Sensitivity analysis of sensors based on La−SnO_2 films to ethanol vapors

© V.A. Davidenko[1], G.V. Tolstyak[2], E.M. Bayan[2], V.V. Petrov[1]

[1] Institute of Nanotechnologies, Electronics and Equipment Engineering, Southern Federal University, Taganrog, Russia
[2] Department of Chemistry, Southern Federal University, Rostov-on-Don, Russia
E-mail: vvpetrov@sfedu.ru

Received April 30, 2025
Revised August 5, 2025
Accepted August 12, 2025

In this work, the gas-sensitive characteristics of gas sensors based on nanocrystalline tin dioxide films modified with 1, 3, and 5 mol.% La^{3+} ions obtained by oxidative pyrolysis were studied. The study of gas-sensitive properties to ethanol vapors with a concentration of 100 ppm was carried out at operating temperatures of 200−400 °C. Gas sensors based on 1La−99SnO_2 film have the highest response values to ethanol vapors at a temperature of 200−250 °C, and sensors based on 3La−97SnO_2 film have the highest response values at a temperature of 350−400 °C.

Keywords: tin dioxide, lanthanum oxide, thin films, gas-sensitive properties, ethanol.

DOI: 10.61011/TPL.2025.12.62807.7958

Unique physical and chemical properties [1] make tin dioxide (SnO_2) one of the most sought-after *n*-type semiconductors. One way to improve its characteristics is to modify it with various metal oxides (specifically, rare earth elements), of which lanthanum is particularly noteworthy [2]. SnO_2 films modified with La^{3+} ions are sensitive to carbon-dioxide gas [3,4]. The response of acetone sensors based on an SnO_2 film with added lanthanum (2%) is 9 times stronger and virtually instantaneous at 350 °C [5]. Nanocomposite fibers based on La_2O_3 and SnO_2 nanocrystals formed by electrospinning [6] feature an ethanol response value of 111 at an operating temperature of 250 °C and response and recovery times of 150 and 742 s, respectively. The authors of [7,8] have synthesized SnO_2 films modified with La^{3+} ions by oxidative pyrolysis. This method allows one to form highly sensitive nanocomposite materials [9]. The aim of the present study is to examine the gas-sensitive characteristics of sensors based on nanocrystalline films of tin dioxide that are modified with La^{3+} ions with a concentration of 1, 3, or 5 mol.% and exposed to ethanol vapor.

The required materials were synthesized by oxidative pyrolysis in several stages. Lanthanum carbonate ($La_2(CO_3)_3$), tin tetrachloride pentahydrate ($SnCl_4 \cdot 5H_2O$), and hydrochloric and abietic acids were the initial materials. The needed amount of salts was calculated so as to form thin films of tin(IV) oxide with 1, 3, or 5 mol.% lanthanum(III). The first step consisted in obtaining an intermediate product: organic Sn^{4+} and La^{3+} salts. The corresponding procedure has been detailed earlier in [7,8]. The produced organic salts of tin(IV) and lanthanum(III) were dissolved in an organic solvent. Precursors for subsequent film formation were obtained this way. At the second stage, thin films of these precursors were applied to a sensor platform. The sensor platform was a polycrystalline aluminum oxide substrate with interdigitated platinum measuring electrodes spaced approximately 100 μm apart formed on its working side. A platinum heater, which could heat films to operating temperatures (600 °C), was on the non-working side of the platform. The sensor platforms were mounted in a standard TO-5 housing. After drying in air, the formed sensor was annealed at 600 °C for 2 h using the film heater. Tin(IV) oxide films containing 1, 3, or 5 mol.% La^{3+} were obtained this way. The thickness of annealed La−SnO_2 films was estimated by stylus profilometry (Alfastep D-100, Kla-Tencor, United States). The obtained value was 120 nm with a determination error of ±20 nm.

The phase composition of films was determined by X-ray diffraction analysis (ARLX'TRA diffractometer, Switzerland). All peaks present in the X-ray patterns of materials containing 1, 3, and 5 mol.% La^{3+} ions (Fig. 1) belong to the tetragonal crystallographic cassiterite phase (SnO_2). The average particle size was estimated by the coherent scattering regions and calculated using the Scherrer formula to be 21−24 nm.

The sensitivity of sensors based on La−SnO_2 films to ethanol vapor with a concentration of 100 ppm was studied using a multifunctional stand for measuring the parameters of gas sensors [9]. The sensors were introduced into a measurement chamber and heated to a specified temperature. The chamber was then purged sequentially with a stream of synthetic air and a mixture of synthetic air and ethanol vapor with a concentration of 100 ppm at a gas flow rate of 200 ml/min. The air−gas supply sequence was repeated several times. Measurements were carried out at working temperatures of 200−400 °C. Figure 2 presents the dynamics of two responses of La−SnO_2 sensors with 1, 3, and 5 mol.% La^{3+} to ethanol vapor at a temperature of 400 °C.

