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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 ^{0}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_2S, NO_2, 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 air 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 loses. 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).

Table 1. Sources of CO emissions.

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
30000–100000ppm	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-reached compounds is present.

It is known that gas analytical devices based on sensors are promosing to determine the content of

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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.

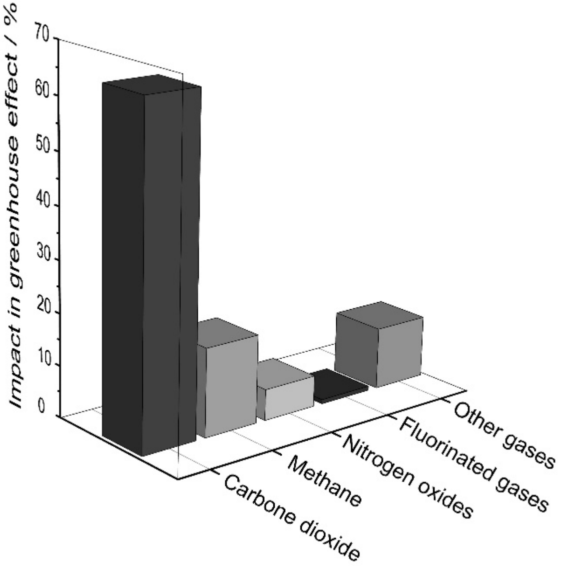

Fig. 1. Impact of different gasses in greenhouse effect.

Table 2. Influence of different CO concentrations on human.

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 monooxide [14] because of their chemical inertness and thus low oxidation rates of CH_4 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 SnO_2 was synthesized by a sol-gel technique. The reagents ($SnCl_4 \times 5H_2O$ and ethylene glycol) were mixed under stirring and excess of ethylene glycol was evaporated in two steps corresponding to a gel formation (120 ^oC) and xerogel formation (150 ^oC). The crystalline SnO_2 was obtained after high temperature treatment (up to 600 ^oC) of the xerogel [12].

For the sensors creation the initial powder of SnO_2 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 $PdCl_2$. After impregnation the plates were dried at 90 ^oC and then calcinated up to 620 ^oC 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 dispersion 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 equal to 100 kV).

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

$$D = k \cdot \lambda / \beta \cdot cos\theta \,, \qquad (1)$$

where D is the XRD particle size; k is a constant close to unity (for our calculation value 0.9 was taken); λ is the wavelength of CuKα radiation (λ= 1,5418 Å); β is a true broadening of a diffraction peak ($\beta = \Delta - b$, where Δ is an experimental broadening and b is an instrumental broadening); θ is a Bragg angle.

For stabilization of the electric characteristics of the sensors they were periodically treated by 930 ppm CH_4 for 30 seconds per 1 hour. During the procedure the temperature of the gas sensitive layer was 405 °C. A ratios R_0/R_{CO} and R_0/R_{CH4} were taken as measures of the sensor responses to CO and CH_4, correspondingly, where R_0 is a value of the sensor electric resistance in air, R_{CO} is a value of the sensor electric resistance in the presence of 1000 ppm CO and R_{CH4} is a value of the sensor electric resistance in the presence of 930 ppm CH_4. The used gas mixtures were certified at the Ukrainian Center of Certification and Metrology. Carbon monoxide- air and methane–air mixtures with lower CO and CH_4 concentrations (less than 1000 and 930 ppm, correspondingly) were obtained through dilution generators.

The values of the sensor signals in air and in the presence of carbon monoxide or methane were measured in a special electric stand [13]. The sensors were sequentially connected to load resistors. The sensor electric resistance was calculated according to the Ohm's law by the next formula:

$$R_s = R \cdot (U_{p.s.} - U_r) / U_r \qquad (2)$$

where $U_{p.s.}$ is a value of voltage supplying by power source at the gas sensitive layer (V); U_r is a value of voltage at the load resistor (V) that depends on the gas composition surrounding the sensor (CO or CH_4 content); R is a known value of electric resistance of the load resistor (Ohm); R_s is a value of the sensor electric resistance (Ohm) in air (R_0) and in the analyzed gas mixture (R_{CO} or R_{CH4}).

Catalytic 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 (Table3). 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 (Table3). 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 (Table3).

Table 3. Particles sizes calculated from TEM and XRD data for initial SnO_2 and different sensor materials (s.m.).

