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SYNTHESIS AND ELECTROPHYSICAL PROPERTIES OF THE CATODIC LAYER OF ANODIC TITANIUM OXIDE FOR PEROVSKITE SOLAR CELLS

Currently, solar cells based on hybrid organo-inorganic perovskite technology are one of the fastest-growing trends in solar energy. The use of this new hybrid perovskite material will make it possible to obtain thinner solar cells, make them flexible, reduce manufacturing costs, and increase the efficiency of photovoltaic conversion.

An important element of perovskite solar cells is the cathodic transport layer, the material for which titanium oxide with semiconducting properties of n-type conductivity is often chosen. This contact is responsible for the extraction of photoinduced electrons from the light-absorbing perovskite layer into the electric circuit of the cell. The cathodic titanium oxide layer provides efficient separation and transport of photoinduced charge carriers from the perovskite layer. Therefore, the electronic conductivity of such a layer is an important parameter to ensure high photovoltaic conversion efficiency.

Ti films of 50-60 nm thickness were deposited on silicon and aluminum foil substrates by electron-beam evaporation in the «Oratoria-9» vacuum unit. Before the vacuum deposition process, the substrates were chemically cleaned and then washed in distilled water and dried in a desiccator at 60 °C. The following modes were used: film deposition rate 0.4 nm·s⁻¹, residual gas pressure in the chamber 10⁻³ Pa, substrate temperature - room temperature.

Electrochemical oxidation of the Ti film was performed in an electrolyte based on a mixture of 2% aqueous oxalic acid solution and 1% aqueous sulfamic acid solution (by mass). A P-5827M potentiostat was used to ensure the maintenance of the set potential value during anodizing. A graphite electrode was used as a cathode. The set value of the potentiostat voltage determined the final thickness of the formed anodic TiO₂ film due to the self-regulating process of anodic oxidation of Ti.

A LEF-3M-1 elipsometer was used to measure the TiO_2 film thickness. Such studies were carried out with titanium films deposited on silicon substrates. For this purpose, Ti films were anodized in an electrolyte at different voltages until the current flow through the oxide ceased completely. After the anodization process, the samples were washed in distilled water and isopropyl alcohol. Then they were air-conditioned at $80\text{ }^\circ\text{C}$ to remove residual water and stabilize the film structure.

The electrophysical properties of the initial and annealed films were studied by I-V spectroscopy. The area of metal electrodes of MDM structures was 10 mm^2 . The volt-ampere characteristics were measured under room conditions.

In this work we studied the optical properties of anodic titanium oxide films formed on aluminum foil. Figure 1 shows the change in the optical density of anodic titanium oxide films from the anodization voltage.

