Perspectives for usage of adsorption semiconductor sensors based on Pd/SnO$_2$ in environmental monitoring of carbon monoxide and methane emission

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Abstract. Nanosized semiconductor sensor materials based on SnO$_2$ with different palladium contents were obtained via zol-gel technology with the use of ethylene glycol and hydrate of tin (VI) chloride as precursors. Morphology and phase composition of nanosized sensor materials were studied by X-ray diffraction and TEM methods. Catalytic activities of the Pd/SnO$_2$ nanomaterials in the reaction of H$_2$ and CO oxidation were investigated. Adsorption semiconductor sensors based on Pd/SnO$_2$ nanomaterials were made by their calcination up to 620 °C in air and the sensors were found to be highly sensitive to presence of CO and CH$_4$ in air ambient. Higher responses to CO of Pd-containing sensors in comparison with their responses to CH$_4$ were confirmed by higher reaction activity of CO in catalytic oxidation reaction. Differences in sensitive properties of the sensors to methane and carbon monoxide were explained by features of the catalytic reactions of methane and carbon monoxide oxidation occurring on surfaces of the gas sensitive layers of the sensors.

1 Introduction

Nowadays, a significant degradation of environment due to an increase in harmful substances emissions from industry, multiple technogenic accidents and uncontrolled usage of the existing resources of the planet is one of the global problems of humanity. It should be noted that such ecological situation is due to the pollution of almost all components of the environment (air, water reservoirs and soils). In particular, such gases as CO, CH$_4$, H$_2$S, NO$_x$, CO$_2$, NH$_3$, SO$_2$ etc. presented in air can lead not only to local significant air pollution by toxic gases, but also to climate change throughout the planet. Therefore, control over the emission of such gases in the environment is one of the necessary challenges, the solution of which will prevent further deterioration of the environment.

Among harmful gases presented in air control of natural gas and carbon monoxide is crucially needed. Natural gas is widely used in chemical industry and is one of the main energy sources. On the other hand, natural gas can combine with air explosively that leads to human’s deaths and economical losses. Since methane is the main component of the natural gas detection of CH$_4$ allows to monitor the natural gas leakages. Besides, methane is also known to be one of the most dangerous greenhouse gases (Fig.1) and, thus, control of the methane emission in atmosphere is important for reduction of global warming.

Carbon monoxide is widely used in industry also, e.g. in synthesis of aldehydes, methanol, phosgene, in oil industry, in metallurgy etc. But the main part of carbon monoxide emission falls on incomplete combustion of carbonaceous substances. In particular, vehicles, coal and wood burning, portable and back-up generators emit large amount of CO in environment (Table 1).

| Concentration     | Source                                                |
|-------------------|-------------------------------------------------------|
| 5–15 ppm          | Near properly-adjusted gas stoves in homes, modern vehicle exhaust emissions |
| <1000 ppm         | Car exhaust fumes after passing through catalytic converter |
| 5000 ppm ppm      | Exhaust from a home wood fire                        |
| 30000–100000 ppm  | Undiluted warm car exhaust without a catalytic converter |

Carbon monoxide emission hazard is attributed mainly to ability of CO molecules almost irreversibly bounded with iron in human blood (with hemoglobin cells) that leads to decrease in its ability to transport oxygen. Deficit of oxygen leads to different symptoms including headache and dizziness (Table 2). If the CO concentration is high enough human death can be occurred. Carbon monoxide is colorless and odorless gas that make detection of its presence in air crucially needed, especially in household where burning of different organic or carbon-reaching compounds is present.

It is known that gas analytical devices based on sensors are promising to determine the content of...
methane and carbon monoxide in air. It should be noted that nowadays a variety of the sensors are being widely developed [1], and they are intended for usage in various branches of science, technology and industrial production. The main areas of the sensors application are [2-8]: control over volatile combustion products in industry, analysis of exhaust gases from automobile transport, quality control of food products, diagnostics of some diseases, studies of cell transformations of living organisms, determination of drugs purity in pharmacology and environmental monitoring.

