

<https://doi.org/10.15407/ujpe66.9.803>

E. OVODOK,¹ M. IVANOVSKAYA,¹ D. KOTSIKAU,² V. KORMOSH,³ P. PYLYP,⁴
V. BILANYCH⁴

¹ Research Institute for Physical-Chemical Problems of the Belarusian State University
(Minsk 220030, Belarus)

² Belarusian State University
(Minsk 220030, Belarus)

³ Research Institute of Analytical Technique of Uzhhorod National University
(Uzhhorod 88000, Ukraine)

⁴ Department of Applied Physics, Uzhhorod National University
(Uzhhorod 88000, Ukraine)

STRUCTURAL CHARACTERIZATION AND GAS SENSING PROPERTIES OF NANO-SIZED TIN DIOXIDE MATERIAL SYNTHESIZED FROM TIN(II) SULFATE

Structural features, surface condition, and gas-sensing properties of the nanocrystalline SnO₂ powders synthesized from SnSO₄ precursor by different methods have been studied. XRD, TEM, BET, and FTIR methods were used for the samples characterization. The gas sensors were fabricated by the thick-film technology from the synthesized SnO₂ powders. The responses of the sensors toward CO and CH₄ gases are measured. It is revealed that the preoxidation of SnSO₄ powder with concentrated sulfuric acid before the hydrolysis results in the lower particle size, higher surface area, improved adsorption activity, and higher sensitivity to reducing gases (CO, CH₄) of the synthesized SnO₂ materials, than in the case of the SnO₂ materials obtained without the preoxidation stage.

Keywords: SnO₂, SnSO₄, FTIR spectroscopy, thick-film sensor, CO, CH₄.

1. Introduction

Tin dioxide is widely used as a solid-state gas sensor material due to its physico-chemical properties, chemical stability, and relatively low cost [1–3]. The thick-film technology is extensively used for the fabrication of gas sensors [4–6]. A finely dispersed SnO₂ powder is required to obtain gas sensors of a good quality by the thick-film technology. N. Yamazoe and coworkers showed that the sensors fabricated from tin dioxide with particle sizes in the interval from 4 to 10 nm generally possess a higher gas sensitivity, than the sensors fabricated from coarser SnO₂ particles [7, 8].

One of the most commonly used methods for the production of SnO₂ materials is the sol-gel approach with a SnCl₄ solution as a precursor [9–11]. However, N. Yamazoe revealed that using SnCl₄ precursor within the unmodified sol-gel method does not provide the possibility to obtain an SnO₂ powder calcinated at 600 °C with the sizes of particles smaller

than 15 nm [7]. C. Xu and coworkers showed that the crystallite size of SnO₂ can be stabilized against the thermal growth, when the stannic acid gel was impregnated with a small amount (5 at. %) of a foreign metal oxides [8]. In our work, we suggest the SnO₂ synthesis route that allows stabilizing the SnO₂ crystallite size during a thermal treatment without adding extraneous metal oxides.

G.W. Wang and coworkers showed that the addition of SO₄²⁻ ions to tin(IV) hydroxide during the SnO₂ synthesis from SnCl₄ caused a notable increase in the surface area of the calcinated oxide [12]. However, the residual chloride ions can degrade the gas-sensitive properties of the SnO₂ sensor materials. H.C. Chiu and C.S. Yeh showed that the presence of Cl⁻ ions change the number of the oxygen species in SnO₂ and decrease the sensitivity of the sensor to ethanol [13]. Thus, using tin sulfate salts as a precursor is reasonable. The presence of Sn(IV) ions in a solution is necessary for the formation of sols, which allows one to get SnO₂ thin film samples and fine dispersed SnO₂ powders. However, tin(IV) sulphate

is easily hydrolyzed by crystal water and humidity of air. For this reason, SnSO_4 salt was chosen as an initial precursor.

In addition, sulphate ions can modify the surface and change the adsorption and catalytic properties of metal oxides. K. Arata and M. Hino found that SnO_2 , TiO_2 , and ZrO_2 calcinated oxides, which were synthesized in the presence of sulphate ions, are characterized by a high concentration of acid centers. The ratio between Lewis and Bronsted acid sites on these oxides can change under a moisture treatment [14]. Surface acid sites influence the catalytic activities of materials. The surface sulfate groups can be directly involved in the process of gas adsorption, or they can act as an activator of reagents in catalytic reactions. An improvement of the sensitivity of Fe_2O_3 – SnO_2 materials to CH_4 under the influence of SO_4^{2-} ions has been established by M. Takana and coworkers [15].

The present work is aimed at the characterization of the structure and gas-sensing properties of SnO_2 materials that are prepared by different routes from the SnSO_4 precursor and are suitable for the production of thick film gas sensors.