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 Å, c= 3.1882 Å. For Pd doped materials no phases corresponded to palladium compounds were found even for materials contained up to 3.31 wt.% Pd. No electron diffraction attributed to palladium containing spices also was observed for all studied 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].

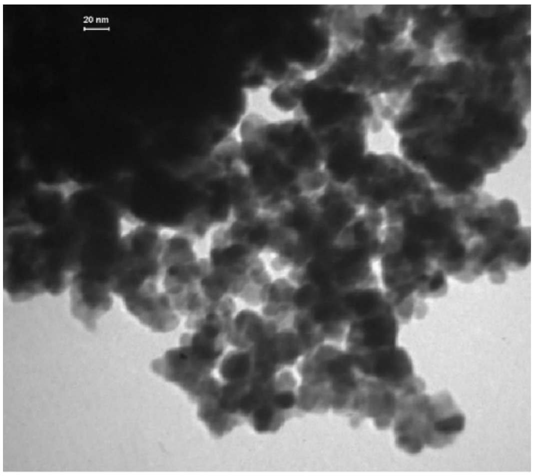

Fig. 2. TEM image of the 1.41 wt.% Pd/SnO_2.

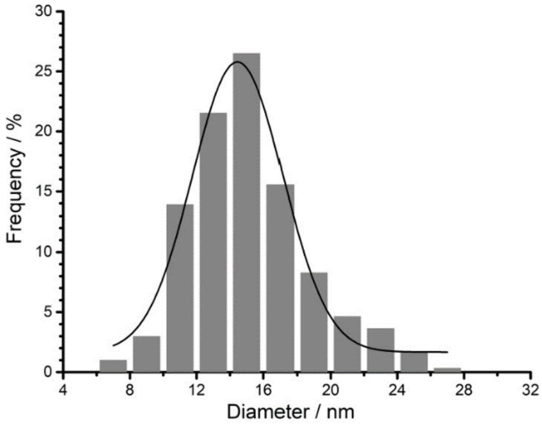

Fig. 3. Histogram of the particles distribution calculated through analysis of TEM data for the samples 1.41 wt.% Pd/SnO_2.

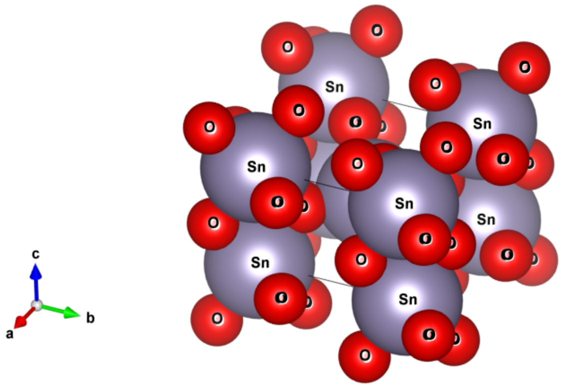

Fig. 4. Crystal structure of tin dioxide calculated by using the XRD data.

3.2 Gas sensitive properties of the sensors

The changes of the values of the sensor electrical resistances in air on the dopant content have an extreme character for both Pd-containing sensors (Table 4). The initial decrease in the electrical resistances in air for the sensors with a low Pd content (0.09-0.23 wt.%) can be attributed to formation of more quantity of oxygen vacancies in tin dioxide crystal structure due to palladium introduction. Such changes can occur at the high temperature treatment process of the sensor formation. It 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 additive 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/SnO_2 at different operation temperatures.

Sensor resistance / kOhm							
T / ºC	**Pd content / wt.%**						
	0.09	**0.31**	**0.62**	**1.41**	**2.28**	**2.42**	**3.31**
405	206	296	392	416	469	395	271
380	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/SnO_2 a change in the responses to CH_4 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/SnO_2) (Table 4). Such correspondence indicates to a common reason that determines both the value of R_0 and γ to methane. This reason is the amount of oxygen chemisorbed on the interface Pd-SnO_2. 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 ºC ($\gamma = 13.5$ for the sensor based on 0.228 wt.% Pd/SnO_2). 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/SnO_2 gas sensitive nanomaterials in oxidation reactions of CO and CH_4.