The baseline resistances of sensors (R_0) were recorded when the chamber was purged with air. With subsequent purging with a mixture of air and ethanol vapor (100 ppm), the sensor resistance decreased. When the readings became stable, the sensor resistance (R_{gas}) was determined. The

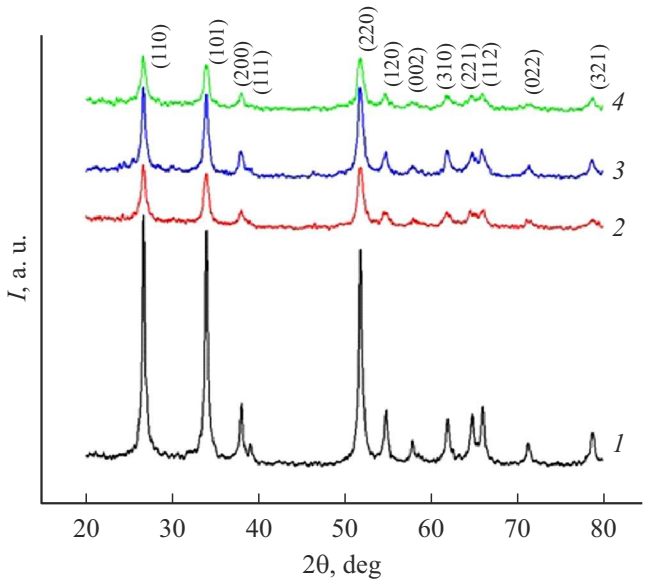

Figure 1. X-ray diffraction patterns of pure (*1*) and modified SnO_2. The concentration of modifying La^{3+} ions is 1 (*2*), 3 (*3*), or 5 mol.% (*4*).

sensor response was calculated as $S = R_0/R_{gas}$. The sensor response time (t_{res}) at the level of 0.9 and the recovery time of sensor resistance at the level of 0.1 (t_{rec}) were also determined. The values of S, t_{res}, and t_{rec} were averaged over the number of measurements. The measurement error was estimated at 5 %.

Figure 3, *a* shows the dependence of the sensor response to ethanol vapor with a concentration of 100 ppm on lanthanum content of the La–SnO_2 film at operating temperatures ranging from 200 to 400 °C. This dependence suggests that the response value of sensors based on the 3La–97SnO_2 thin film at operating temperatures of 200–250 °C is 31–72 % lower than that of sensors based on films of other compositions. At 300–350 °C, the 1La–99SnO_2 film features a 1–60 % stronger response. At 400 °C, the response value of sensors based on the 3La–97SnO_2 film is 17–21 % higher than that of sensors based on films of other compositions. This is seen clearly from the dependence of the sensor response on operating temperature (Fig. 3, *b*). It should be noted that the response value of the sensor based on a SnO_2 film, which was synthesized using the same procedure without the addition of lanthanum compounds, to ethanol with a concentration of 100 ppm was 1.6 and 2.1 at 350 and 400 °C, respectively. The response at lower temperatures was zero.

This behavior is attributable to the fact that metal oxides contain adsorbed oxygen molecules and ions (O_2^-) at temperatures up to 250–300 °C and atomic oxygen ions (O^{2-} and O^-) at higher temperatures [10,11]. It was demonstrated in [12] that the conversion of ethanol on the surface of gas-sensitive materials depends only on adsorbed oxygen. Ethanol dissociates through the formation of an ionic bond between oxygen in the molecule and an unsaturated metal atom of the active surface site (M_s), while a hydrogen atom of ethanol binds to nearby oxygen anion O_s:

$$CH_3CH_2OH + O_s + M_s \rightarrow CH_3CH_2O{-}M_{ads} + O{-}H_{ads} + V_{O_s}$$

$$\rightarrow CH_3CHO + H{-}M_{ads} + O{-}H_{ads} + V_{O_s}$$

$$\rightarrow CH_3CHO + M_s + H_2O + V_{O_s}.$$

The intermixing of M_{ads}–H and OH_{ads} produces an H_2O molecule, oxygen vacancy V_{O_s}, and partially reduced metal atom M_s. At temperatures above 250–300 °C, the emergence of a large number of oxygen ions due to the dissociation of O_2 molecules leads to a right shift of the reaction (toward the reaction products). The presence of a large number of metal ions will shift the reaction to the left, proving an explanation for the low response values of sensors based on the 5La–95SnO_2 film. It is known [7] that 3La–97SnO_2 films have a maximum surface potential of 57.5 mV, which is 2.2–4.6 times higher than that of films of other compositions. An intense surface electric field [9] contributes to a stronger response of the sensor based on 3La–97SnO_2 at higher temperatures.