![Impact of different gases in greenhouse effect](image)

**Fig. 1.** Impact of different gases in greenhouse effect.

| Concentration | Effect                                                                 |
|---------------|------------------------------------------------------------------------|
| 35 ppm        | Headache and dizziness within six to eight hours of exposure           |
| 400 ppm       | Frontal headache within one to two hours                               |
| 800 ppm       | Dizziness, nausea, and convulsions within 45 min; insensible within 2 hours |
| 1600 ppm      | Headache, increased heart rate, dizziness, and nausea within 20 min; death in less than 2 hours |
| 6400 ppm      | Headache and dizziness in one to two minutes. Convulsions, respiratory arrest, and death in less than 20 minutes. |
| 12800 ppm     | Unconsciousness after 2–3 breaths. Death in less than three minutes.   |

The gas sensors are widely used to detect leakages of toxic and explosive gases and monitor their content in air of both domestic premises and industrial production [9]. Cheap and reliable, with low power consumption, such sensors are widely used. Requirements for them are growing and, in particular, the main characteristics of the sensors - sensitivity, selectivity, response time, relaxation, gas measurement range, stability etc. should be improved [10]. The adsorption semiconductor sensors are perspective to determine presence of both carbon monoxide and methane in air due to combination of their high sensitivity to reducing gases and operational characteristics [11-13]. But the adsorption semiconductor sensors have poor sensitivity to methane and carbon monoxide [14] because of their chemical inertness and thus low oxidation rates of CH₄ and CO by oxygen, chemisorbed on the gas sensitive layer of the sensor.

To create highly sensitive adsorption semiconductor sensors intended to detect toxic and explosive gases leakages it is very important to develop new more sensitive functional nanomaterials [9, 15]. It is known that the main semiconductor material of a sensitive layer of such sensor is tin dioxide due to its chemical and thermal stability [16, 17]. However, it has low sensitivities to gases [18]. One of the effective ways to improve variety functional properties of materials, including their sensitivity, is to use them in a nanosized state [19-21]. In particular, the usage of nanosized semiconductor as the gas sensitive material can lead to increase in the sensor response to reducing gases (such as carbon monoxide and methane) through increase in contribution of surface processes into bulk properties (conductivity) of the semiconductor [14, 22].

Another way to increase the sensor responses to carbon monoxide and methane is introduction of catalytically active additives into the gas sensitive layer of the sensors [23]. Palladium, platinum, gold, oxides of transition and rare earth metals can be such active components [24, 25]. Among the known catalysts for oxidation of carbon monoxide and methane, palladium is one of the most effective [26].

Therefore, development of new nanosized semiconductor gas sensitive materials based on tin dioxide containing catalytically active components, in particular, palladium, should be considered as promising in order to obtain highly sensitive adsorption semiconductor sensors intended to detect carbon monoxide and methane.

The aim of this work is creation of palladium-containing nanosized materials based on tin dioxide for development of the adsorption semiconductor sensors to carbon monoxide and methane.

### 2 Experimental techniques

Initial SnO₂ was synthesized by a sol-gel technique. The reagents (SnCl₄·5H₂O and ethylene glycol) were mixed under stirring and excess of ethylene glycol was evaporated in two steps corresponding to a gel formation (120 °C) and xerogel formation (150 °C). The crystalline SnO₂ was obtained after high temperature treatment (up to 600 °C) of the xerogel [12].

For the sensors creation the initial powder of SnO₂ was mixed with a binder (10% carboxymethylcellulose solution in water) to form a paste that was applied on a ceramic sensor plate between platinum measuring electrodes [13]. Palladium was introduced into a gas sensitive layer by a wet impregnation technique using water solutions of PdCl₂. After impregnation the plates were dried at 90 °C and then calcinated up to 620 °C in
air. Gas sensitive materials and catalysts were prepared by the same procedure as the sensors.

In the sensor materials added palladium content were determined by X-ray fluorescence analysis with the energy dispersive X-ray spectrometer ElvaX EXS - 01.

Morphology of the gas sensitive materials was studied by transmission electron microscopy (TEM) using the SELMI PEM-125K electron microscope (accelerating voltage was 100 kV).

