact that the number of nanotubes per 1 cm^2 is reducing due to increased internal nanotubes diameter.

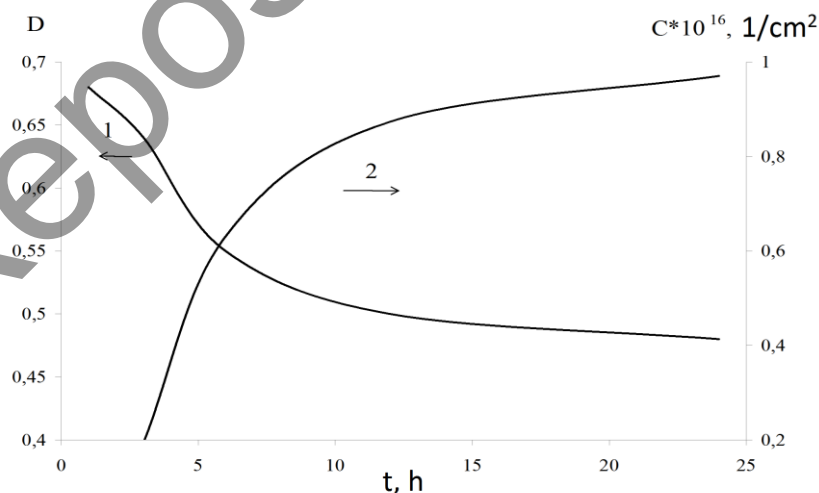
Picture 2 shows the isotherms of nitrogen adsorption.



Picture 2. The isotherms of films adsorption, obtained at different voltages

According to the classification of the IUPAC, the obtained isotherms have II adsorption type, which corresponds with multilayer adsorption [20]. With pressure increasing the isotherm asymptotically approaches the straight line $P/P_0 = 1$. In the initial part of the isotherm it has a convex shape, which indicates the strong interaction of adsorbate with the adsorbent. In addition, the adsorption isotherm for all the samples have the same form, which indicates the identity of the porous structure of the films, which differ from each other in the volume of adsorbed gas.

Also the molecules sorption into the porous film of titanium dioxide was investigated. For this purpose sorption of the Z-907 (cis-Bis (isothiocyanato) (2,2'-bipyridyl-4,4'-dicarboxylato) (4,4'-diononyl-2'-bipyridyl) ruthenium (II)) dye molecules was carried from the ethanol solution into the pores of TiO_2 films, prepared in the electrolyte: ethyleneglycol + NH_4F 0.5 wt.% + H_2O 3 wt. % at a anodizing voltage of 20 V.



The presented data shows that with increasing time of sorption the optical density of the solution decreases, which indicates a decrease in the concentration of molecules in solution and flow physisorption of molecules on the surface of the TiO_2 film.

The number of molecules adsorbed per unit area was determined by the change in optical density D before and after the sorption.

$$C_s = \frac{N_A \cdot c \cdot V'}{S} \left(1 - \frac{D_1}{D_2}\right), \quad (1)$$

where: N_A - the Avogadro constant; c - the phosphor molecules concentration in solution; V' - the volume of solution; S - area of the adsorbent; D_1 and D_2 - optical density of the solution before and after adsorption.

It was established that with increasing adsorption time the concentration of molecules on the surface of the film increases, and then reaches saturation.

4. Conclusion

Thus, by the two stage electrochemical anodization there are highly ordered titanium dioxide nanotubes, perpendicular to the plane of the titanium foil, formed on the surface of the titanium foil. It was found that with increasing anodizing voltage the internal diameter, growth rate and nanotubes interporous distance is increasing. The specific surface area and total pore volume begin to decrease due to the falling number of nanotubes per unit area. With increasing time sorption the optical density of the solution decreases, the density of molecules on the surface of the film is increasing, and then reaches saturation.

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