MANUFACTURE AND INVESTIGATIONS OF ANODIZED TITANIUM OXIDE PHOTOANODES

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1. Introduction

Photoelectrolysis of water, first reported in 1972 by Fujishima and Honda [1], has recently attracted renewed interest since it offers a renewable, non-polluting approach to hydrogen production [2, 3]. Interest in semiconductor photoanodes made of the titanium dioxide, which is characterized as highly stable against photocorrosion and is relatively inexpensive, has renewed. Thus, a possibility to manufacture nanostructured photoanodes, owing to high surface area and improved charge separation kinetics, became basic direction of the investigations [4-7]. The aim of this work was the manufacture of semiconductor photoanodes made of thin-film titanium oxide by anodization of pure titanium plates at an invariable voltage and investigation of their photoelectrochemical properties.

2. Manufacture of titanium oxide photoanodes

We used a technology of manufacturing of titanium oxide thin films by an anodization of titanium sheets in aqueous solutions of hydrofluoric acid at an invariable voltage. Anodic or electrochemical oxidation is a process of oxide films manufacture on the surface of metals or semiconductors at anodic polarization in oxygen-containing media. The main point of the anodic oxidation consists at the titanium oxide layer deposition on a surface of a titanium plate not from a solution. We have the product of the oxidation of the titanium anode. Advantages of this method are low power-consuming anodic oxidation process and its ecological purity, simple setups, a possibility of manufacturing films with different morphological structures and complex geometric configurations, a high-scale of controllability process of the growth of films allowing fabrication of the films with reproducible and stable characteristics.

The commercial titanium plate (anode with the area ~1 cm^2) and platinum counterelectrode were located in a teflon vessel. Preliminary titanium plates (trademark BT1-0 with content 99.31 at.% Ti and 0.69 at.% Al) were ungreased, etched in 20% solution of nitric acid with the adding of hydrofluoric acid and washed in cold bidistilled water. The aqueous solution containing 0.5 weight % HF was used for an anodic oxidation process. Titanium oxide films have been grown at voltages U_{growth}=10, 15, 20, 25, and 30 V. The anodizing voltages were kept constant during

the entire process. The growth time of films was 20 minutes. The acetic acid was added in electrolyte (in ratio 0.5 weight %HF:CH3COOH=7:1) for hardening films which were growing at voltage below 20 V. The acetic acid does not influence the morphology of titanium oxide thin films. All anodization experiments were carried out at room temperature with continuously agitation of an electric stirrer. Films were carefully washed out in the distilled water and were dried at temperature 50^0C after growing.

It is known that as-prepared films are amorphous. Therefore the subsequent annealing was carried out for their crystallization. The prepared films were exposed to the subsequent annealing immediately after growing in the air at temperature 550^0C (with of rate of heating ~ 20C/min) during 1 hour.

3. Results and discussion

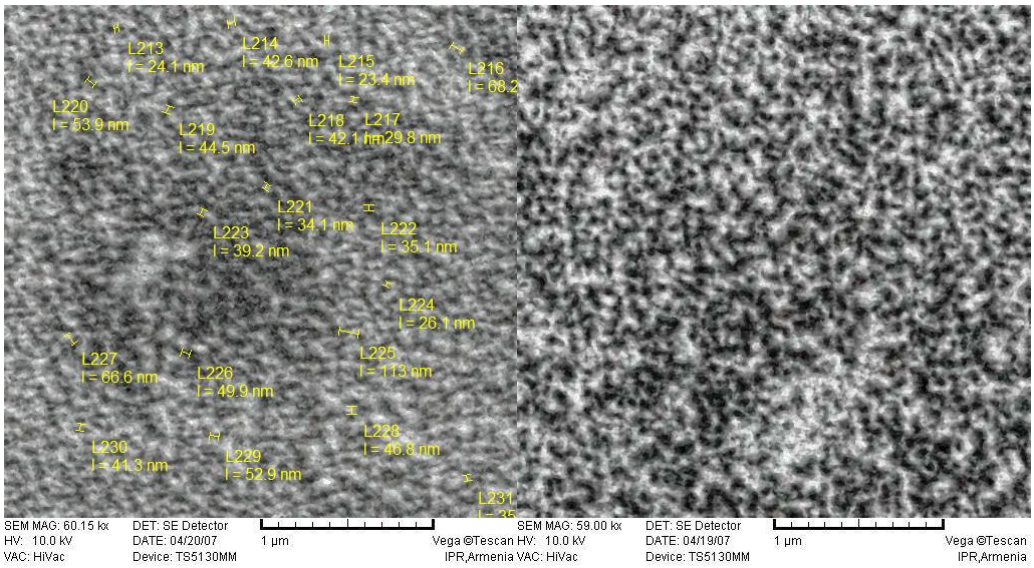
The analysis of element structure of titanium oxide thin films was carried out. As-prepared amorphous films before annealing contained about identical amount of titanium and oxygen and ~ 5 at.% fluorine. Results of investigations of element structure of films after annealing in the air are presented in Table 1. It is seen that the amount of fluorine sharply decreases and the contents of oxygen increases during annealing in the air that provides manufacturing TiO_2 phase.

