St. Petersburg Polytechnic University Journal. Physics and Mathematics. 2022 Vol. 15, No. 3.3
Научно-технические ведомости СПбГПУ. Физико-математические науки. 15 (3.3) 2022

Conference materials
UDC 546.05; 538.975
DOI: https://doi.org/10.18721/JPM.153.352

Surface and electrophysical properties study of thin TiO_2-SnO_2 nanocomposite films

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Abstract. Thin nanocomposite films based on pure tin dioxide with a low content of titanium oxide (0, 1, 3, and 5 mol %) were obtained by solid-phase low-temperature pyrolysis. The thickness of the films obtained was up to 200 nm. The particle size of the TiO_2-SnO_2 nanomaterial lies in the range of 7–13 nm. Atomic force microscopy (AFM) showed that the films have a granular structure with a height difference of 11–114 nm. The surface of the film with a Ti concentration of 5 mol.% has a higher roughness compared to other samples. Force microscopy with a Kelvin probe (KPFM) revealed a surface potential, indicating the existence of a strong surface electric field. A small addition of titanium dioxide (1%) to the tin dioxide structure leads to the appearance of peak values of the surface potential, the value of which reaches 1325 mV. Studies of the temperature dependences of the obtained samples showed that the pure SnO_2 film has the maximum resistance values and high nonlinearity. However, with a small addition of titanium dioxide (1%) to tin dioxide, the electrical resistance of the nanosized material sharply decreases and has indicators 4–5 orders of magnitude lower than those of pure SnO_2 films.

Keywords: nanomaterials, thin films, pyrolysis, tin dioxide, titanium dioxide, surface potential, electrical properties

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

Citation: Gulyaeva I. A., Ivanishcheva A. P., Volkova M. G., Bayan E. M., Petrov V. V., Surface and electrophysical properties study of thin TiO_2-SnO_2 nanocomposite films. St. Petersburg State Polytechnical University Journal. Physics and Mathematics, 15 (3.3) (2022) 265–270. DOI: https://doi.org/10.18721/JPM.153.352

Материалы конференции
УДК 546.05; 538.975
DOI: https://doi.org/10.18721/JPM.153.352

Исследование поверхностных и электрофизических свойств тонких нанокомпозитных пленок состава TiO_2-SnO_2

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Аннотация. Методом твердофазного низкотемпературного пиролиза были получены тонкие нанокомпозитные пленки на основе чистого диоксида олова с низким содержанием оксида титана (0, 1, 3 и 5 мол. %). Атомно-силовой микроскопией (АСМ) показано, что пленки имеют зернистую структуру с перепадом высот 11–114 нм. Методом Кельвин-зондовой силовой микроскопии (КЗСМ) на поверхности TiO_2-SnO_2

пленок с мольным соотношением Ti:Sn равным 1:99 обнаружен высокий поверхностный потенциал потенциала (V_b = 1325 мВ), показывающий существование сильного поверхностного электрического поля.

Ключевые слова: наноматериалы, тонкие пленки, пиролиз, диоксид олова, диоксид титана, поверхностный потенциал, электрофизические свойства

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

Ссылка при цитировании: Гуляева И. А., Иванищева А. П., Волкова М. Г., Баян Е. М., Петров В. В., Исследование поверхностных и электрофизических свойств тонких нанокомпозитных пленок состава TiO_2-SnO_2 // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2022. Т. 15. № 3.3. С. 265–270. DOI: https://doi.org/10.18721/JPM.153.352

Introduction

Inorganic oxide nanomaterials based on tin and titanium dioxides are widely used to create electronic devices, photocatalysts, solar cell electrodes and gas sensors [1–3]. Titanium dioxide is the most commonly used as a photocatalyst, but the width of its band gap does not allow it to be used when irradiated with visible light, so various modifying additives are used for this purpose [4]. One of these additives is tin ions (4+), since the close radius allows you to replace titanium in the crystal lattice [5–6]. Tin dioxide has chemical and thermal stability, and due to the combination of high conductivity and high potential for the release of excess oxygen, Electrodes based on SnO_2 also contribute to the complete oxidation of organic compounds [7]. Another reason for the combined use of these oxides may be a similar type of crystallization, since both tin dioxide and titanium dioxide can be crystallized in the structure of rutile [8].