X-ray diffraction (XRD) analysis of the materials was conducted by using a Bruker D8 Advance with CuKa radiation. Estimation of the XRD particle sizes was performed by a Scherrer equation: [27]:

\[ D = \frac{k \lambda}{\beta \cos\theta}, \]

where \( D \) is the XRD particle size; \( k \) is a constant close to unity (for our calculation value 0.9 was taken); \( \lambda \) is the wavelength of CuKa radiation (\( \lambda = 1.5418 \text{ Å} \)); \( \beta \) is a true broadening of a diffraction peak (\( \beta = \Delta - b \), where \( \Delta \) is an experimental broadening and \( b \) is an instrumental broadening); \( \theta \) is a Bragg angle.

For stabilization of the electric characteristics of the sensors they were periodically treated by 930 ppm CH\(_4\) load resistor (Ohm); electric resistance was calculated according to the Ohm’s law by

\[ R = \frac{V}{I} \]

For Pd doped materials no catalyst activities of the Pd/SnO\(_2\) nanomaterials were studied in flow-type reactors using gaseous mixtures 1000 ppm CO or 930 ppm CH\(_4\) with air. Analysis of the gas mixture components was carried out by a chromatographic method using a chromatograph Shimadzu GC-14. The weight of the analyzed catalyst was 200 mg. The temperature of 100% CO or CH\(_4\) conversion (T\(_{100}\)) was taken as a measure of the catalytic activity of the samples.

3 Results and discussion

3.1 Morphologies of the sensor materials

It was shown that the initial tin dioxide consists of particles with predominantly spherical shape with an average size 10-11 nm estimated by TEM (Table 3). High temperature treatment of the sensor material based on the initial SnO\(_2\) without any dopants results in an increase in its particle size up to 19-20 nm (Table 3). Introduction into the sensor material a low amount of palladium is enough to prevent the semiconductor particles enlargement during sintering up to 620 °C. Therefore, for all studied gas sensitive materials with palladium additives the average particle size observed by TEM was 14-15 nm (Table 3).

| Materials               | TEM size / nm | XRD size / nm |
|-------------------------|---------------|---------------|
| Initial SnO\(_2\)       | 10 – 11       | 6.7           |
| SnO\(_2\) (s.m.)        | 19 – 20       | 20.1          |
| 0.31 wt.% Pd/SnO\(_2\) (s.m.) | 14 – 15 | 12.8          |
| 1.41 wt.% Pd/SnO\(_2\) (s.m.) | 14 – 15 | 12.4          |

TEM observation of semiconductor gas sensitive materials revealed their nanoscale nature (Fig. 2). The semiconductor nanoparticles for Pd/SnO\(_2\) are spherical shaped with particle distribution range from 6 to c.a. 30 nm (Fig. 3). It should be noted that particles size in sensor materials are larger in comparison with initial SnO\(_2\) (Table 3). This fact can be explained by particles agglomeration and enlargement during high temperature treatment during formation of gas sensitive layer of the sensors [28].

According to the XRD data the cassiterite phase (Fig.4) was detected for Pd-containing sensor materials (ICDD PDF-2 Version 2.0602 (2006), card no. 00-041-1445). Calculated parameter of SnO\(_2\) unit cell (Fig.4) was:

\[ a = b = 4.7382 \text{ Å}, c = 3.1882 \text{ Å} \]

For Pd doped materials no electron diffraction attributed to palladium compounds were found even for materials contained up to 3.31 wt.% Pd. No electron diffraction attributed to palladium compounds was detected for Pd/SnO\(_2\) materials. The absence of diffraction from Pd-containing particles (metallic Pd, PdO, etc.) for both XRD and electron diffraction methods can be explained by high palladium dispersion on tin dioxide surface and/or probably due to large number of defects in palladium species [27].