2. Material and Methods

Two methods of synthesis of a SnO_2 powder from the SnSO_4 precursor were used.

Method I. The SnO_2 powder was obtained by the hydrolysis of a SnSO_4 solution and a subsequent thermal treatment of the precipitated oxyhydroxide. Here, 100 ml of a SnSO_4 solution ($C = 50$ g/l) was prepared by dissolving the freshly recrystallized SnSO_4 salt in distilled water acidified with sulfuric acid (pH 2). An ammonia solution ($C = 5$ wt. %) was added dropwise to a SnSO_4 solution until pH 8 was reached.

The obtained precipitate was separated by the centrifugation and washed 3 times with distilled water. 50 ml of distilled water and 0.1 ml of concentrated sulfuric acid were added to the precipitate. Then the suspension was ultrasonicated ($f = 22$ kHz, $P = 130$ W) for 2 min. The resultant precipitate was dried at 50 °C and calcinated for 1 h at 600 °C ($\text{SnO}_2(\text{I})$).

Method II. The preoxidation of SnSO_4 salt with concentrated sulfuric acid was carried out before the hydrolysis. Typically, 5 g of the freshly recrystallized

SnSO_4 powder was added to 5.5 ml of concentrated H_2SO_4 acid. The suspension was heated at 200 °C during 10 min. At the end of the reaction, the solution was diluted with distilled water up to 100 ml. Then an ammonia solution ($C = 5\%$) was added dropwise until pH 8 was reached.

The obtained precipitate was separated by the centrifugation and washed 3 times with distilled water. 50 ml of distilled water and 0.1 ml of concentrated sulfuric acid were added to the precipitate. Then the suspension was ultrasonicated ($f = 22$ kHz, $P = 130$ W) for 2 min. A transparent sol was obtained under such treatment. The resultant sol was dried at 50 °C and calcinated at 600 °C ($\text{SnO}_2(\text{II})$). Method II was developed by us for obtaining a highly dispersed calcinated SnO_2 powder.

The phase composition of the materials was characterized by the X-ray diffraction (XRD) analysis. The XRD analysis was carried out on a PANalytical X'Pert PRO MRD (multipurpose research diffractometer, Holland) with a modular construction using Cu K_α –radiation. The fine structural features of the SnO_2 crystallites were revealed by the transmission electron microscopy (TEM). The TEM examinations were performed on a *LEO 906E* transmission electron microscope. The specific area (S_{BET}) was calculated by the BET (Brunauer–Emmett–Teller) method from nitrogen adsorption isotherms measured by a Gemini V2.00 surface analyzer (Micromeritics Instrument Corp.) at -196 °C. The state of the surface of samples was examined by the Fourier transform infrared spectroscopy (FTIR). The FTIR analysis was carried out on an AVATAR FTIR-330 spectrometer supplied with a smart diffuse reflectance accessory in the wavenumber range from 400 to 4000 cm^{-1} .

The gas sensors were fabricated by the thick-film technology. The SnO_2 powders were grinded thoroughly with ethanol in an agate mortar. Then the obtained paste was deposited onto polycrystalline Al_2O_3 substrates ($1.6 \times 1.6 \times 0.25$ mm^3) supplied with a Pt interdigitated electrode on the front side and a Pt-heater on the rear side. The sensor elements were annealed at 570 °C for 3 h in air. The thickness of the oxide sensitive layer was about 15 mkm.

$\text{SnO}_2(\text{I})$ and $\text{SnO}_2(\text{II})$ sensors were fabricated from the SnO_2 powders synthesized by methods I and II, respectively. A contact electric potential was applied to the heater, and a resistance of the sensing layer was measured in air (R_{air}) and in air-gas mixtures

(R_{gas}). The sensor response (G) was calculated as $R_{\text{air}}/R_{\text{gas}}$. The response measurements were carried out in air-gas mixtures with a CH_4 concentration of 1000 ppm and with a CO concentration of 1000 ppm (30% relative humidity) at different working temperatures. Concentration dependences of the resistances of sensors at the CO detection were obtained at determined optimal operation temperatures.

3. Results and Discussion

3.1. Structure, morphology, and surface state

The X-ray diffraction patterns of the as-prepared and the annealed at 600 °C samples are shown in Fig. 1. The structural parameters of the samples are summarized in Table. According to the XRD data, the as-prepared sample synthesized by method I contains the $\text{Sn}_6\text{O}_4(\text{OH})_4$ phase (JCPDS 84-2157) and SnO_2 rutile phase (JCPDS 88-0287).

