Conference materials
UDC 546.05; 538.975
DOI: https://doi.org/10.18721/JPM.153.350

The effect of the seed layer on the TiO_2 nanotubes coatings quality grown on the glass substrates by hydrothermal synthesis

M. G. Volkova [1, 2]✉, A. P. Ivanishcheva [2], V. V. Petrov [2], E.M. Bayan [1]

[1] Southern Federal University, Rostov-on-Don, Russia;

[2] Research and Education Centre "Microsystem technics and multisensor monitoring systems", Southern Federal University, Taganrog, Russia

✉ mvol@sfedu.ru

Abstract. Coatings of titanium dioxide nanotubes were obtained on glass substrates by hydrothermal synthesis method. The influence of the seed layer synthesis method on the coatings quality was studied. The synthesized materials are nanoscale, crystallized in a mixed anatase-rutile modification. It was shown that for seed layers deposited by low-temperature solid-phase pyrolysis technique, the coatings are more homogeneous than for seed layers deposited by sol-gel method. In addition, a tendency to agglomeration was noted for nanotubes grown on a seed layer deposited by the sol-gel method. The electrophysical properties study showed that for materials with a seed layer obtained by the sol-gel method, the resistance is an order of magnitude higher than for materials with a seed layer synthesized by low-temperature pyrolysis technique. The activation energy (Ea) for titanium dioxide nanotubes (seed layer is applied by sol-gel method) was 0.74 eV, and for the sample obtained by low-temperature pyrolysis Ea was 0.68 eV.

Keywords: titanium dioxide, thin films, hydrothermal synthesis, seed layer, nanotubes

Funding: This work was financially supported by the RFBR, project No. 20-07-00653 A.

Citation: Volkova M. G., Ivanishcheva A. P., Petrov V. V., Bayan E. M., The effect of the seed layer on the TiO_2 nanotubes coatings quality grown on the glass substrates by hydrothermal synthesis. St. Petersburg State Polytechnical University Journal. Physics and Mathematics, 15 (3.3) (2022) 255–259. DOI: https://doi.org/10.18721/JPM.153.350

Материалы конференции
УДК 546.05; 538.975
DOI: https://doi.org/10.18721/JPM.153.350

Влияние затравочного слоя на качество покрытий из нанотрубок TiO_2 выращенных на стеклянных подложках гидротермальным методом

М. Г. Волкова [1, 2]✉, А. П. Иванищева [2], В. В. Петров [2], Е. М. Баян [1]

[1] Южный федеральный университет, Ростов-на-Дону, Россия;

[2] НОЦ «Микросистемная техника и мультисенсорные мониторинговые системы», Южный федеральный университет, Таганрог, Россия

✉ mvol@sfedu.ru

Аннотация. Покрытия из нанотрубок диоксида титана были получены на стеклянных подложках гидротермальным методом. В ходе работы было изучено влияние метода синтеза затравочного слоя на получаемые покрытия. Синтезированные материалы наноразмерны, кристаллизуются в смешанной анатазно-рутильной модификации. Показано, что для затравочных слоев, нанесенных методом низкотемпературного твердофазного пиролиза, покрытия более однородные, чем для затравочных слоев, нанесенных золь-гель методом. Кроме того, для нанотрубок выращенных на затравочном слое, нанесенном золь-гель методом, была отмечена склонность к агломерации. Изучение электрофизических свойств показало, что для материалов с затравочным слоем, полученным золь-гель методом, сопротивление на порядок выше, чем для материалов с затравочным слоем синтезированным низкотемпературным пиролизом. Энергия активации (Ea) для нанотрубок диоксида титана, где затравочный слой нанесен золь-гель методом составила 0.74 эВ, а для образца, полученного методом низкотемпературного пиролиза – 0.68 эВ.

Ключевые слова: диоксид титана, тонкие пленки, гидротермальны синтез, затравочный слой, нанотрубки

Финансирование: Работа выполнена при финансовой поддержке гранта РФФИ № 20-07-00653 А.

