Preparation and properties of nanoscale titanium dioxide film for transport layer of *n*-type photovoltaic cell

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The influence of anodization voltage on the thickness of anodic TiO_2 films formed by electrochemical oxidation of titanium has been investigated. Activation energies were determined from the temperature dependence of conductivity. The possibility of obtaining TiO_2 anodic films with resistivity from 3.0 to 5.0 $\mu\Omega \cdot$ m and electronic type of conductivity is shown.

Keywords: Solar energy, titanium oxide, photovoltaic cells, transport layers, electronic conductivity.

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1. Introduction

One of the promising areas of applying films based on wide-band semiconductor TiO_2 with electronic conductivity is solar power engineering [1,2]. The technique of electrochemical Ti oxidation is affordable, allows controlling the thickness of the obtained films with great precision, and provides high uniformity and formation rate. Obtaining TiO_2 films with semiconducting properties by low-temperature electrochemical oxidation makes it possible to use such material as an electronic transport layer in perovskite photovoltaic cells [3]. Therefore, the study of electronic properties of nanoscale TiO_2 films, as well as ways to increase their conductive properties is a pressing task.

2. Experimental part

Ti films with a thickness of 50−60 nm were deposited on Al-foil samples by magnetron sputtering in Ar medium. Electrochemical oxidation of Ti films was carried out in an electrolyte based on a mixture of 2% aqueous solution of $C_2H_2O_4$ and 1% aqueous solution of H_3NSO_3 in a two-electrode cell. Anodic TiO_2 films were prepared by electrochemical oxidation of Ti at U_a anodising voltages of 5 to 40 V followed by holding until the current dropped completely. The anodising current was considered to drop to 10% of the initial value. The films were then annealed in an air atmosphere at 140°C for 30 min.

The surface of the samples with TiO_2 films formed by electrochemical oxidation of titanium film on aluminium foil (Ti-Al) showed different interference colouration as shown in Figure 1. The colour of the film in visible light was determined by the optical difference of the path between two interfering rays: the one reflected from the upper surface and the one leaving the film after reflection from the lower surface. The results depend on the thickness of the TiO_2 film, which was measured using an LEF-3M-1 ellipsometer. The error of the highly sensitive optical ellipsometry method, which was used to determine the thickness of the anodic oxide film, did not exceed 2%. The error of the resistivity measurement of the anodic oxide film did not exceed 10%.

3. Results and discussion

In Figure 2, *a*, showing the dependence of the anodic oxide film thickness on U_a, two characteristic areas can be distinguished. The first plot (up to 30 V inclusive) — a linear dependence with a formation factor (the ratio of the formed film thickness to U_a in the potentiostatic regime) of 1.4 nm/V and the second plot (above 30 V) — a linear dependence with a formation factor of about 1.55 nm/V. The increase of the formation factor up to 1.55 nm/V (second section) indicates the complete oxidation of Ti film and the beginning of Al oxidation. As is known, the coefficient for anodic Al_2O_3 is 1.65 nm/V. Therefore, for the anodic films formed at voltages > 30 V, an increase in the anodic film formation ratio will be observed, which agrees well with the data for the second site.

The effect of U_a on the electrical conductivity of anodic TiO_2 films after heat treatment was studied by measuring the electrical resistivity using Ni contact pads formed by vacuum sputtering. As can be seen from Figure 2, *b*, a decrease in resistivity is observed at U_a up to 3.0 $\mu\Omega \cdot$ m, and an increase after 40 V is observed. It is assumed that this is due to the appearance of additional mechanical stresses in the film due to its compaction by filling micropores in TiO_2 with aluminium oxide during the anodisation process.