The as-prepared sample synthesized by method II is characterized by wide diffraction peaks assigned to the SnO_2 rutile phase (JCPDS 88-0287). The rutile phase predominates in the all samples calcinated at 600 °C. Traces of the SnO phase were additionally observed in the $\text{SnO}_2(\text{I})$ sample. The width of diffraction peaks in the patterns of the $\text{SnO}_2(\text{II})$ sample is much higher, than in the case of $\text{SnO}_2(\text{I})$ sample. The average size of the rutile SnO_2 crystallites was estimated by the Debye–Scherrer equation from the width of the (110) reflexion. The $\text{SnO}_2(\text{I})$ sample is characterized by an average crystallite size of about 24 nm. The $\text{SnO}_2(\text{II})$ sample consists from smaller crystallites (5.5 nm). The lattice parameters were calculated for the calcinated SnO_2 samples. The unit cell parameters of the $\text{SnO}_2(\text{I})$ sample correspond well to the reference data ($a = 0.4738$ nm, $c = 0.3187$ nm) [16]. In contrast, the a parameter of the $\text{SnO}_2(\text{II})$ sample is slightly lower (0.4723 nm), and the c parameter is slightly higher (0.3199 nm), than the values given in the literature [16]. The formation of a defective lattice is caused by the influence of sulphate groups under the dehydration and crystallization processes of initial particles during the synthesis of the $\text{SnO}_2(\text{II})$ sample.

According to the TEM data, the $\text{SnO}_2(\text{I})$ and $\text{SnO}_2(\text{II})$ samples are polycrystalline (Fig. 2). The particles have a similar morphology close to the spherical one. However, they are characterized by differ-

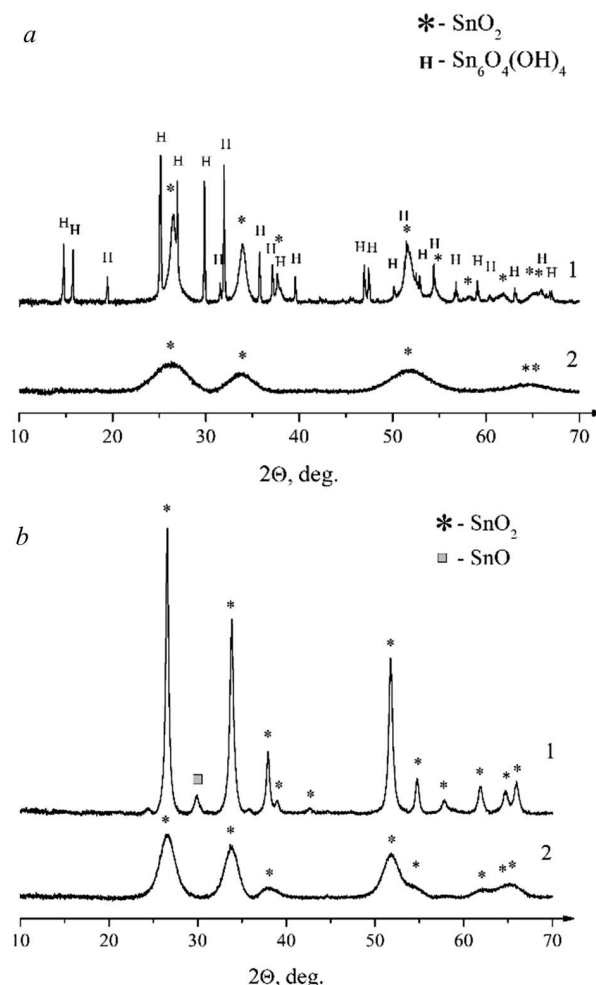


Fig. 1. X-ray diffraction patterns of as-prepared (a) and calcinated at 600 °C (b) samples synthesized by method I (1) and method II (2)

ent sizes. The particle size estimated for the $\text{SnO}_2(\text{II})$ sample is 5.5 nm, and that for the $\text{SnO}_2(\text{I})$ sample is 27 nm. The TEM data are in agreement with the crystallite size calculated from XRD patterns.

The specific surface area of the samples was measured by means of the BET analysis, which shows that the surface areas are 17.9 m²/g and 70.4 m²/g for $\text{SnO}_2(\text{I})$ and $\text{SnO}_2(\text{II})$ powders, respectively. Thus, method II allows one to synthesize a SnO_2 powder, which is characterized by a high surface area and a low crystallite size after the calcination at 600 °C.

The described structural differences of the SnO_2 samples are determined by the chemical processes, which take place during the syntheses.