Ссылка при цитировании: Волкова М. Г., Иванищева А. П., Петров В. В., Баян Е. М. Влияние затравочного слоя на качество покрытий из нанотрубок TiO_2 выращенных на стеклянных подложках гидротермальным методом // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2022. Т. 15. № 3.3. С. 255–259. DOI: https://doi.org/10.18721/JPM.153.350

Introduction

Semiconductor oxide materials are the most commonly used in almost all areas of modern industry. Thin films nanomaterials coatings based on zinc oxide, tin dioxide or titanium dioxide can be used as gas-sensitive sensors [1], photocatalysts [2], optical devices [3], etc. The simultaneous use of various oxides and the creation of composite materials based on them also leads to properties improvement of the target products [4]. For example, the use of zinc and tin (IV) oxides leads to a significant improvement in gas-sensitive properties due to the appearance of a potential barrier at the boundary of the ZnO/SnO_2 heterojunction [5].

The study of film materials with a certain structure, such as nanorods, nanotubes, nanocubes, etc., is of particular interest, since such materials will have a larger surface area and a concentration of defects, which in turn can lead to improved gas-sensitive or photocatalytic properties [6]. However, smooth nanowires adsorb gases only on their surfaces, which creates serious obstacles to achieving highly sensitive properties, therefore porous nanowires are most interesting to study because of their high surface-to-volume ratio and porous structure, which allows gases to be absorbed not only on the surface, but also throughout the volume. Despite the fact that nanotubes and nanorods have similar morphology, nanotubes will have greater porosity and surface area, which is also more preferable for obtaining promising functional nanomaterials [7].

Nanostructured titanium dioxide is one of the most promising multifunctional inorganic materials due to its unique physical and chemical properties. TiO_2 coatings can be used in a wide range of applications, including catalysis, self-cleaning surfaces, gas sensors, solar cells, etc. [8]. There are various methods for producing TiO_2 films, among which are chemical (sol-gel, pyrolysis methods, deposition methods) and mixed physico-chemical methods (electrodeposition, atomic layer deposition, etc.) [9]. However, using hydrothermal synthesis, it is possible to obtain high-purity nanostructures with a given morphology at a relatively low temperature.

Obtaining high-quality coatings from nanotubes is possible in the presence of a seed layer without pores and cracks, therefore, the most important step in the nanostructure's growth is the choice of the seed layer synthesis method [10]. The most common synthesis methods are pyrolysis technique and sol-gel method, as the simplest and most cost-effective. Spray pyrolysis methods are widely known and most commonly used, but the solid-phase pyrolysis method is less common. In the course of previous studies, the authors developed and successfully applied film materials synthesis method based on zinc and tin (IV) oxides [11], therefore, the production of film materials based on titanium dioxide by this method seemed to be the most preferable. The sol-gel method is also a relatively simple technology, but a serious disadvantage may be poor reproducibility and the inability to obtain homogeneous coatings [12]. Therefore, the purpose of this work was to study the effect of the seed layer synthesis method on the quality of TiO_2 nanotubes coatings obtained by hydrothermal synthesis.

Materials and Methods

Titanium tetrachloride, titanium butoxide, organic acid, 1,4-dioxane, sodium hydroxide and distilled water were selected as precursors to produce TiO_2-nanotubes films coatings. Nanostructured film coatings were obtained in two stages. The first stage included the preparation of a seed layer using sol-gel method or low-temperature solid-phase pyrolysis technique. In the first case, the titanium tetrachloride hydrolysis product was applied once to pre-prepared glass substrates.

In the second case, the seed layer was synthesized in the melt by the interaction of titanium butoxide and organic acid. The resulting melt was cooled, crushed, and after dissolution in 1,4-dioxane, it was also applied once to the prepared substrates. The substrates with the applied solutions were subjected to temperature treatment in a muffle furnace for two hours at a temperature of 550 °C. Cooling was carried out in air together with a muffle furnace, which allows us to obtain homogeneous coatings without cracks.