Calculation by the Scherrer equation shows different SnO\(_2\) particle sizes for the sensor materials without any additives and the Pd-containing samples (Table 3). The XRD sizes for them are quite smaller than corresponding TEM sizes (12-13 and 14-15 nm respectively). This may be caused by additional defects on the tin dioxide surface [29].
It was found that introduction of Pd into SnO₂ leads to increasing surface charge carriers concentration. Further increase in dopant content leads to increasing the electrical resistance (Table 4) that can be caused by formation of an interface between the palladium particles and tin dioxide support. The interface consists of active centers for the oxygen chemisorption [30]. Therefore, the increase in the electrical resistance with an increase in the palladium content (from 0.23 wt.% to 1.41 wt.%) is caused by the increase in amount of oxygen chemisorbed on the longer interface between the catalytically active and tin dioxide. Further increase in the palladium content leads to the enlargement of the particles of the catalytically active additives and to their aggregation. As a result, the length of the interface begins to decrease and the amount of chemisorbed oxygen decreases too. This leads to decrease in the electrical resistances of the sensors with a large content of the catalytically active Pd additives (Table 4).

### Table 4. Electrical resistance in air of the sensors based on Pd/SnO₂ at different operation temperatures.

| T / °C | Sensor resistance / kOhm |
|--------|--------------------------|
| 405    | 0.09: 206 / 296 / 392 / 416 / 469 / 395 / 271 | 0.31: 218 / 357 / 625 / 681 / 739 / 569 / 399 |
| 350    | 217 / 372 / 852 / 963 / 1005 / 720 / 507 |
| 325    | 211 / 354 / 1001 / 1243 / 1311 / 809 / 542 |
| 295    | 192 / 290 / 977 / 1428 / 1355 / 828 / 523 |
| 260    | 152 / 200 / 790 / 1276 / 928 / 592 / 434 |
| 225    | 106 / 99 / 397 / 660 / 609 / 377 / 240 |

For the sensors based on Pd/SnO₂ a change in the response to CH₄ on palladium content correlate with the change in the electrical resistances at the various sensor operation temperatures (Table 5). The highest responses to methane and the highest values of the electrical resistances in air are observed for the same sensor composition (based on 1.41 wt.% Pd/SnO₂) (Table 4). Such correspondence indicates to a common reason that determines both the value of R₀ and γ to methane. This reason is the amount of oxygen chemisorbed on the interface Pd-SnO₂. The electrical resistance in air depends on the number of electrons localized on the chemisorbed oxygen. On the other hand, the response of the sensor is determined by the rate of the reaction that also depends on the amount of chemisorbed oxygen [14].

It was established that the dependences of the Pd-containing sensor responses (γ) to 1000 ppm CO on palladium content are extremal (with maximum at 0.228 wt.% Pd) for all studied operation temperatures (Fig. 5). The highest response was observed at 380 °C (γ = 13.5 for the sensor based on 0.228 wt.% Pd/SnO₂). The shift of maximal CO response value in comparison with response to methane for the sensors with lower Pd loading can be explained by differences in catalytic activities of Pd/SnO₂ gas sensitive nanomaterials in oxidation reactions of CO and CH₄.

It was found that introduction of Pd into SnO₂ materials leads to increase in their catalytic activities in
both CO and CH4 oxidation reactions. Maximal differences of temperatures of CO and CH4 total conversions (ΔT_max) for nanomaterials Pd/SnO<sub>2</sub> in comparison with nanosized SnO<sub>2</sub> are equal to 240 and 185°C, respectively. It was found that Pd/SnO<sub>2</sub> materials are much more active in CO oxidation reaction in comparison with CH4. For the catalyst 2.3wt.% Pd/SnO<sub>2</sub> temperature of total conversion is equal to 110 °C in CO oxidation reaction and 415 °C in CH4 oxidation reaction. Such difference in catalytic activity may be due to the chemical inertness of methane molecules. Since the optimal operating temperatures of the sensors (when their significant response values are observed) are quite high. It should be noted that optimal operation temperatures are much higher than the temperature of 100% CO conversion on the corresponding Pd/SnO<sub>2</sub> materials, it can be assumed that a significant amount of products of the CO oxidation reaction occurred on the surface of palladium clusters will prevent access of reagents (CO and O<sub>2</sub>) to the interface Pd-SnO<sub>2</sub>, that is responsible for the formation of the responses of the sensors. This leads to the shift of the maximal response of the sensors to CO in the area of the sensors with the lower palladium content. For these sensors, due to the higher rate of CO oxidation, the effect of blocking the interface of Pd-SnO<sub>2</sub> by CO oxidation products is much greater compared to sensors based on Pd/SnO<sub>2</sub> materials with palladium content higher than 0.228 wt.%, though the additional introduction of palladium increases the interface as evidenced by the increase in the electrical resistance of the sensors (Table 4). It should be noted that the final exclusion of oxygen chemisorbed at the interface Pd-SnO<sub>2</sub> from the formation of the sensor response to CO occurred probably for the sensors with Pd concentration > 1 wt.%. This leads decrease in response of such sensors to the level of the sensors based on undoped tin dioxide (Fig. 5).