Structural characteristics of the SnO₂ samples synthesized from SnSO₄ by methods I and II

Method of synthesis	Phase composition of as-prepared samples	Phase composition of samples calcinated at 600 °C	d_{aver} , nm (XRD)	a parameter, nm	c parameter, nm	d_{aver} , nm (TEM)	Specific surface area, m ² /g (BET)
Method I	Sn ₆ O ₄ (OH) ₄ SnO ₂	SnO ₂ SnO	24±1	0.4738	0.3187	27	17.9
Method II	SnO ₂ · xH ₂ O	SnO ₂	5.5±1	0.4723	0.3199	5.5	70.4

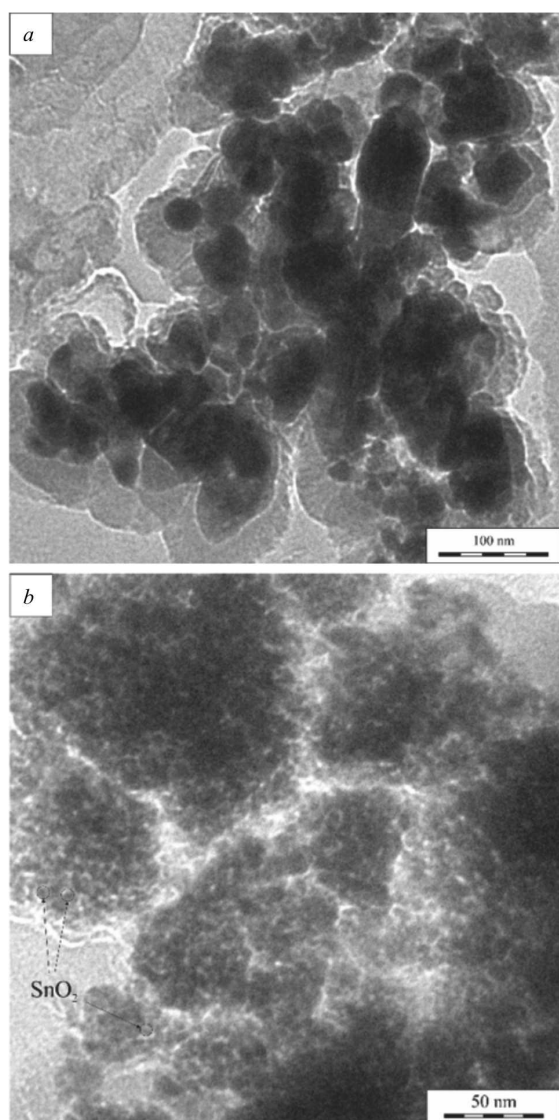
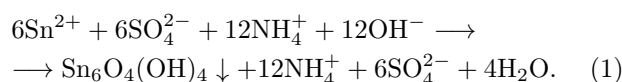


Fig. 2. TEM images of the SnO₂ samples (600 °C) synthesized by (a) method I and (b) method II

In method I, tin(II) oxyhydroxide is precipitated by the hydrolysis of SnSO₄ with an ammonia solution (Eq. (1))

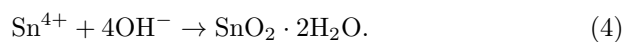


The Sn₆O₄(OH)₄ crystalline phase with traces of the SnO₂ rutile phase is observed in the dried precipitate. Ultrasonification during the synthesis induces a partial decomposition and the oxidation of tin(II) oxyhydroxide to SnO₂. According to FTIR data, a certain amount of SO₄²⁻ groups is preserved on the surface of Sn(OH)₂ particles after the drying (Fig. 3, a). Then tin(II) oxyhydroxide decomposes to SnO and oxidizes to SnO₂ under the heating up to 600 °C.

In method II, Sn²⁺ ions are oxidized to Sn⁴⁺ ions by concentrated sulfuric acid at the first stage of the synthesis (Eq. (2) and (3))



After this treatment, Sn⁴⁺ and SO₄²⁻ ions, as well as traces of non-oxidized Sn²⁺ ions, present in the resultant solution. The amount of the remained Sn²⁺ ions can be varied by the duration of the heating. A polymerized tin oxyhydroxide is formed during the hydrolysis of Sn⁴⁺ ions by an ammonia solution (Eq. (4))



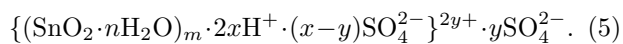
The product consists of polynuclear complexes interconnected by bridging OH-groups, in which H₂O molecules are located in the coordination environment of tin ions. In the core of the generated particles, tin atoms have coordination of oxygen atoms

similar to SnO₂ oxide. Hydroxyl groups and hydrogen bonded water molecules cover the SnO₂ core. Sulfate ions are intercalated in these particles and coordinated by tin ions. Annealing the sample at 600 °C induces the dehydration of the initial particles and the crystallization and growth of tin dioxide crystallites.

FTIR spectra illustrated in Fig. 3 show that sulfate ions are observed in both SnO₂·2H₂O and Sn₆O₄(OH)₄ precipitates after the washing and drying. However, as-prepared SnO₂(I) and SnO₂(II) samples are characterized by quantitative and qualitative differences in the interval of the vibrational mode of [SO₄]²⁻ groups.