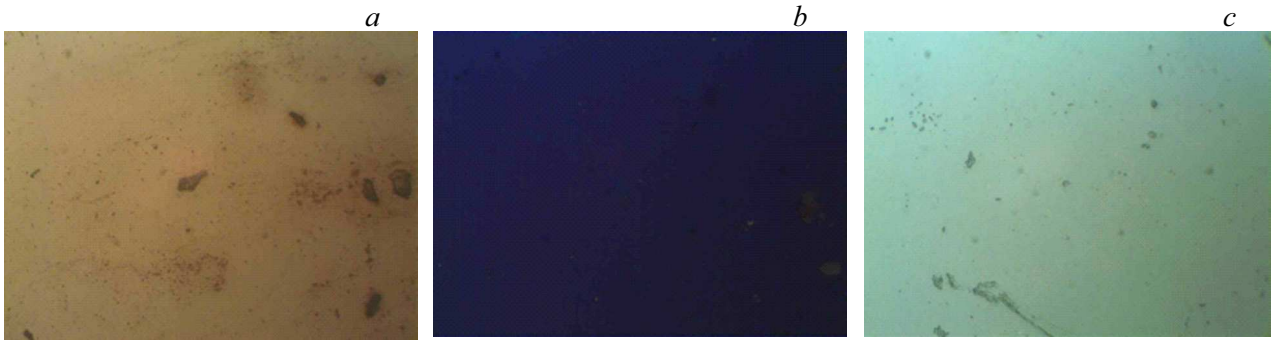

Figure 1. The interference colour dependence of TiO_2 film on U_a: *a* — 5 V (9 nm), *b* — 15 V (22 nm), *c* — 40 V (60 nm).

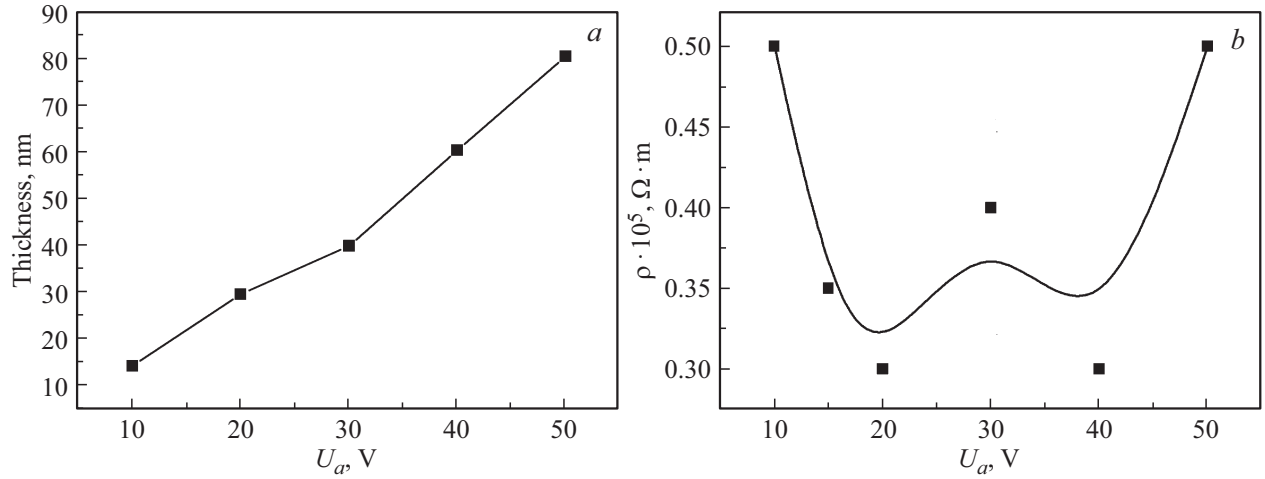

Figure 2. The effect of U_a for the Ti-Al structure (thickness of Ti 60 nm) on the parameters of the anodic film TiO_2: *a* — for the thickness, *b* — for the resistivity.

To reduce mechanical stresses, the samples were annealed at 413 K for 30 min.

According to the literature, titanium dioxide behaves as an *n*-type [4] semiconductor. In this case, electrons from the metal electrode have the opportunity to tunnel directly to the traps formed during the anodic oxidation of Ti near the bottom of the conduction band.