Table 5. Response to 930 ppm CH4 in air of the sensors based on Pd/SnO<sub>2</sub> at different operation temperatures.

| T / °C | 0.09 | 0.31 | 0.62 | 1.41 | 2.28 | 2.42 | 3.31 |
|-------|------|------|------|------|------|------|------|
| 405   | 3.0  | 9.2  | 10.1 | 9.1  | 9.0  | 8.9  | 6.1  |
| 380   | 2.2  | 8.1  | 11.5 | 12.0 | 11.3 | 10.7 | 7.8  |
| 350   | 1.6  | 6.4  | 11.1 | 12.4 | 11.1 | 10.5 | 7.8  |
| 325   | 1.3  | 4.6  | 8.4  | 10.1 | 8.7  | 8.4  | 6.4  |
| 295   | 1.0  | 3.0  | 5.3  | 7.0  | 5.7  | 5.4  | 4.2  |
| 260   | 1.0  | 1.7  | 2.7  | 3.6  | 2.5  | 2.4  | 2.5  |
| 225   | 1.0  | 1.2  | 1.3  | 1.6  | 1.6  | 1.3  | 1.4  |

The temperatures of CH4 total conversion are higher in comparison with the sensor operation temperatures. This results in include of the full interface Pd-SnO<sub>2</sub> length in the formation of the sensor responses to methane. This assumption is consistent with the fact that the maximal responses to methane and values of electrical resistances in air are observed for the sensors with the same palladium content (Tables 4, 5).

The response time and relaxation time of the optimal CO and CH4 sensors based on Pd/SnO<sub>2</sub> obtained in this work and characteristics of the sensors known in the literature are presented in Table 6. As it can be seen, the dynamic characteristics and response values of the sensors with 0.228 wt.% Pd to CO and 1.41 wt.% to CH4 obtained in this work are better than literature data.

Table 6. Sensor responses and dynamic characteristics of the developed sensors and known in the literature.

| Sensitive layer content of nanosystem | Gas concentration, ppm | Sensor response | Temperature, °C | Response time, sec | Recovery time, sec | References |
|--------------------------------------|------------------------|----------------|----------------|-------------------|------------------|------------|
| SnO2 porous nanosolid                | 4000                   | 9.2            | 300            | 28                | 252              | [31]       |
| 0.2mol%Pd/1mol%Hf/SnO2               | 3000                   | 1.3            | 350            | 100               | 50               | [32]       |
| 5%Pd/SnO2/CuO                        | 2000                   | 1.32           | 200            | 7                 | 10               | [33]       |
| 5%Pd/SnO2/graphene nanocomposites    | 1600                   | 1.1            | 26             | 120               | 120              | [34]       |
| 0.228wt.%Pd/SnO2                     | 1000                   | 13.5           | 380            | 5.5               | 15.2             | this work  |
| SnO2/MoO3                             | 300                    | 2.4            | 300            | 1430              | 1524             | [35]       |
| 2.8 wt%Al/ZnOnanorods                | 100                    | 1.6            | 350            | 480               | 240              | [36]       |
| SnO2/Au multilayered heterostructure  | 100                    | 3.07           | 300            | 58.6              | 77.7             | [37]       |
| Co3O4 nanoparticle                   | 25                     | 2.1            | 200            | 120               | 600              | [38]       |

Fig. 5. Responses to 1000 ppm CO of the sensors based on Pd/SnO2 on palladium content at different operation temperatures of the sensors.