A free sulfate ion is characterized by the T_d symmetry. Two vibrational modes (ν_3 and ν_4) of four fundamental oscillations are active in IR spectroscopy. When sulfate ions are bounded with particles, their symmetry decreases from T_d to C_{2V} or C_{3V}, and additional bands can appear in IR spectra. The vibrational modes of bidentate bonded sulfate groups are observed in the IR spectra of the as-prepared SnO₂(I) sample: $\nu_1 = 948 \text{ cm}^{-1}$, $\nu_3 = 1015, 1115, 1246 \text{ cm}^{-1}$, and $\nu_4 = 605, 661 \text{ cm}^{-1}$ [17]. The bands assigned to $\nu_1 = 948 \text{ cm}^{-1}$, $\nu_3 = 1027, 1105$, and a shoulder at 1182, $\nu_4 =$ shoulders at 600 and 642 cm⁻¹ vibrations of bidentate bonded [SO₄]²⁻ groups are detected in the FTIR spectra of the as-prepared sample synthesized by method II. The frequencies of the bands vary from sample to sample due to the difference in the energy state of surface tin atoms, which coordinate sulfate groups.

The intensities of the ν_1 and ν_3 vibrational modes of [SO₄]²⁻ group are considerably higher for the as-prepared SnO₂(II) sample, than for the as-prepared SnO₂(I) sample. This is due to a higher sorption capacity of the particles in a sol, than in a precipitate. In the case of the sol, sulfate ions can be incorporated in the micelle structure and remain in the structure during the subsequent drying of the sample (Eq. (5))



The IR spectra of the as-prepared samples show the absorbance in the interval from 2500 to 3750 cm⁻¹. This broad band is assigned to the stretching OH vibrations in hydroxyl groups and adsorbed water ($\nu(\text{OH})$) [17]. The band at 1660 cm⁻¹ characterizes the deformation HOH vibrations ($\delta(\text{HOH})$). The intensity and width of the $\nu(\text{OH})$ bands are noticeably

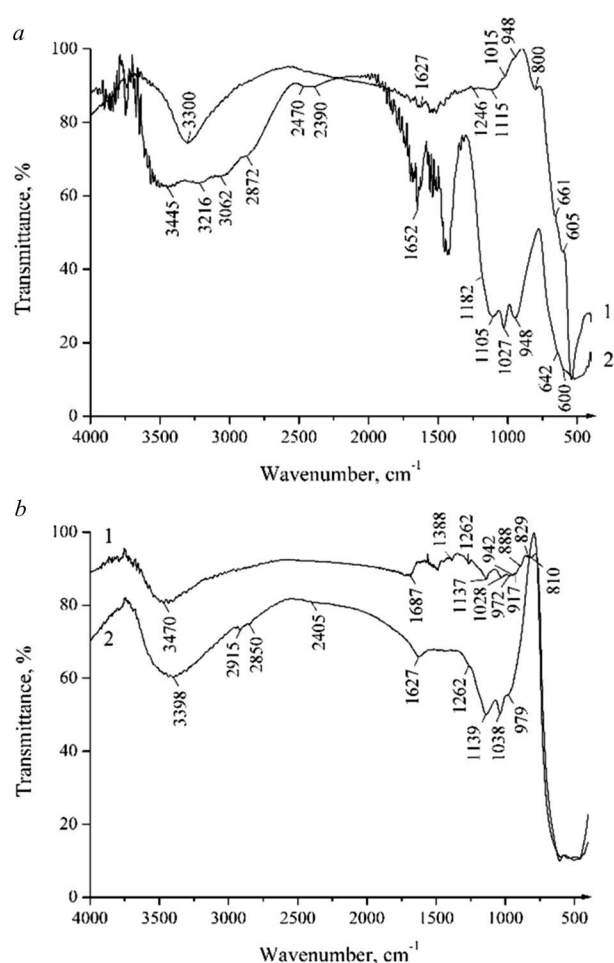


Fig. 3. FTIR spectra of as-prepared (a) and calcinated at 600 °C (b) samples synthesized by method I (1) and method II (2)

higher for the as-prepared SnO₂(II) sample, than for the as-prepared SnO₂(I) sample. Furthermore, the local maxima of the absorption at 3445, 3216, 3062, and 2872 cm⁻¹ in the band of $\nu(\text{OH})$ vibrations and additional bands for $\delta(\text{HOH})$ vibrations are observed in the IR spectrum of the as-prepared SnO₂(II) sample. The features of the spectrum related to the position of the $\nu(\text{OH})$ and $\delta(\text{OH})$ vibrations indicate the formation of hydrogen bonds between SO₄²⁻ and OH-groups. In addition, the presented IR data confirm the assumption that sulfate ions are incorporated in the micelle structure of SnO₂·nH₂O hydrosol.