Modification of SnO_2 films with titanium dioxide allows to improve various properties of the nanocomposite material, including electrophysical [9–10]. For example, the work [11] describes the properties of nanostructures based on Ti-SnO_2 films, among the factors that ensure the success of the use of these materials as electrodes are listed: (1) The structure of the core-shell of the Ti-SnO_2 network are listed: (1) The structure of the core-shell of the Ti-SnO_2 network, consisting of Ti inside a shell of SnO_2 nanocrystals, is favorable for the diffusion of lithium ions during cyclic charge-discharge. (2) The Ti in the composite acts as an effective mechanical support for relieving the stress caused by the intercalation–deintercalation of lithium, which can play a crucial role in the excellent lithium storage capacity and the cyclic capacity of the electrode. (3) Mesopores formed by 3D microstructures also contribute to the improvement of the electrochemical characteristics of the electrode, possibly because they facilitate the diffusion of the electrolyte or lithium ions during charge-discharge processes.

The purpose of this work was to study surface (surface morphology and surface electric potential) and electrophysical (temperature dependence of electrical resistance) properties synthesized by solid-phase low-temperature pyrolysis of thin films TiO_2-SnO_2.

Materials and Methods

To obtain thin film materials TiO_2-SnO_2 with a ratio of Ti:Sn = 0:100, 1:99, 3:97, 5:95 by the method of solid-phase low-temperature pyrolysis, tin salts ($SnCl_4 \cdot 5H$) were used as precursors for the synthesis of thin films TiO_2-SnO_2 and titanium ($(C_4H_9O)_4Ti$). The resulting salts were dissolved in 1,4-dioxane and applied three times to the prepared silicon and polycore substrates. Each layer was dried in air and in a drying oven at a temperature of 120 °C. The final temperature treatment was carried out in a muffle furnace at a temperature of 600 °C for two hours. The synthesis conditions were selected according to previous studies [12].

According to X-ray phase analysis, the resulting films have a crystal structure of cassiterite, regardless of the concentration of the additives administered. The resulting reflexes are somewhat expanded, which is typical for film nanocrystalline materials. Diffraction maxima of other phases are not detected. Synthesized TiO_2-SnO_2 is characterized by a decrease in both particle sizes from 36 to 22 nm and the degree of crystallization from 68% to 45% with an increase in the concentration of titanium from 0 to 5 mol. %, which may be due to an increase in the concentration of defects and a less “ideal” crystal structure.

The study of the surface morphology and surface potential of the obtained films was carried out using the Ntegra probe nanolaboratory (NT-MDT SI, Russia). For this purpose, the samples were first examined using atomic force microscopy, and then Kelvin-probe force microscopy was used. In the study, the AFM and KPFM methods used the NSG10/Pt cantilever with a force constant of 11.2 N/m (TipsNano, Estonia) and a radius of curvature of about 25 nm.

To process the results of AFM measurements, the Image Analysis (NT-MDT) program was used, with the help of which the roughness parameters were estimated, the root value of roughness (Sq, Root Mean Square) and the maximum height difference (S_y, Peak-to-peak)). On the basis of the KPFM measurements, the values of the surface potential V_b were determined. To compare the surface potentials on different film samples, the difference between the maximum and minimum values ΔV_b was used, the values of which were averaged according to the sample.

Studies of the electrophysical properties of the obtained film samples were carried out on a software and hardware measuring complex that allows measuring the dependence of resistance on temperature [13].

Results and Discussion

Fig. 1 shows AFM scans of studied samples of TiO_2-SnO_2 films with a Ti:Sn ratio of 0:100, 1:99, 3:97, 5:95 mol.% with a size of 3×3 μm^2.

Table 1 shows roughness (S_q, nm), maximum elevation differences (S_y, nm), as well as surface potential values (V_b, mV) and its average values (ΔV_b, mV) for each of the samples obtained.