Table 6. Sensor responses and dynamic characteristics of the developed sensors and known in the literature.

| Sensitive layer content of nanosysytems | Gas concentration, ppm | Sensor response | Temperature, °C | Response time, sec | Recovery time, sec | References |
|----------------------------------------|------------------------|----------------|----------------|-------------------|------------------|------------|
| SnO2 porous nanosolid                  | 4000                   | 9.2            | 300            | 28                | 252              | [31]       |
| SnO2+PtO/PdPt                          | 1000                   | 1.7            | 150            | 50                | 270              | [39]       |
| 1.41wt% Pd/SnO2                        | 1000                   | 12.4           | 350            | 6                 | 10               | this work  |
| SnO2 nanoparticle                      | 500                    | 1.5            | -              | 24                | 36               | [40]       |
For the sensors with maximum responses that based on the materials 0.228% Pd/SnO\textsubscript{2} for CO and 1.41% Pd/SnO\textsubscript{2} for CH\textsubscript{4}, the dependences of their signal values in the presence of different CO and CH\textsubscript{4} concentrations in air correspondingly were studied. It was found that the sensors can measure CO in the range of 20-1000 ppm and CH\textsubscript{4} in the range of 50-930 ppm. It should be noted that the studied dependences are practically linear in these ranges of measured concentration. These results indicate to possibility of using the obtained sensors to measure with good dynamic characteristics presence of CO and CH\textsubscript{4} in a wide concentration range in air.

4 Conclusions

The synthesized nanosized material based on SnO\textsubscript{2} with palladium additives allowed to create adsorption semiconductor sensors with enhanced response intended to measure different concentrations of CO and CH\textsubscript{4} in air. The sensors containing 1.41 wt.% palladium demonstrate the highest response to CH\textsubscript{4} at 350 °C and the sensors containing 0.228wt.% palladium exhibit the maximum response to CO at 380°C. The higher sensitivities of the sensors to CO compared to CH\textsubscript{4} is explained by the mechanism of the sensor response formation, which is based on the occurring the catalytic oxidation reaction of gases on the surface of the sensors with involving of chemisorbed oxygen adsorbed from air on the semiconductor surface. The sensors obtained in the work have good dynamic properties and a wide range of carbon monoxide and methane detection, that is necessary to provide fast analysis of the environment using sensor gas analyzers based on the created sensors.

