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Optical and electrophysical properties of La-SnO_2 films

© A.P. Starnikova[1], V.V. Petrov[1], G.V. Tolstyak[2], I.A. Gulyaeva[1], E.M. Bayan[2]

[1] Institute of Nanotechnologies, Electronics and Equipment Engineering, Southern Federal University, Taganrog, Russia
[2] Chemical Faculty, South Federal University, Rostov-on-Don, Russia

E-mail: starnikova@sfedu.ru; vvpetrov@sfedu.ru

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In this work, the optical and electrophysical properties of tin dioxide thin films containing 1−5% La^{3+}, obtained by oxidative pyrolysis, were studied using atomic force and Kelvin probe force microscopy, X-ray diffraction, and spectrophotometry. The films are optically transparent, homogeneous, and formed by crystallites 21−24 nm in size. The SnO_2 film with 3% La^{3+} has the highest values of activation energy, roughness, and surface potential.

Keywords: thin films, tin dioxide, activation energy, optical properties, transparency.

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1. Introduction

Tin dioxide is one of the most sought-after semiconductor of *n*-type due to its unique electric and optical properties [1]. To improve its characteristics, various additives are introduced, among which lanthanum is deemed to be rather promising, since it has $4f$ electron sublevel [2]. Composite films based on $La_2O_3-SnO_2$ are multifunctional and are of interest for use in gas sensors [3] and other areas [4]. Inclusion of 2 wt% La^{3+} causes increase in the sensitivity of film SnO_2 9 times to acetone and reduction of response time to 2.8 s at operating temperature 350°C [5]. Sensors were produced on the basis of $La-SnO_2$ and La−ZnO, sensitive to CO_2 with concentrations of not below 500 ppm in the wide humidity range [6,7]. Doping with ions La^{3+} also influences optical properties of zinc oxide films, which maintained transparency $> 80\%$ and had a narrowed prohibited zone from 3.275 to 3.125 eV [8]. The objective of this paper was to study optical, electrophysical and structural properties of thin nanocrystalline films based on SnO_2, modified with 1, 3 and 5 mol.% ions La^{3+}, which were synthesized by oxidation pyrolysis method.

2. Results and discussion

The source substances to produce films of pure and ion-modified La^{3+} SnO_2, $La_2(CO_3)_3$, $SnCl_4 \cdot 5H_2O$, hydrochloric and abietinic acids were used. The synthesis was carried out using oxidation pyrolysis method on substrates of polycore, glass and silicon under annealing for 2 h at 600°C using the previously described method [9].

Morphology of the surface and microstructure of nanofilms are the key factors that determine their properties, therefore, the study paid the special attention thereto. The methods of atomic force and Kelvin probe force microscopy with the help of probe laboratory Ntegra (NT-MDT, Russia) assessed the maximum elevation difference (S_y) and distribution of potential on film surface (V_b) (see Figure 1, *a*).

It is shown that films SnO_2 with content of 3% La^{3+} have maximum roughness with elevation difference (S_y), reaching 150 nm. This is 1.4−3 times higher than in the specimens with other content of La^{3+}. Value V_b correlates with distribution of values S_y. The maximum value V_b, equal to 57.5 mV, is also available for film SnO_2 with content of 3% La^{3+}. Values V_b in other specimens are 2.2−4.6 times less.

Phase composition of films was determined by X-ray diffraction analysis (diffractometer ARLX'TRA, Switzerland). All peaks present in X-ray patterns of materials containing 1, 3, 5% La^{3+}, belong to tetragonal crystallographic phase SnO_2, tin stone (Figure 1, *b*). Other phases were not found. Average dimensions of crystallites were assessed by areas of coherent scattering calculated using Scherrer formula and amounted to 21−24 nm.