Table 1

Surface characteristics of TiO_2-SnO_2 films

Ti:Sn, mol.%	S_y, nm	S_q, nm	V_b, mV	ΔV_b, mV
0:100	11.0	1.4	4	4
1:99	34.3	4.1	1325	141
3:99	60.2	7.4	326	39
5:99	114.6	12.6	126	17

AFM studies have shown that TiO_2-SnO_2 films have a granular structure, and the roughness of films increases with increasing concentration of titanium dioxide. The least roughness has a film SnO_2 (S_y = 11.0 nm), and TiO_2-SnO_2 film with a concentration of Ti 5 mol.% has the highest roughness (S_y=114.6 nm).

Studies of KPFM have shown that the lowest value of the surface potential (V_b = 4 mV) is characteristic of the tin oxide film – Fig. 1, *h*. This is due to the fact that the contact of two crystallites of tin dioxide contributes to the formation of a low surface potential. However, a small addition (1 mol.%) of titanium dioxide to the structure of tin dioxide leads to the appearance of peak values of the surface potential, the value of which reaches 1325 mV. It is known that the electron output work of titanium dioxide (4.7 eV) [14] is somewhat less than that of tin oxide (4.8–4.9 eV). [15, 16].

When the crystallites TiO_2 and SnO_2 come into contact, electrons will pass from titanium dioxide to tin dioxide, and regions with large local surface potential values of V_b should arise. The latter indicates the existence on the surface of such a film of a strong (up to 10^7 V/cm) electric field, which can significantly affect the transfer of charge carriers in it and the processes occurring on its surface [17].

Fig. 2 shows the dependence of electrical resistance on inverse temperature.

Pure SnO2 film has maximum resistance values and high nonlinearity. However, with a small addition of titanium dioxide (1%) to tin dioxide, the electrical resistance of the nanoscale material is sharply reduced and has indicators 4–5 orders of magnitude lower than pure SnO_2 films. This may also be a consequence of the presence of a high surface electric field in TiO_2-SnO_2 films