References

1. B. Eggins, Chemical and biological sensors (Technosphere, Moscow, 2005)
2. D. Kohl, Function and applications of gas sensors. J. Phys. D: Appl. Phys. 34, R125 (2001). doi:10.1088/0022-3727/34/19/201
3. N. Docquier, S.Candel, Combustion control and sensors: a review. Prog. Energy Combust. Sci. 28, 107-150 (2002). doi:10.1016/S0360-1285(01)00009-0
4. S. Ampuero, J.O. Bosset, The electronic nose applied to dairy products: a review. Sens. Actuators, B: Chem. 94, 1-12 (2003). doi:10.1016/S0925-4005(03)00321-6
5. D. Nicolas-Debarnot, F. Poncin-Epaillard, Polyaniline as a new sensitive layer for gas sensors. Anal. Chim. Acta 475, 1-15 (2003). doi:10.1016/S0003-2670(02)01229-1
6. A.J. Haes, R.P. Van Duyne, A unified view of propagating and localized surface plasmon resonance biosensors. Anal. Bioanal. Chem. 379, 920-930 (2004). doi:10.1007/s00216-004-2708-9
7. B. Timmer, W. Othhuis, A. van den Berg, Ammonia sensors and their applications - a review. Sens. Actuators, B. Chemical 107, 666-677 (2005). doi:10.1016/j.snb.2004.11.054
8. J. Riu, A. Maroto, F.X. Rius, Nanosensors in environmental analysis. Talanta 69, 288-301 (2006). doi:10.1016/j.talanta.2005.09.045
9. T. Anukunprasert, C. Saiwan, E. Traversa, The development of gas sensor for carbon monoxide monitoring using nanostucture of Nb-TiO\textsubscript{2}. Sci. Technol. Adv. Mater. 6, 359-363 (2005). doi:10.1016/j.stam.2005.02.020
10. G. Eranna, B.C. Joshi, D.P. Runthala, R.P. Gupta, Oxide Materials for Development of Integrated Gas Sensors—A Comprehensive Review. Crit. Rev. Solid State Mater. Sci. 29, 111-188 (2004). doi:10.1080/10408430490888977
11. K. Ho, M.T. Itamura, M. Kelley, R.C. Hughes, Review of Chemical Sensors for In-Situ Monitoring of Volatile Contaminants. (University Libraries UNT Digital Library, 2001), https://digital.library.unt.edu/ark:/67531/metadc722940. Accessed 26 June 2020
12. L.P. Oleksen, N.P., Maksymovych, I.P. Matushko, A.I., Buvalio, N.M. Derkachenko, Hydrogen sensitivity of sensors based on CoO/SnO\textsubscript{2}/SbO\textsubscript{2} nanomaterials obtained by the sol-gel method. Russ. J. Phys. Chem. A 87(2), 265-269 (2013). doi:10.1134/S1066362213020222
13. G. Fedorenko, L. Oleksenko, N. Maksymovych, Oxide Nanomaterials Based on SnO\textsubscript{2} for Semiconductor Hydrogen Sensors. Adv. Mater. Sci. Eng. 13, 1 (2019). doi:10.1155/2019/5190235
14. Mine Safety Appliances Company (MSA), Gas detection handbook. 5th ed. (MSA, USA, 2007)
15. M. Zhang, Z. Yuan, J. Song, C. Zheng, Improvement and mechanism for the fast response of a Pt/TiO\textsubscript{2} gas sensor. Sens. Actuators B Chem. 148, 87-92 (2010). doi:10.1016/j.snb.2010.05.001
16. M. Batzill, U.Diebold, The surface and materials science of tin oxide. Prog. Surf. Sci. 79 (2-4), 47-154 (2005). doi:10.1016/j.progsurf.2005.09.002
17. A.V. Marikutsa, M.N. Rumyantseva, A.M. Gaskov, M. Batzill, U.Diebold, Basics in relation with gas sensing phenomena. Part I. Physical and chemical properties and sensor signal formation. Inorg. Mat. 51, 1329-1347. (2015). doi:10.1134/S00036818651150304X
18. T.A. Miller, S.D. Bakrania, C. Perez, M.S. Wooldridge, In Functional Nanomaterials, ed. by K.E. Geckeler, E. Rosenberg (American Scientific Publishers, 2006) p. 515
19. A. Gurlo, Nanosensors: towards morphological control of gas sensing activity. SnO\textsubscript{2}, In\textsubscript{2}O\textsubscript{3}, ZnO and WO\textsubscript{3} case studies. Nanoscale. 3, 154-165 (2011). doi:10.1039/C0NR00560F
20. N. Barsan, U. Weimar, Conduction Model of Metal Oxide Gas Sensors. J. Electroceram. 7, 143-167 (2001), doi: 10.1023/A:1014405811371
21. G.A. Ozin, A.C. Arsenault. *Nanochemistry: A Chemical Approach to Nanomaterials* (RSC Publishing, London, 2005) p. 876

22. N. Yamazoe, K. Shimano, New perspectives of gas sensor technology. Sens. Actuators B **138**, 100-107 (2009). doi: 10.1016/j.snb.2009.01.023

23. D. Abbaspazeha, R. Ghasempoura, F. Rahimi, A. Iraji zad, Sens. Transducers J. **73**, 819 (2006)

24. L.P. Oleksenko, V.K. Yatsimirsky, G.M. Telbiz, L.V. Lutsenko, Adv. Sci. Technol. **22**, 535 (2004)

25. L.P. Oleksenko, L.V. Lutsenko, Catalytic activity of bimetal-containing Co,Pd systems in the oxidation of carbon monoxide. Russ. J. Phys. Chem. A **87**, 180-184 (2011). doi: 10.1134/S0036024411020210