At the second stage, TiO_2 nanotubes were obtained by hydrothermal synthesis. To achieve this, the substrates with the applied seed layer were placed in a cell for hydrothermal synthesis, a solution of 10 M sodium hydroxide and titanium dioxide powder were added (the cell load did not exceed 80%). Hydrothermal treatment was carried out for 24 hours at a temperature of 160 °C. At the end of the nanostructure growth procedure, the samples were washed with distilled water to the neutral medium of the solution and dried in air. The synthesized materials were examined by X-ray diffraction analysis (XRD, ARLX'TRA diffractometer, Thermo ARL, CuKα radiation) and scanning electron microscopy (SEM, scanning electron microscope Nova Nanoab 600). The study of the electrical resistance dependence on the reverse temperature was carried out according to the previously described method [1].

Results and Discussion

According to the results of XRD, for film materials obtained by low-temperature pyrolysis at the first stage of synthesis, a mixed structure of anatase and rutile is shown. Calculations of the crystallite sizes according to the Scherrer equation showed that the average size is 9 and 13 nm for the anatase and rutile phases, respectively. XRD patterns of materials after hydrothermal treatment do not have clearly crystallized peaks, which allow us to indirectly judge the presence of nanoscale titanium dioxide materials (Fig. 1).

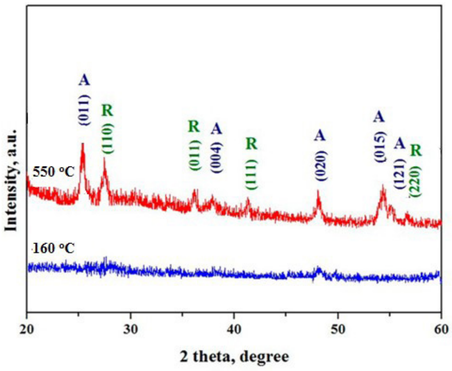

Fig. 1. XRD patterns of TiO_2-materials obtained by low-temperature pyrolysis (red curve) and hydrothermal method (blue curve), anatase is A, rutile is R

According to SEM data, nanostructured titanium dioxide coatings obtained by hydrothermal method (the seed layer is applied by pyrolysis) are nanotubes with a diameter of about 10 nm, a length of several microns; the tubes are extended, sometimes curved, rolled into balls of 3–5 microns in size (Fig. 2, *a*). For nanostructures synthesized by the hydrothermal method with a seed layer applied using sol-gel technology, a slightly different nature of the nanotubes growth is shown. The resulting structures are thin nanotubes with a diameter of several tens of nanometers, extended, and sometimes curved, with a length of several microns. On the tubes surface there are island agglomerates consisting of tubes tangles (Fig. 2, *b*), which may be due to the uneven application of the seed layer as a result of an imperfect synthesis method.

The electrophysical properties of the obtained film were measured using a software and hardware measuring complex that allows detecting the dependence of resistance on temperature,

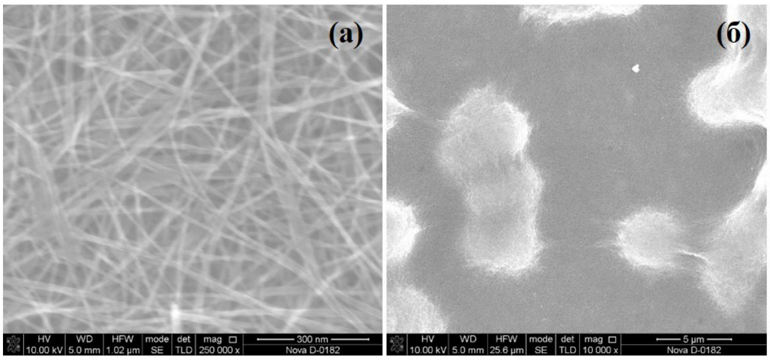

Fig. 2. SEM-image of TiO_2-nanotubes (seed layer was deposited using low-temperature pyrolysis (*a*) and sol-gel method (*b*)

as well as the activation energy of conductivity [13]. To achieve this, V-Ni contacts were formed on top of nanotubes by thermal vacuum evaporation. The dependence of the electrical resistance on the reverse temperature is shown in Fig. 3.