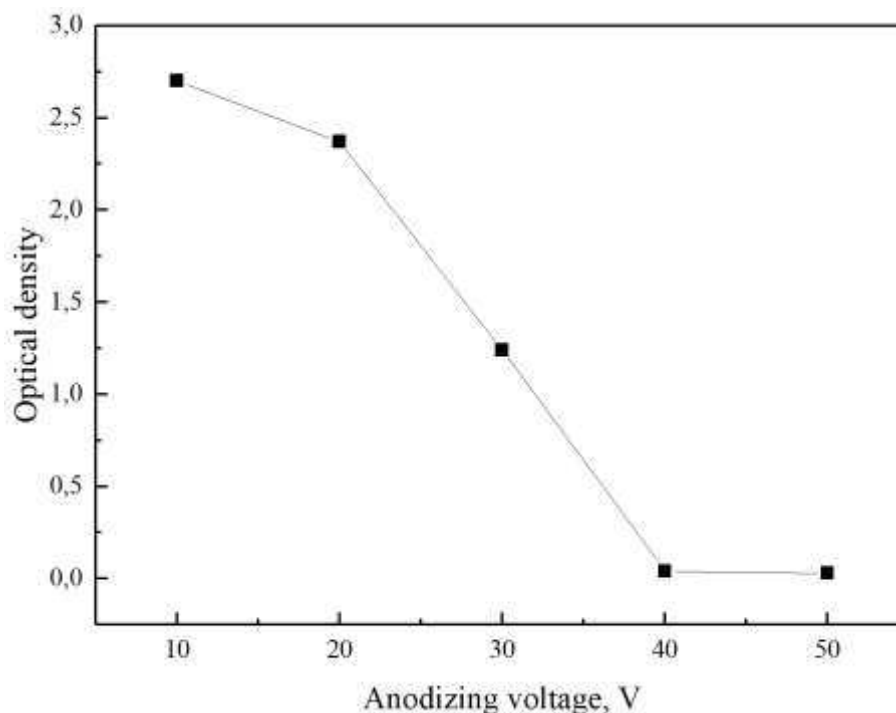


Figure 1 – Change in the optical density of the TiO_2 anodic film as a function of the anodization voltage

As can be seen from the figure 1, up to 30 V the anodic films are optically opaque. Starting from 40 V the anodic films become optically transparent in the visible region of the spectrum. Transition of anodic films to the structure with high transparency for voltages above 40 V is explained by complete oxidation of titanium film and reaching the anodization front to aluminum. It is known that anodic aluminum oxide films are characterized by high transparency in the visible range. Consequently, at

voltages > 40 V, the process of anodic oxidation of aluminum begins and a thin layer of aluminum oxide is formed at the titanium oxide-aluminum interface. In order to elucidate in more detail the mechanism of anodic oxidation of Ti film on Al foil, the influence of anodizing voltage on the thickness of the anodic films was studied.

Figure 2 shows the change in anodic film thickness with the anodizing voltage.

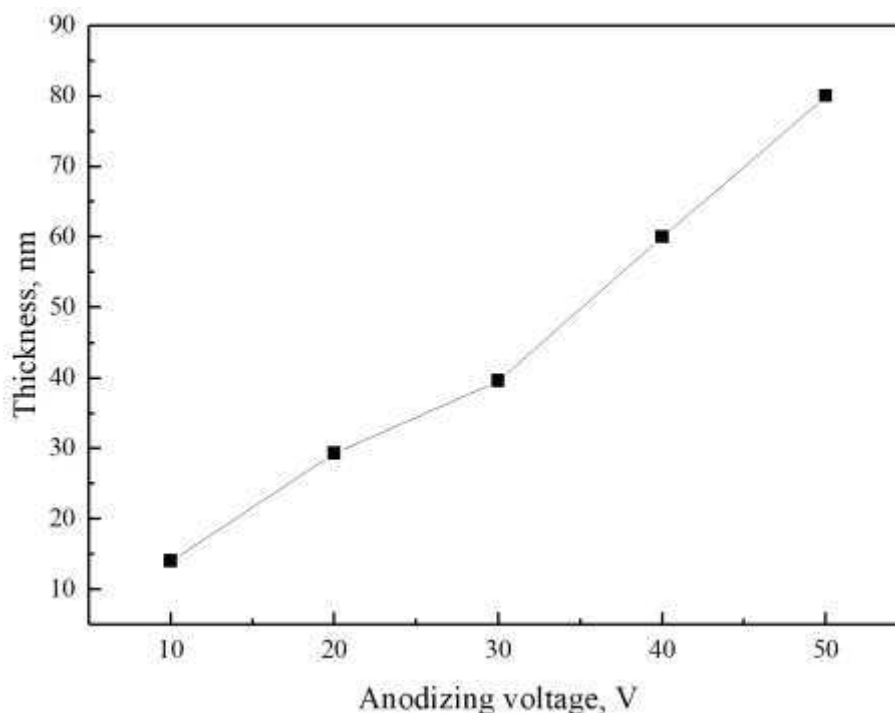


Figure 2 – Change in TiO_2 anodic film thickness as a function of anodizing voltage