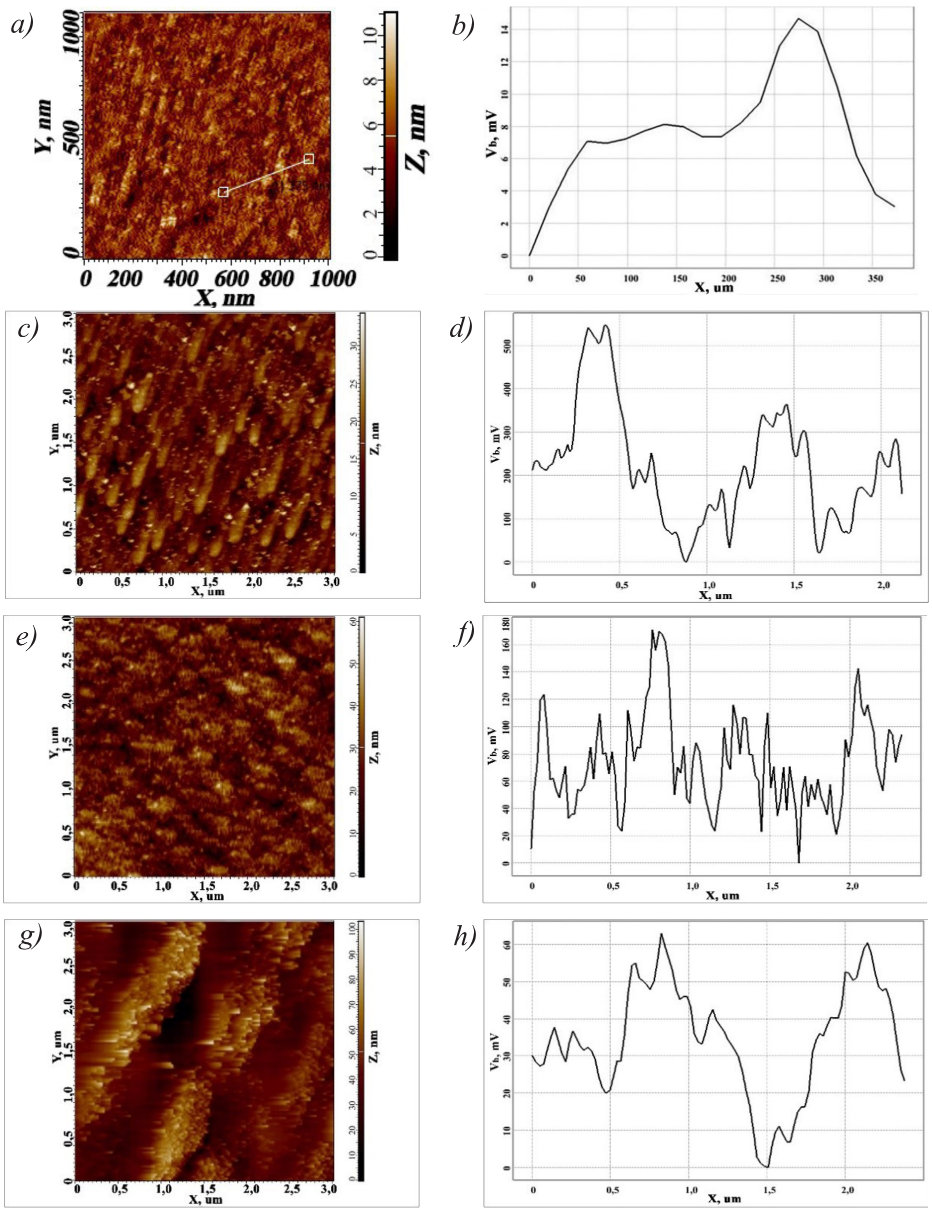

Fig. 1. AFM elevation scans (*a*, *c*, *e*) and their corresponding surface potential distribution (*b*, *d*, *f*) over the surface TiO_2-SnO_2 films with a Ti:Sn mole ratio of 0:100 (*a*, *b*), 1:99 (*c*, *d*), 3:97 (*e*, *f*) and 5:95 (*g*, *h*) mol. %

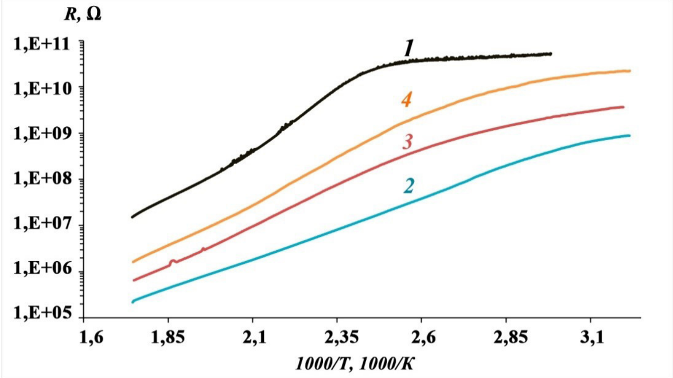

Fig. 2. Dependence of R on 1000/T for TiO_2-SnO_2 films with a molar ratio of Ti:Sn equal to 0:100 (curve1), 1:99 (curve 2), 3:97 (curve 3) and 5:95 (curve 4) mol. %

with a Ti:Sn molar ratio of 1:99. A higher content of titanium dioxide additives (3 and 5%) shows a higher resistance than that of sample c (1%). At the same time, the dependence of electrical resistance on the reverse temperature for the resulting films is close to linear.

Conclusion

Nanoscale films of TiO_2-SnO_2 composition with controlled thickness were formed by solid-phase low-temperature pyrolysis. The KPFM method detected a surface potential on their surface, showing the existence of a high surface electric field. The resulting TiO_2-SnO_2 films can be used as solar cell electrodes and gas-sensitive materials for gas sensors.

Acknowledgments

We would like to express our gratitude to the staff of the Laboratory for Technology of Functional Nanomaterials of the Institute of Nanotechnology, Electronics and Equipment Engineering of the Southern Federal University for their help in conducting AFM and KFM studies.

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Received 13.07.2022. Approved after reviewing 25.07.2022. Accepted 26.07.2022.