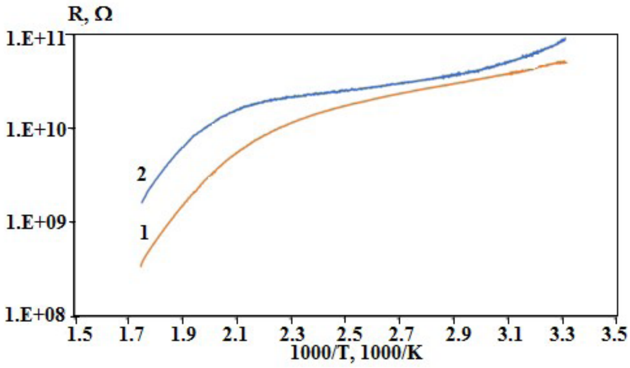

Fig. 3. R-1000/T dependence of TiO_2-nanotubes (seed layer was deposited using low-temperature pyrolysis (curve 1) and sol-gel method (curve 2))

Titanium dioxide nanotubes grown on the seed layer synthesized by low-temperature pyrolysis (Fig. 3, curve 1) and sol-gel method (curve 2), have a similar character and high nonlinearity. With an increase in the heating temperature in the temperature range of 30–130 °C, a slight decrease in the resistance is observed. In the temperature range of 150–300 °C, there is a sharp decrease in resistance by 1.5 orders of magnitude. The structure with TiO_2 nanotubes grown on the seed layer deposited by the sol-gel method has a resistance an order of magnitude higher than TiO_2 nanotubes grown on the seed layer synthesized by low-temperature pyrolysis. This may be a consequence of the amorphous structure of TiO_2 nanotubes with a seed layer deposited by the sol-gel method. The same conclusions are confirmed by the calculation of the activation energy of conductivity (Ea) carried out in the temperature range of 200–300 °C. For titanium dioxide nanotubes, grown on the seed layer applied by sol-gel method, the Ea was 0.74 eV, and for the sample with seed layer obtained by low-temperature pyrolysis, the Ea was 0.68 eV.

Conclusion

Coatings of titanium dioxide nanotubes were obtained by hydrothermal method. It was shown that when a seed layer was applied by low-temperature pyrolysis technique, it is possible to obtain smaller diameter tubes and a better coating, without the presence of agglomerates. The presence of a large number of “stuck together” particles in the material with sol-gel seed layer application can be explained by the uneven distribution of nanotube growth centers. The study of electrophysical properties showed that for materials with a seed layer obtained by the sol-gel method, the resistance is an order of magnitude higher than for materials with a seed layer synthesized by low-temperature pyrolysis. This can be explained by the more amorphous structure of materials with a seed layer obtained by the sol-gel method, which confirms the calculation of the activation energy – for these materials it is higher than for materials with a seed layer deposited by low-temperature pyrolysis.

Acknowledgments

The authors are grateful to the Laboratory for Technology of Functional Nanomaterials of the Institute of Nanotechnology, Electronics and Equipment Engineering of the Southern Federal University for SEM studies conducting.

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THE AUTHORS

VOLKOVA Maria G.
mvol@sfedu.ru
ORCID: 0000-0001-9483-162X

PETROV Viktor V.
vvpetrov@sfedu.ru
ORCID: 0000-0003-3725-6053

IVANISHCHEVA Alexandra P.
starnikova@sfedu.ru
ORCID: 0000-0002-3779-8242

BAYAN Ekaterina M.
ekbayan@sfedu.ru
ORCID: 0000-0002-8445-9139

Received 13.07.2022. Approved after reviewing 15.07.2022. Accepted 15.07.2022.