As can be seen from the figure, the linear graph can be divided into two characteristic sections: 1 (up to and including 30 V) - linear graph with a forming factor (slope of a linear graph) of 1.4 nm/V and 2 (over 30 V) - linear graph with a forming factor of about 1.55 nm/V. The results obtained can be explained as follows. It is known that the forming factor for anodic titanium oxide is 1.4 nm/V. This value agrees well with the data for the first section of the voltage graph of the anodic film thickness, which testifies to the formation of the anodic titanium oxide only. At anodizing voltages starting from 40 V, an increase in the anodic film formation coefficient up to 1.55 nm/V is observed (second section). This result is related to the complete oxidation of the titanium film and the beginning of aluminum oxidation. As is known, the forming factor for the anodic aluminum oxide is 1.65 nm/V. Therefore, an increase in the forming factor is observed for the anodic films.

The influence of anodizing voltage on the electrical resistivity of anodic titanium oxide films was studied. Figure 3 shows the graphs of the resistivity of the anodic films on the anodization voltage.

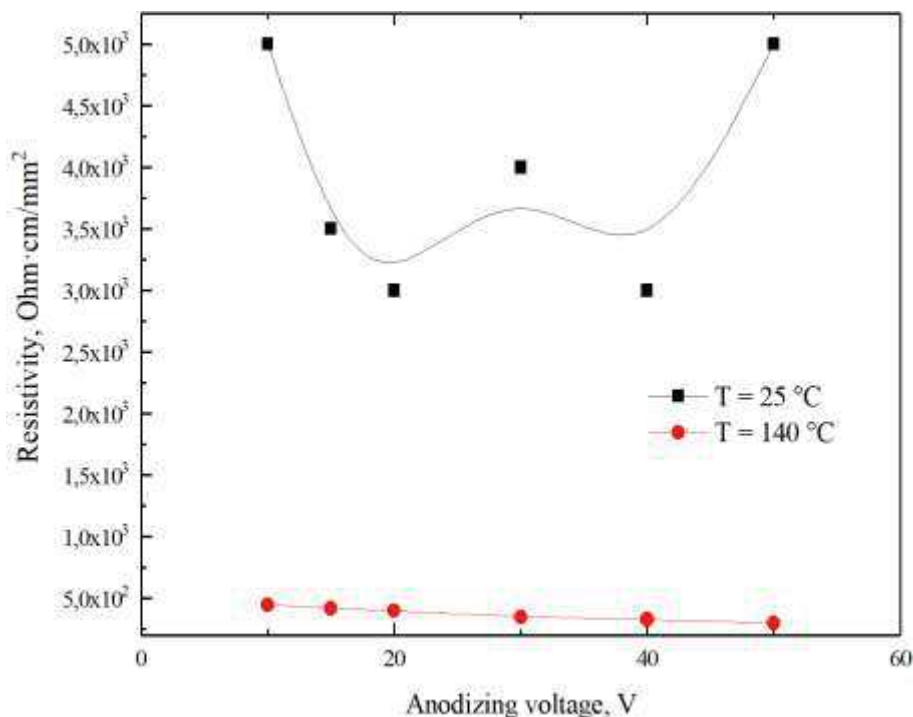


Figure 3 – Change in anodic TiO₂ film resistivity as a function of anodizing voltage for freshly anodized samples and after annealing at 140 °C for 30 min

As can be seen from the figure, as the anodizing voltage increases from 10 to 30 V, there is a slight decrease in the resistivity. With the beginning of electrochemical oxidation of aluminum (at a voltage > 40 V), the resistivity of the anodic film increases. We believe that in this case, it is associated with the appearance of additional mechanical stresses in the anodic film due to the filling of pores in TiO₂ with aluminum oxide during the anodization process. To reduce the mechanical stresses in the anodic film, the samples were annealed at 140 °C for 30 min.

Also from Figure 3 we can see that annealing of the anodic films obtained at 50 V led to a significant decrease in resistivity.

In addition to the resistivity value, it is important to determine the conductivity mechanism of the semiconductor oxide film. Therefore, using a thermal probe, it was found that all the anodic films had n-type conductivity. The electrical transfer in the anodic TiO₂ film is due to electronic processes and is related to the electronic mechanism of conductivity by localized states.