Figure 4 presents the temperature dependences of the response and recovery times of sensors based on La–SnO_2 films. Since the t_{res} and t_{rec} values depended only weakly on the film composition at each temperature, they were represented by a single curve. It is evident that adsorption-desorption mechanisms change at 300–350 °C, which may also be attributed to the presence of molecular and atomic oxygen ions within different temperature ranges. The value of t_{res} decreases by a factor of 1.26 at 200–300 °C, reaching a minimum of 230 s at 300 °C. The value of t_{rec} increases by a factor of 3, reaching its maximum at the same temperature. Within the temperature range of 350–400 °C, the values of t_{res} and t_{rec} decrease by a factor of 1.09 and 1.96, respectively.

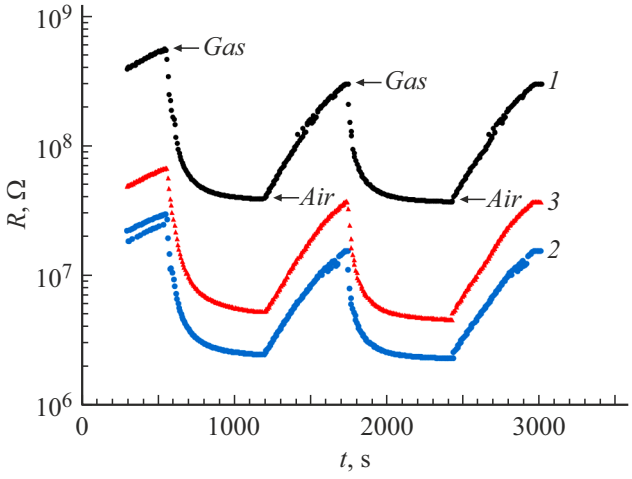

Figure 2. Dynamics of resistance variation of La–SnO_2 sensors with 1 (*1*), 3 (*2*), and 5 mol.% (*3*) La^{3+} exposed to ethanol vapor (100 ppm) at a temperature of 400 °C.

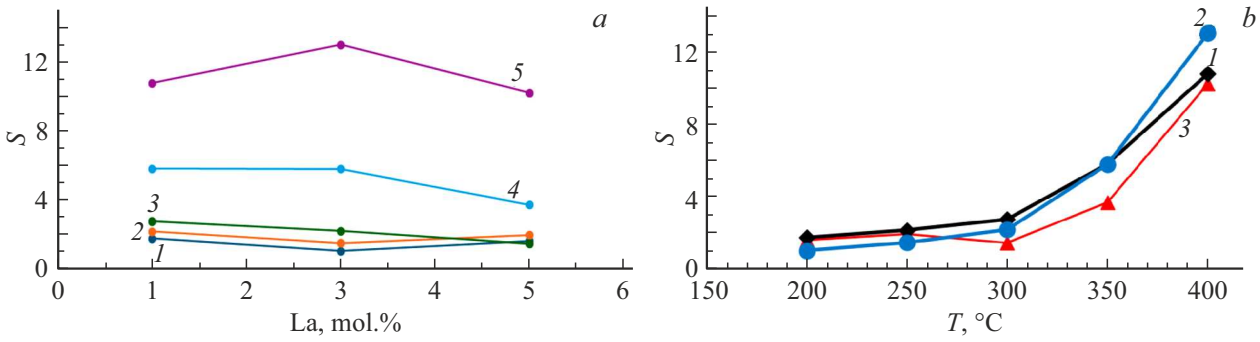

Figure 3. Dependences of the response of sensors to ethanol vapors with a concentration of 100 ppm: *a* — on lanthanum content of the La–SnO_2 film at operating temperatures of 200 (*1*), 250 (*2*), 300 (*3*), 350 (*4*), and 400 °C (5); *b* — on operating temperature for sensors based on 1La–99SnO_2 (*1*), 3La–97SnO_2 (*2*), and 5La–95SnO_2 (*3*).

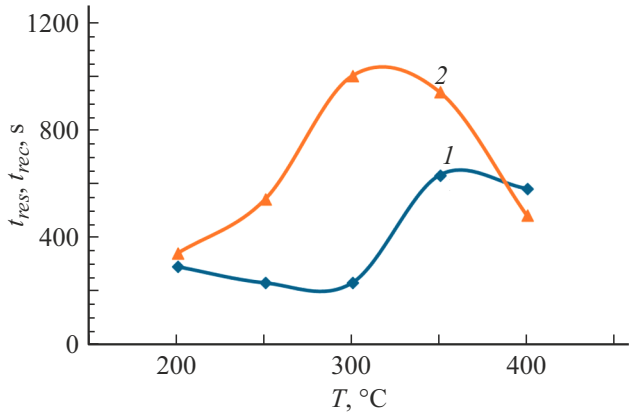

Figure 4. Temperature dependences of the response (*1*) and recovery (*2*) times of sensors based on La–SnO_2 films.