It was found that introduction of Pd into SnO_2 materials leads to increase in their catalytic activities in both CO and CH_4 oxidation reactions. Maximal differences of temperatures of CO and CH_4 total conversions (ΔT_{100}) for nanomaterials Pd/SnO_2 in comparison with nanosized SnO_2 are equal to 240 and 185^0C, respectively. It was found that Pd/SnO_2 materials are much more active in CO oxidation reaction in comparison with CH_4. For the catalyst 2.3wt.% Pd/SnO_2 temperature of total conversion is equal to 110 ^0C in CO oxidation reaction and 415 ^0C in CH_4 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_2 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_2) to the interface Pd-SnO_2, 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_2 interface by CO oxidation products is much greater compared to sensors based on Pd/SnO_2 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_2 from the formation of the sensor response to CO occurred probably for the sensors with Pd concentration > 1 wt.%. This leads do 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 CH_4 in air of the sensors based on Pd/SnO_2 at different operation temperatures.

T / °C	**Sensor response**						
	Pd content / wt.%						
	0.09	**0.31**	**0.62**	**1.41**	**2.28**	**2.42**	**3.31**
405	3.0	9.2	10.1	9.7	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 CH_4 total conversion are higher in comparison with the sensor operation temperatures. This results in include of the full interface Pd-SnO_2 length in the formation of the sensor responses to methane. This assumption is in 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 CH_4 sensors based on Pd/SnO_2 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 1.41wt.% to CH_4 obtained in this work are better than literature data.

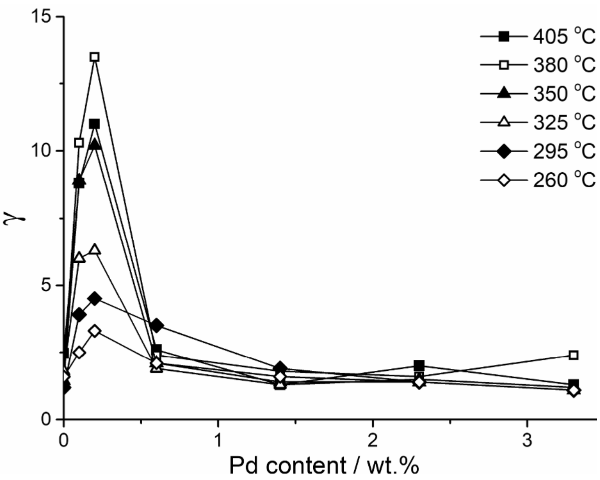

Fig. 5. Responses to 1000 ppm CO of the sensors based on Pd/SnO_2 on palladium content at different operation temperatures of the sensors.

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**
Sensors to CO						
SnO_2 porous nanosolid	4000	9.2	300	28	252	[31]
0.2mol%Pd/ 1mol%Fe/SnO_2	3000	1.3	350	100	50	[32]
7%PdO/SnO_2/ CuO	2000	1.32	200	7	10	[33]
5%Pd/SnO_2/ graphene nanocomposites	1600	1.1	26	120	120	[34]
0.228wt% Pd/ SnO_2	1000	13.5	380	5.5	15.2	this work
SnO_2/MoO_3	300	2.4	300	1430	1524	[35]
2.8 wt%Al/ ZnOnanorods	100	1.6	350	480	240	[36]
SnO_2/Au multilayered hetero-structure	100	3.07	300	58.6	77.7	[37]
Co_3O_4 nano-structured	25	2.1	200	120	600	[38]
Sensors to CH_4						
SnO_2 porous nanosolid	4000	9	440	112	3222	[31]
SnO_2-rGO-PdPt	1000	1.7	150	50	270	[39]
1.41wt% Pd/ SnO_2	1000	12.4	350	6	10	this work
SnO_2 nanoparticle	500	1.5	-	24	36	[40]

For the sensors with maximum responses that based on the materials 0.228% Pd/SnO_2 for CO and 1.41% Pd/SnO_2 for CH_4, the dependences of their signal values in the presence of different CO and CH_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_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_4 in a wide concentration range in air.

4 Conclusions

The synthesized nanosized material based on SnO_2 with palladium additives allowed to create adsorption semiconductor sensors with enhanced response intended to measure different concentrations of CO and CH_4 in air. The sensors containing 1.41 wt.% palladium demonstrate the highest response to CH_4 at 350 °C and the sensors containing 0.228wt.% palladium exhibit the maximum response to CO at 380^0C. The higher sensitivities of the sensors to CO compared to CH_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 monooxide and methane detection, that is necessary to provide fast analysis of the environment using sensor gas analyzers based on the created sensors.

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