The $\nu[\text{SO}_4]^{2-}$ bands have a low intensity in the FTIR spectrum of the calcinated SnO₂(I) sample, whereas a high intensity of these bands is revealed

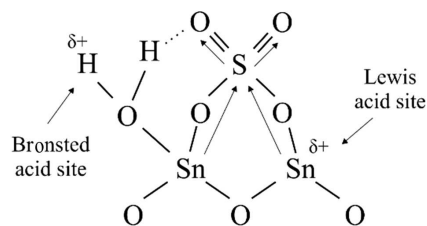


Fig. 4. Scheme of acid centers on SnO₂ surface modified with sulphate groups

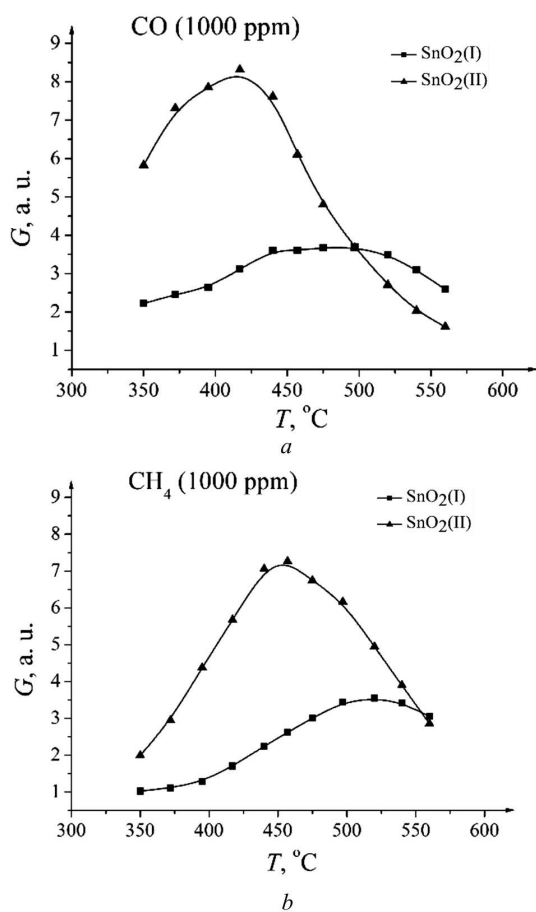


Fig. 5. The dependences of response vs working temperature for SnO₂ (I and II) sensors at the detection of CO (1000 ppm) (a) and CH₄ (1000 ppm) gases (b)

in the spectrum of the SnO₂(II) sample after the calcination (see Fig. 3, b). The triplet of [SO₄]²⁻ vibrational bands is observed for the calcinated SnO₂(II) sample, but the maxima of the bands are shifted to higher wavenumbers (979, 1038, 1139 cm⁻¹) comparing to the as-prepared sample. Moreover, in the

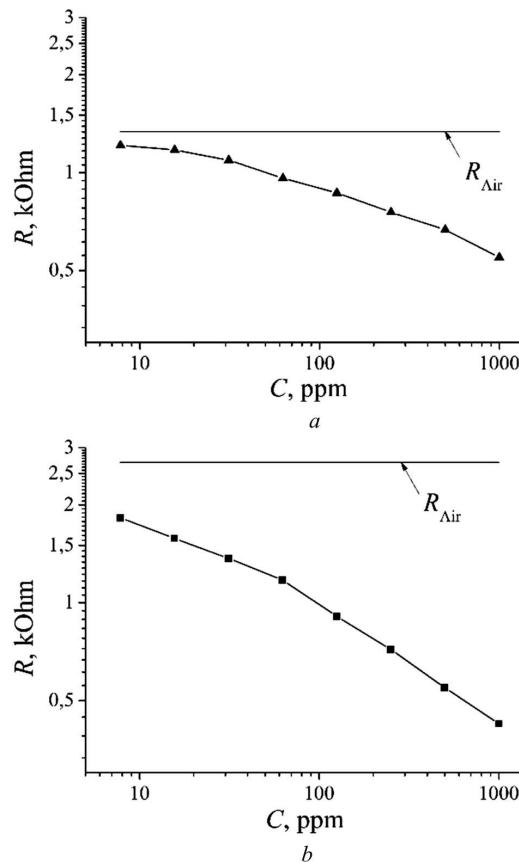


Fig. 6. Dependences of the electric resistance of SnO₂ (I) sensor (a) and SnO₂ (II) sensor (b) on the concentration of CO in air

spectrum of the SnO₂(II) sample annealed at 600 °C, a wide band attributed to $\nu(\text{OH})$ vibrations is observed. Note that the local maxima are resolved less in this interval, than for the as-prepared sample. The adsorption maximum of the $\nu(\text{OH})$ band is observed at 3470 cm⁻¹, and the small peaks are detected at 2915, 2855, 2405 cm⁻¹. These peaks indicate that hydrogen-bonded OH groups are presented on the oxide surface. The interaction between SO₄²⁻-ions and OH-groups influences the state of the surface adsorption centers of SnO₂ oxide.