Film transmission spectra were obtained on a spectrophotometer UV-1100 ECOVIEW at room temperature in the range of 200−1000 nm. Transmission at wavelengths 325−1000 nm makes more than 85% for film containing 1% La^{3+}; more than 98% — for films containing 3 and 5% La^{3+} (Figure 2). Optical widths of prohibited areas obtained by Tauc plots are 3.55 eV for film containing 1% La^{3+}; 3.75 eV — for film containing 3% La^{3+} and 4.32 eV — for film containing 5% La^{3+}. For pure tin dioxide the width of the prohibited area is 3.6 eV, and for lanthanum oxide — 4.3 eV [10]. The latter indicates a considerable influence of low lanthanum concentrations on optical properties of composite films La_2O_3-SnO_2.

After thermal treatment, contact metallization V-Ni with thickness of 200 nm was applied on the films by vacuum thermal evaporation method. Using the method described in [11], temperature dependence of electric

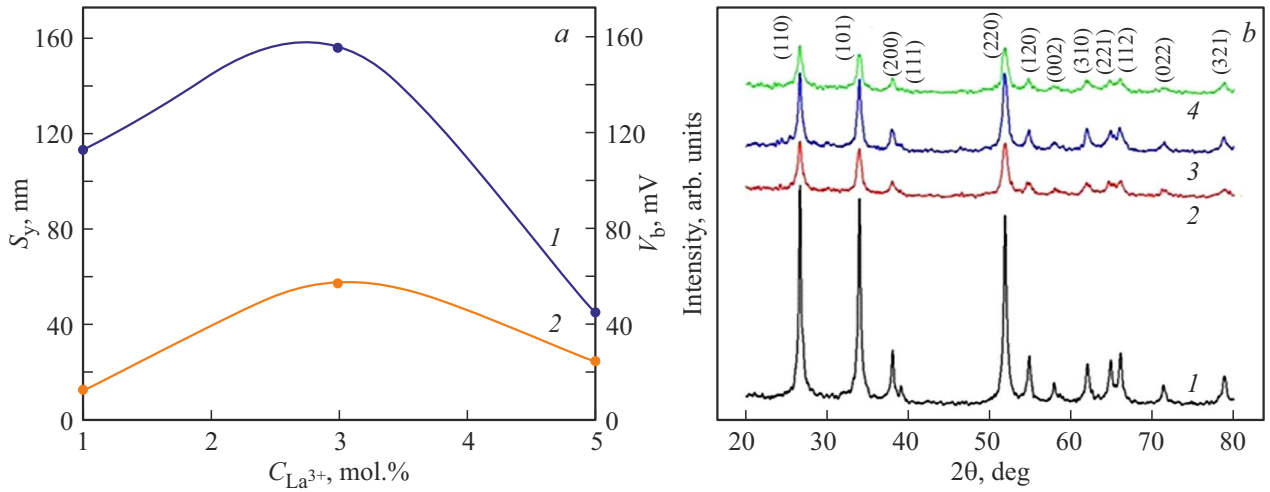

Figure 1. Dependence of values of maximum elevation difference (1) and surface potential (2) on content of ions La^{3+} in films SnO_2 (*a*) of X-ray pattern SnO_2 (*1*), SnO_2, modified with 1 (*2*), 3 (*3*), 5 (*4*)% La^{3+} (*b*).

conductivity (G) and current-voltage curves (CVC) of the produced structures was measured. CVC La-SnO_2 of films at temperatures above room temperature was of linear nature, which indicates non-straightening nature of contact metallization. Based on studies of temperature dependences of electric conductivity, the activation values were calculated in two temperature ranges 30–140°C and 140–230°C. Activation energy of conductivity (E_a) was assessed using Arrhenius equation: $G = G_0 \cdot \exp(-E_a/k \cdot T)$, where E_a — conductivity activation energy, k — Boltzmann constant, and G_0 — coefficient taking into account the volume conductivity of the material. For samples containing 1, 3 and 5% La^{3+} in SnO_2 values E_a in temperature range 30–140°C made 0.14; 0.09; 0.07 eV accordingly, and in temperature range 140–300°C E_a made 0.44; 0.87; 0.84 eV, accordingly (Figure 3).