Figure 3 shows the dependences of the resistance of the TiO_2 thin film on the heating and cooling temperature.

As can be seen from Figure 3, in the low-temperature region (up to 353 K) local electronic levels give the greatest contribution to the conductivity of the oxide film (1st section). The increase in conductivity is due to the fact that local electronic levels provide the possibility of additional electronic transitions. The temperature region > 353 K (2-nd plot) indicates a possible transition to another conduction mechanism.

The values of the conductive activation energy were calculated for the 1-th (low-temperature, up to 353 K) and 2-th (high-temperature, > 353 K) parts of the temperature dependence and had values of 0.07 and 0.1 eV in the Arrhenius [5] approximation, respectively.

The experimental results are in good agreement with the model of the influence of intrinsic electrically active defects in titanium dioxide. The concentration of such defects may be predominant, and the *n*-type conductivity is determined not by charged oxygen vacancies in the nonmetal sublattice, but by excessive inter-nodal defects Ti^{+3}. This removes the apparent contradiction in the detected low values of defect activation for *n*-type conduction samples with the predominance of typical defects in the oxygen sublattice. A low value of the activation energy of Ti^{+3}, close to that observed in our experiments, was found in [6]. The state of electrons at small levels was analysed by EPR, and the activation with electron transfer to the conduction band — by infrared spectroscopy. The discussed ideas also correlate with the character of change of electrophysical properties in the „heating-cooling“ cycle, where there is a partial decrease in the deviation from stoichiometry inside the homogeneity region of titanium dioxide during annealing in air (the concentration of Ti^{+3} decreases and the resistance increases), which is reflected in the curvature of the dependence and a slight increase in the slope in the Arrhenius coordinates.

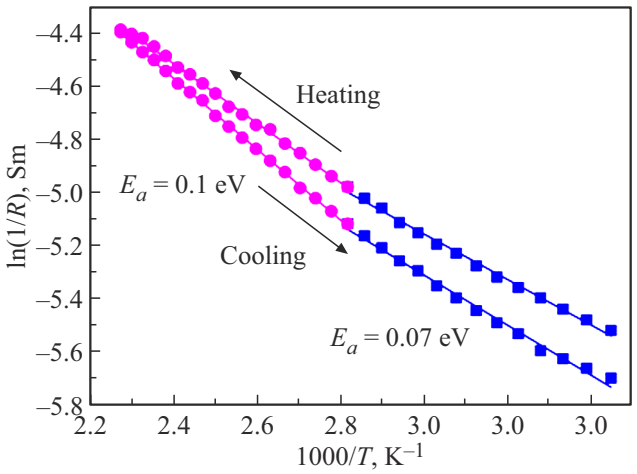

Figure 3. The Arrhenius curve for anodic oxide film TiO_2 (30 nm) during heating-cooling cycle.

Other possible mechanisms for the formation of small electronic levels with the participation of adsorbed water [7] have also been discussed in the literature.

Additional studies will be carried out to further develop the modelling concepts.

4. Conclusion

It was shown that the surface of samples with TiO_2 films after electrochemical oxidation of Ti-Al-structures at voltages in the range of 5–50 V had different interference colouring. It was found that for the films formed at voltages > 30 V, an increase in the anodic film formation ratio was observed. Analysis of the influence of U_a on the value of resistivity (Figure 2) showed that the anodic oxide films TiO_2 obtained at anodisation voltages of 15–40 V possess the minimum values of resistivity. The activation energies for the low-temperature (0.07 eV) and high-temperature (0.1 eV) parts of the graph were determined in Arrhenius coordinates. It is shown that the formation of TiO_x with partial oxidation of aluminium allows to obtain anodic oxide films with low resistivity in the range from 3.0 to 5.0 $\mu\Omega \cdot$ m and electronic type of conductivity.

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Conflict of interest

The authors declare that they have no conflict of interest.

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