Thus, according to the IR data, the surfaces of the SnO₂(I) and SnO₂(II) samples contain unequal amounts of [SO₄]²⁻ groups. The as-prepared SnO₂(II) sample has a high amount of surface hydroxyl groups and adsorbed water, which forms hydrogen bonds with [SO₄]²⁻ groups. Furthermore, sulphate groups are included directly in the micelle

structure. Sulphate groups influence the processes of dehydration and crystallization of oxide. As a result, the SnO₂(II) sample calcinated at 600 °C is characterized by a low particle size and a high surface area and contains a high amount of surface sulfate groups. The sulphate groups are bidentates bound with tin cations. Surface SO₄²⁻ ions create Bronsted acid sites and improve acceptor properties of the surface Sn⁴⁺ lattice cations (Lewis acid sites) due to the inductive interaction (Fig. 4). Surface acid sites are active in the adsorption and dissociation of gas molecules. Kustov and coworkers showed that the modification of ZrO₂ with SO₄²⁻ anions results in a strengthening of the surface Lewis acid sites represented by low-coordinated zirconium ions, which promotes the adsorption of CO molecules [18].

Gas-sensing properties

We now consider the gas-sensing properties of SnO₂ thick-film sensors. In order to determine the optimum operating temperatures, the response of the sensors to CO and CH₄ (1000 ppm) are tested as a function of the operating temperature, as shown in Fig. 5. The response of the SnO₂(II) sensor to CO and CH₄ is about 2.5 times higher, than the response of the SnO₂(I) sensor over a wide interval of working temperatures (see Fig. 5, *a*, *b*). The response maxima of the SnO₂(II) sensor to both gases are observed at lower temperatures, than iforn the SnO₂(I) sensor. The former has the maximum response to CO at a lower operation temperature, than to CH₄. In the interval of temperatures from 350 to 375 °C, the highest difference between the responses of the SnO₂(II) sensor to CO and CH₄ is observed. This operation mode is suitable for the selective detection of carbon monoxide.

Further, we measured changes in the sensor resistance at different concentrations of CO at the optimal operation temperature. Figure 6 shows the dependences of the electric resistance of the sensors on the concentration of CO in air. The SnO₂(II) sensor is characterized by a higher sensitivity to CO as compared with the SnO₂(I) sensor. Carbon monoxide can be detected by the SnO₂(II) sensor at concentrations smaller than 10 ppm.

The gas-sensing properties of the SnO₂(II) sensor are caused, on the one hand, by structural features of the SnO₂ powder. The small size of SnO₂ particles

($d = 5.5$ nm), which is comparable with the doubled thickness of the space-charge layer ($L \approx 3$ nm) [7], provides a high sensitivity of the SnO₂(II) sensor to reducing gases. The high surface area of the powder promotes the absorption of gases. On the other hand, surface sulfate groups increase the strength of the Lewis acid sites and promote the CO adsorption on the oxide surface.

4. Conclusions

SnO₂ powders were synthesized from tin(II) sulphate by different routes. The preoxidation of a SnSO₄ powder with concentrated H₂SO₄ prior to the hydrolysis stage allowed us to obtain the SnO₂ powder, which is characterized by the 5.5-nm average particle size and a high surface area (70.4 m²/g) after the calcination at 600 °C. The high concentration of SO₄²⁻ groups is observed on the surface of this sample. The thick-film SnO₂(II) gas sensor is characterized by a higher response to CO and CH₄ gases and a lower optimal working temperature as compared to the SnO₂(I) sensor. The SnO₂(II) sensor can be used for the detection of CO concentrations smaller, than 10 ppm. The improvement of the gas sensing properties of tin(IV) oxide layers is caused by their structural features and the effect of SO₄²⁻ ions on the adsorption properties of the oxide surface.

This work was performed within the framework of an international Ukrainian-Belarusian grant (Belarusian RFFR grants No. X21YKPI-002).