It was shown that in the range 30–140°C with increase of La^{3+} content in the films, the temperature dependence

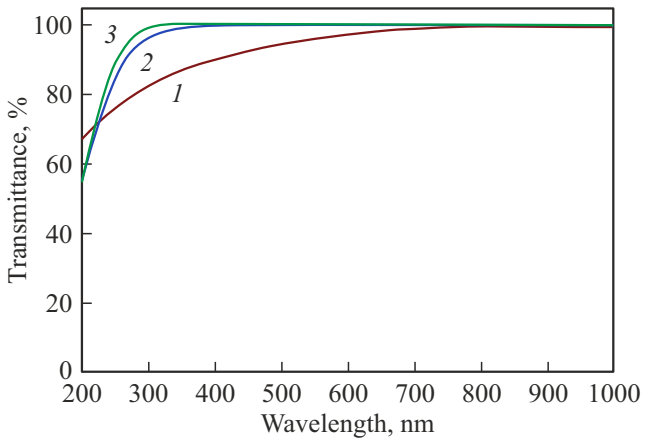

Figure 2. Transmission spectra of films SnO_2, modified with 1 (*1*), 3 (*2*), 5 (*3*)% La^{3+}.

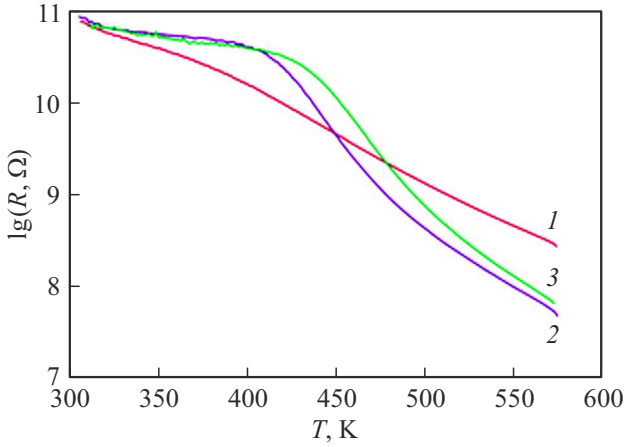

Figure 3. Dependences of resistance logarithm of films SnO_2, modified with 1 (*1*), 3 (*2*), 5 (*3*)% La^{3+} on temperature.

of electric conductivity decreases. This is explained by the binding of oxygen vacancies with ions La^{3+}. At temperatures above 140°C for the film containing 1% La^{3+}, activation energy is 0.44 eV, which is close to the values of energy level occurrence corresponding to the oxygen vacancies in the prohibited area of SnO_2. However, for the films containing 3 and 5% La^{3+} the activation energy values are nearly twice higher and are equal to 0.87 and 0.84 eV, accordingly. It may be related, on the one hand, to appearance of deep levels in prohibited area of SnO_2 that are related to ionization of adsorbed oxygen, and on the other hand, to formation of nanocrystallites La_2O_3.

3. Conclusion

All produced films of SnO_2, containing La^{3+}, are homogeneous, formed by crystallites with size of 21–24 nm,

have transmission of more than 85% in the range of 325–1000 nm. Introduction of 1–3% La^{3+} causes a more drastic reduction of temperature dependence of electric conductivity, which makes it possible to use them as gas sensitive layers of gas sensors. The highest values of activation energy, parameters of roughness and surface potential are of the tin dioxide film with content of 3% La^{3+}. The latter may be related to formation of composite structure of the film, which was previously observed in papers [12,13]. Determination of the optical absorption edge demonstrated that the increase in concentration La^{3+} causes increase of the prohibited area width from 3.55 to 4.32 eV.

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Conflict of interest

The authors declare that they have no conflict of interest.

Authors' contributions:

V.V. Petrov — conceptualization, data analysis, article text editing; G.V. Tolstyak — material synthesis, article text writing, XPS, optical properties, electrophysical measurements; I.A. Gulyaeva — AFM, KPFM measurements; A.P. Starnikova — electrophysical measurements; E.M. Bayan — methodology, data analysis, article text writing and editing.

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