Table 1

U_{growth}, V	The element structure of films			Thickness of film, nm	Average diameter of pores, nm	Average walls thickness of pores, nm	The rate of hydrogen evolution, μmol/h.cm^2
	Ti, at.%	O, at.%	F, at.%				
10	26.15	71.99	1.86	51.744	19.8	45.7	179
15	31.55	66.57	1.88	200	22.4	36.4	194
20	31.50	68.50	-	317.1	26	55	272
25	33.10	65.64	1.26	.3	29.2	45.5	216
30	30.21	67.73	2.06	200.6	27.9	47.5	220

SEM analysis showed that obtained titanium oxide thin films have nanoporous structure with a typical pore size of 20-30 nm. The SEM image of prepared titanium oxide films after the annealing is shown in Fig. 1. Thickness of films, the average diameter and walls thicknesses of pores are determined (Table 1). The greatest thickness of films is obtained at 20 V. Increase in both voltage and duration of process of anodizing does not lead to increase in thickness of a film because titanium oxide can be etched at a high rate in HF solution even in the absence of an anodizing voltage. Laboratory conditions for the investigation of the photoelectrolysis current were carried out under the mercury lamp illumination with power of 250 W. These measurements were carried out in heterogeneous photoelectrochemical cell (anodic and cathodic compartments were separated by the ion-exchange membrane (trademark MF-4CK) and were

filled with aqueous 5N NaOH and 5N H_2SO_4 electrolyte, correspondingly). The current-voltage characteristics of manufactured photoanodes made of thin film titanium oxide were measured in the same heterogeneous photoelectrochemical cell using the automatized setup connected to the computer. These measurements were carried out in darkness and under mercury lamp with power of 250 W. Light intensity was kept constant during measurements.



a) b)

Fig. 1. The SEM images of films prepared at voltages 10 V (a), and 30 V (b).

Typical current-voltage characteristics of prepared thin-film nanoporous titanium oxide photoanodes are presented in Fig. 2a. The dark current is practically absent. The anodic photocurrent onset potential is equal to ~-0.8 V.

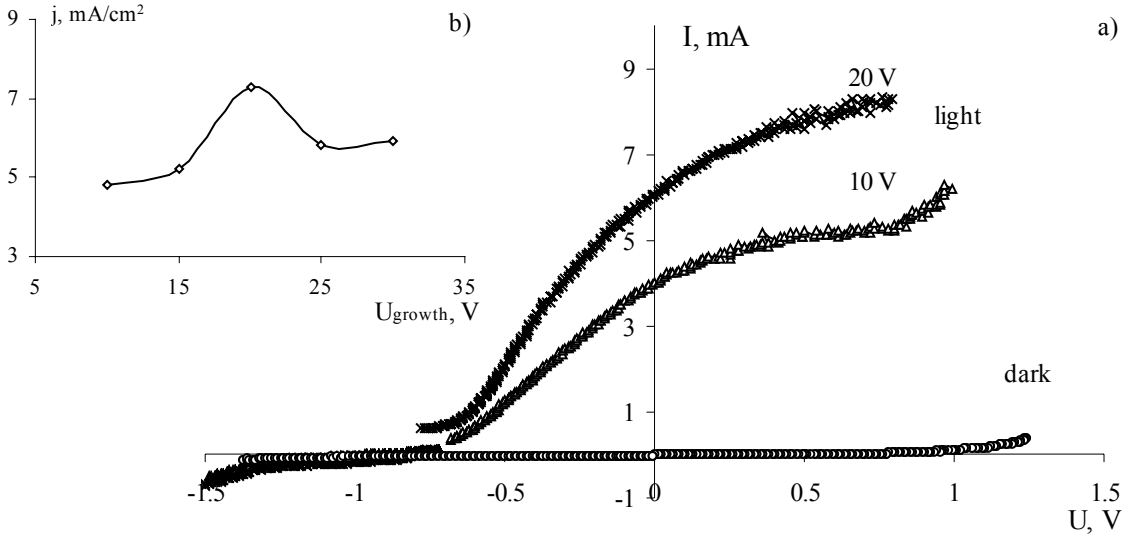


Fig. 2. a) The current-voltage characteristics of photoanodes made of thin -film titanium oxide grown at 10 and 20 V during 20 minutes and annealed during one hour. b) Dependence of the photocurrent on the voltage, at which the titanium oxide film growth was carried out.

The dependence of photocurrent density on the anodizing voltage of a film was investigated (Fig. 2b). The greatest photocurrent was observed on the photoanodes which have been grown at 20 V. Notice that these photoanodes have the greatest thickness of films and walls thickness of pores at rather small diameters of pores. Probably, these photoanodes have a largest effective working surface. The rate of the hydrogen evolution was equal ~ 276 μmol/h.cm^2 for photoanode made of thin film titanium oxide grown at 20 V during 20 minutes under the mercury lamp illumination with power of 250 W.

4. Conclusion

Thus, we have manufactured thin-film nanoporous photoanodes made of titanium oxide by a method of the anodization of commercial titanium plate in the aqueous solution containing 0.5 % HF at the constant voltage (10, 15, 20, 25 and 30V) during 20 minutes and the subsequent annealing immediately after growing in the air at temperature 550^{0}C during one hour. Element and structural analyses of films are carried out. Thickness of films, the average diameter and walls thicknesses of pores are determined. The current-voltage characteristics are investigated. The greatest rate of the hydrogen evolution was observed on the thickest films (~ 300 nm), which were anodizing at 20 V.

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