1. M. Batzill, U. Diebold. The surface and materials science of tin oxide. *Prog. Surf. Sci.* **79**, 45 (2005).
2. W. Göpel, K.D. Schierbaum. SnO₂ sensors: current status and future prospects. *Sens. Actuator B Chem.* **26**, 1 (1995).
3. D. Kohl. Surface processes in the detection of reducing gases with SnO₂-based devices. *Sens. Actuator.* **18**, 71 (1989).
4. G. Martinelli, M. C. Carotta. Thick-film gas sensors. *Sens. Actuator B Chem.* **23**, 157 (1995).
5. S.P. Patil, V.L. Patil, S.S. Shendage, N.S. Harale, S.A. Vanalakar, J.H. Kim, P.S. Patil. Spray pyrolyzed indium oxide thick films as NO₂ gas sensor. *Ceram. Int.* **42**, 16160 (2016).
6. D.C. Pugh, S.M. Hailes, I.P. Parkin. A gas-sensing array produced from screen-printed, zeolite-modified chromium titanate. *Meas. Sci. Technol.* **26**, 085102 (2015).
7. N. Yamazoe. New approaches for improving semiconductor gas sensors. *Sens. Actuator B Chem.* **5**, 7 (1991).

8. C. Xu, J. Tamaki, N. Miura, N. Yamazoe, Grain size effects on gas sensitivity of porous SnO₂-based elements. *Sens. Actuator B Chem.* **3**, 147 (1991).
9. S.M. Badalyan, M.N. Rumyantseva, S.A. Nikolaev, A.V. Marikutsa, V.V. Smirnov, A.S. Alikhanian, A.M. Gaskov. Effect of Au and NiO catalysts on the NO₂ sensing properties of nanocrystalline SnO₂, *Inorg. Mater.* **46**, 232 (2010).
10. D. Wang, Y. Chen, Z. Liu, L. Li, C. Shi, H. Qin, J. Hu. CO₂-sensing properties and mechanism of nano-SnO₂ thick-film sensor. *Sens. Actuator B Chem.* **227**, 73 (2016).
11. K. Suematsu, K. Yamada, M. Yuasa, T. Kida, K. Shimano. Evaluation of Oxygen Adsorption Based on the Electric Properties of SnO₂ Semiconductor Gas Sensors. *Sensor. Mater.* **28**, 1211 (2016).
12. G.W. Wang, H. Hattori, K. Tanabe. The enhancement of acid strength and catalytic activity of SnO₂ by the addition of sulfate ion. *Chem. Lett.* **12**, 277 (1983).
13. H.C. Chiu, C.S. Yeh. Hydrothermal synthesis of SnO₂ nanoparticles and their gas-sensing of alcohol. *J. Phys. Chem. B* **111**, 7256 (2007).
14. K. Arata, M. Hino. Preparation of superacids by metal oxides and their catalytic action. *Mater. Chem. Phys.* **26**, 213 (1990).
15. M. Takano, Y. Bando, N. Nakanishi, M. Sakai, H. Okinaka. Characterization of fine particles of the α -Fe₂O₃-SnO₂ system with residual SO₄²⁻ ions on the surface. *J. Solid State Chem.* **68**, 153 (1987).
16. A.A. Bolzan, C. Fong, B.J. Kennedy, C.J. Howard. Structural studies of rutile-type metal dioxides. *Acta Crystallogr. Sect. B* **53**, 373 (1997).
17. K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (John Wiley & Sons, Ltd. 1986).
18. L.M. Kustov, V.B. Kazansky, F. Figueras, D. Tichit. Investigation of the acidic properties of ZrO₂ modified by SO₄²⁻ anions. *J. Catal.* **150**, 143 (1994).

Received 24.12.20

Е.А. Оводок, М.І. Івановська, Д.А. Котиков,
В.В. Кормош, П.П. Пилип, В.С. Біланч

СТРУКТУРНІ ХАРАКТЕРИСТИКИ
І ГАЗОЧУТЛИВІ ВЛАСТИВОСТІ НАНОРОЗМІРНИХ
МАТЕРІАЛІВ ДІОКСИДУ ОЛОВА,
СИНТЕЗОВАНИХ ІЗ СУЛЬФАТУ ОЛОВА

Досліджено структурні особливості, стан поверхні та газо-чутливі властивості нанокристалічних порошоків SnO₂, синтезованих із прекурсора SnSO₄ різними методами. Для вимірювання характеристик зразків використовувалися методи XRD, TEM, BET і FTIR. Газові сенсори виготовлялися за товстоплівковою технологією з синтезованих порошоків SnO₂. Проведено вимірювання реакції отриманих датчиків на гази CO і CH₄. Виявлено, що попереднє окислення порошку SnSO₄ концентрованою сірчаною кислотою перед гідролізом приводить до меншого розміру частинок, більшої площі поверхні, поліпшеної адсорбційної активності і більшої чутливості до відновних газів (CO, CH₄) синтезованих матеріалів SnO₂, ніж у випадку матеріалів SnO₂, отриманих без стадії попереднього окислення.

Ключові слова: SnO₂, SnSO₄, спектроскопія FTIR, товстоплівковий датчик, CO, CH₄.