The gas-sensitive characteristics of gas sensors based on La–SnO_2 nanocrystalline films, which were obtained by oxidative pyrolysis, exposed to ethanol vapor with a concentration of 100 ppm were studied. At operating temperatures of 200 °C, the sensor based on the 1La–99SnO_2 film had the highest response values (1.8). The corresponding response and recovery times were 290 and 340 s, respectively. The maximum response value (13) was obtained in experiments with the sensor based on the 3La–97SnO_2 film at a temperature of 400 °C. The corresponding response and recovery times were 580 and 480 s, respectively.

Authors' contributions

V.A. Davidenko fabricated gas sensors, performed gas sensitivity measurements, and drafted the manuscript; G.V. Tolstyak synthesized the materials, performed X-ray diffraction analysis, and drafted the manuscript; E.M. Bayan devised the synthesis procedure, performed data analysis, and drafted and edited the manuscript; V.V. Petrov was responsible for conceptualization, financing, data analysis, and editing of the manuscript.

Funding

This study was supported by grant No. 24-29-00203 from the Russian Science Foundation (https://rscf.ru/project/24-29-00203/) and was performed at the Southern Federal University.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] E.P. Nascimento, H.C. Firmino, G.A. Neves, R.R. Menezes, Ceram. Int., **48** (6), 7405 (2022). DOI: 10.1016/j.ceramint.2021.12.123
[2] M. Kumar, A. Rahman, J. Photochem. Photobiol. A, **452**, 115553 (2024). DOI: 10.1016/j.jphotochem.2024.115553
[3] M. Andreev, V. Platonov, D. Filatova, E. Galitskaya, S. Polomoshnov, S. Generalov, A. Nikolaeva, V. Amelichev, O. Zhdaneev, V. Krivetskiy, Sensors, **21** (21), 7297 (2021). DOI: 10.3390/s21217297
[4] Kh. Abdelkarem, R. Saad, A.M. El Sayed, M.I. Fathy, M. Shaban, H. Hamdy, Sci. Rep., **13**, 18398 (2023). DOI: 10.1038/s41598-023-45196-y
[5] N. Tammanoon, A. Wisitsoraat, D. Phokharatkul, A. Tuantranont, S. Phanichphant, V. Yordsri, C. Liewhiran, Sensors Actuators B, **262**, 245 (2018). DOI: 10.1016/j.snb.2018.01.238
[6] G. Li, J. Hou, M. Hilal, H. Kim, Z. Chen, Y. Cui, J.-H. Kim, Z. Cai, Sensors, **24**, 6839 (2024). DOI: 10.3390/s24216839
[7] A.P. Starnikova, V.V. Petrov, G.V. Tolstyak, I.A. Gulyaeva, E.M. Bayan, Phys. Solid State, **66** (12), 2017 (2024). DOI: 10.61011/PSS.2024.12.60177.6360PA.
[8] G.V. Tolstyak, I.A. Gulyaeva, V.V. Petrov, E.M. Bayan, Nauchno-tekh. Vedomosti SPbGPU. Fiz.-Mat. Nauki, **17** (3.2), 266 (2024) (in Russian). DOI: 10.18721/JPM.173.253
[9] V.V. Petrov, A.P. Ivanishcheva, M.G. Volkova, V.Yu. Storozhenko, I.A. Gulyaeva, I.V. Pankov, V.A. Volochaev, S.A. Khubezhov, E.M. Bayan, Nanomaterials, **12**, 2025 (2022). DOI: 10.3390/nano12122025

[10] Y.-D. Wang, X.-H. Wu, Q. Su, Y.-F. Li, Z.-L. Zhou, Solid-State Electron., **45** (2), 347 (2001). DOI: 10.1016/s0038-1101(00)00231-8
[11] E. Comini, V. Guidi, C. Malagù, G. Martinelli, Z. Pan, G. Sberveglieri, Z.L. Wang, J. Phys. Chem. B, **108** (6), 1882 (2004). DOI: 10.1021/jp036693y
[12] M. Stankova, X. Vilanova, J. Calderer, E. Llobet, J. Brezmes, I. Gràcia, C. Cané, X. Correig, Sensors Actuators B, **113**, 241 (2006). DOI: 10.1016/j.snb.2005.02.056

Translated by D.Safin