26. G.I. Golodets, *Heterogeneous Catalytic Reactions Involving Molecular Oxygen* (Elsevier, Amsterdam, 1983) p. 878

27. C. Hammond, *The basics of crystallography and diffraction* (Oxford university press, Oxford, 2009) p. 432

28. C. Xu, J. Tamaki, N. Miura, N. Yamazoe, Stabilization of SnO2 ultrafine particles by additives. J. Mater. Sci. **27**, 963-971 (1992). doi: 10.1007/BF01197649

29. H. Borchert, E.V. Shevchenko, A. Robert et al., Determination of nanocrystal sizes: a comparison of TEM, SAXS, and XRD studies of highly monodisperse CoPt3 particles. Langmuir **21**, 1931-1936 (2005). doi: 10.1021/la0477183

30. W.P. Kang, C.K. Kim, Performance analysis of a new metal-insulator-semiconductor capacitor incorporated with Pt-SnO2 catalytic layers for the detection of O2 and CO gases. J. Appl. Phys. **75**, 4237-4242 (1994). doi: 10.1063/1.356012

31. Q. Yu, K. Wang, C. Luan, Y. Geng, G. Lian, D. Cui, A dual-functional highly responsive gas sensor fabricated from SnO2 porous nanosolid. Sens. Actuators, B **159**, 271-276 (2011). doi: 10.1016/j.snb.2011.07.003

32. X.T. Yin, X.M. Guo, Selectivity and sensitivity of Pd-loaded and Fe-doped SnO2 sensor for CO detection. Sens. Actuators B **200**, 213-218 (2014). doi: 10.1016/j.snb.2014.04.026

33. S. Javanmardi, Sh. NasrSfahani, M.H. Sheikh, Facile synthesis of PdO/SnO2/CuO nanocomposite with enhanced carbon monoxide gas sensing performance at low operating temperature. Mater. Res. Bull. **118**, 110496 (2019). doi: 10.1016/j.materresbull.2019.110496

34. M. Shojaee, S. NasrSfahani, M.H. Sheikh, Hydrothermally synthesized Pd-loaded SnO2/partially reduced graphene oxide nanocomposite for effective detection of carbon monoxide at room temperature. Sens. Actuators B **254**, 457-467 (2018). doi: 10.1016/j.snb.2017.07.083

35. R. Nadimicherla, H.-Y. Li, K. Tian, X. Guo, SnO2 doped MoO3 nanofibers and their carbon monoxide gas sensing performances. Solid State Ion. **300**, 128-134 (2017). doi: 10.1016/j.ssi.2016.12.022

36. S.K. Lim, S.H. Hong, S.H. Hwang, W.M. Choi, S. Kim, H. Park, M.G Jeong, Synthesis of Al-doped ZnO Nanorods via Microemulsion Method and Their Application as a CO Gas Sensor. J. Mater. Sci. Technol. **31**, 639-644 (2015). doi: 10.1016/j.jmst.2014.12.004

37. B. Rehman, N.K. Bhatta, S. Vihari, S.K. Jain, P. Vashishtha, G. Gupta, SnO2/Au multilayer heterostructure for efficient CO sensing. Mater. Chem. Phys. **244**, 122741 (2020). doi: 10.1016/j.matchemphys.2020.122741

38. S. Vetter, S. Haffer, T. Wagner, M. Tiemann, Nanostructured Co3O4 as a CO gas sensor: Temperature-dependent behavior. Sens. Actuators B **206**, 133-138 (2015). doi: 10.1016/j.snb.2014.09.025

39. Sh. Navazani, A. Shokuhfar, M. Hassanisadi, A. Di Carlo, N. Yaghoobi Nia, A. Agresti, A PdPt decorated SnO2-rGO nanohybrid for high-performance resistive sensing of methane. J. Taiwan Inst. Chem.Eng. **95**, 438-451 (2019). doi: 10.1016/j.jtice.2018.08.019

40. P.G. Choi, N. Izu, N. Shirahata, Y. Masuda, Improvement of sensing properties for SnO2 gas sensor by tuning of exposed crystal face. Sens. Actuators, B **296**, 126655 (2019). doi: 10.1016/j.snb.2019.126655