

Article

Selective Determination of Hydrogen Sulfide Using SnO₂–Ag Sensor Working in Non-Stationary Temperature Regime

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Abstract: The application of a non-stationary regime of temperature modulation in metal oxide semiconductor sensor based on SnO₂–Ag leads not only to a strongly increased sensor response, but also to a considerably improved sensor selectivity toward hydrogen sulfide. Selectivity with respect to other reducing gases (CO, NH₃, H₂) is about five orders of magnitude, enabling a correct selective determination of H₂S in the presence of interfering gas components.

Keywords: sensitivity; MOX sensor; temperature modulation; qualitative analysis; quantitative analysis



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1. Introduction

Hydrogen sulfide H₂S is a heavy, colorless gas with high corrosivity and flammability. Hydrogen sulfide is a highly hazardous chemical with a characteristic foul odor. Its impurity in the air, even at low concentrations, has a strong negative effect on the mucous membranes of the eyes, nasopharynx and pulmonary tract. This effect forces us to consider any undetectable hydrogen sulfide leaks to be quite dangerous [1].

Metal oxide semiconductor gas sensors are known to be sensitive and simple gas analytical devices. For this reason, they are widely used for measuring the concentrations of toxic and explosive gases. It is generally recognized that the main disadvantage of these sensors is their insufficient selectivity [2]. However, semiconductor sensors show more selectivity in detecting hydrogen sulfide compared to other gases. This is related to the features of the sorption process of H₂S on the surface of metal oxide semiconductors, which can cause reversible conversion of some oxides to sulfides with a higher level of electrical conductivity or with a different type of conductivity. This process can contribute in a very important way to the sensor response. For example, the additives of copper (+2) change the phase composition of the gas-sensitive layer when adsorbing hydrogen sulfide [3,4].

Currently, the most commonly used material for gas sensors of H₂S is tin dioxide with the addition of copper (II) oxide. High sensitivity and selectivity have been demonstrated, for example, using nanofibers obtained from SnO₂ and coated with CuO [5,6]. In these papers, the authors compared the responses of CuO decorated and pure SnO₂ nanofibers (~50–100 nm in diameter) and demonstrated a dramatic increase in H₂S response in the case of application of CuO loading. A completely different method of fabrication (growth from gas phase) was used but showed a similar result in [7,8]. The sensors based on SnO₂ nanowires coated with CuO nanoparticles demonstrated a three-order of magnitude response to 20 ppm of H₂S. This seems to be typical of such nanofibers with a diameter of 50–100 nm coated with CuO nano-particles with the size of few tens of nm.

The sensing mechanism to H_2S was investigated in [9] using thin films of $\text{SnO}_2\text{:CuO}$ obtained by thermal sputtering. The results were rather interesting; the authors demonstrated that their material interacts with H_2S so that the copper presented in it forms CuS (as a result of interaction with gas), whereas SnO_2 remains unchanged. This fact confirms the formation of CuS and respective disappearance of the p-n junction in $\text{SnO}_2\text{:CuO}$ structure as a dominant mechanism of the sensor response to hydrogen sulfide. However, the humidity has an untoward effect on this structure. In the humid atmosphere, the authors found that the formation of Cu(OH)_2 causes sensor signal drifting. The hydroxide can be removed by sensor heating (400°C) or by treatment with H_2S .

Gas-sensitive material consisting of hollow nano-spheres coated with CuO was applied in medical analysis (halitosis diagnostics) for H_2S detection slightly influenced by changes in humidity level [10]. The coating of hollow nanospheres composed of SnO_2 with CuO increases the signal to H_2S by an order of magnitude and leads to an appropriate increase in selectivity to volatile organic compounds (VOCs). A multilayer thin film structure $\text{SnO}_2\text{--CuO}$ demonstrated a four-order of magnitude response and a short response time of about 2 s to 20 ppm of H_2S [11]. This is again in line with other publications on $\text{SnO}_2\text{--CuO}$ material used for H_2S detection.

In the paper [12], the authors analyzed the influence of diffusion in nanoparticles of SnO_2 and CuO on the sensor properties of gas sensors. The diffusion coefficient is of the order $10^{-14}\text{--}10^{-15}\text{ cm}^2/\text{s}$ at 573 K . This very high value of diffusion coefficient (characteristic time of diffusion in 10 nm nanoparticles is of the order of 100–1000 s) could lead to strong instability of the sensor even at relatively low operation temperature. This value should be considered with prudence because it contradicts the results of other researchers. In [13], the sensing properties of thin film structures of CuO/SnO_2 were investigated. In spite of these very interesting results obtained with the application of relatively unusual methods of fabrication of heterostructures of tin dioxide (n-semiconductor) with CuO decoration (p-semiconductor), the most common method of their fabrication is the application of sol-gel process [14].

Along with the additives of copper oxide, for the determination of hydrogen sulfide concentrations, the sensors with silver decoration were also used. Silver oxide is similar to copper oxide; it is also soft oxidizer, which can, in the presence of H_2S , be converted to silver sulfide, which has high electrical conductivity. The transition of silver oxide to silver sulfide gives a strong contribution to the analytical signal of the sensor [15,16]. The additives of silver to nanocrystalline SnO_2 increases its response and significantly improves the selectivity to hydrogen sulfide, if tin dioxide is prepared in the form of nano-structured film [17], as nano-wires [18], or as thin film developed using spray pyrolysis of tin tetrachloride [19].

Tin dioxide is not the only material that, when decorated with copper or silver nanoparticles, demonstrates improved sensitivity and selectivity to hydrogen sulfide. Nanocrystalline LaCoO_3 modified by Ag nanoparticles has improved sensitivity and selectivity to H_2S [20]. The same effect was found at the investigation of graphene decorated with silver nanoparticles [21] and with Ag -doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ films, which demonstrate 100-fold response to 10 ppm of H_2S [22].

Of course, pure tin dioxide [23], or SnO_2 with Pt [24], or fullerene additives [25] can be used as well for the determination of H_2S concentrations. However, the decoration of tin dioxide with copper or silver oxides increases very strongly the sensor response, this material seems to be the most sensitive solution for the manufacturing the sensors of hydrogen sulfide.

In some experiments, copper oxide was not the additive to other materials, but the main sensing material of gas sensor. For example, a highly sensitive sensor was obtained at the application of Pd -doped CuO nanoflowers [26]. In this publication, the authors performed an interesting thermodynamic analysis of the processes in CuO . It was shown that at a low temperature ($\sim 80^\circ\text{C}$), the formation of CuS dominates, and therefore, this temperature is optimal for H_2S sensing. However, to accelerate the recovery of the sensor,

that is, the formation of CuO, it is desirable to heat the sensing material up to ~ 300 °C. This heating–cooling cycle enables the combination of high sensor response and short recovery time (~ 12 s instead of >3000 s at constant temperature operation mode). As well, the unsintered nanowire of copper (II) oxide [27] and sensor properties of CuO/NiO nanofoil demonstrate good sensitivity and selectivity toward hydrogen sulfide [28]. CuO nanoparticles could be used also as a filler for polymer composite. This composite enables the low temperature operation and low power consumption of a gas sensor.

Other sensing materials, such as zinc oxide without any additives, were also successfully used for the determination of hydrogen sulfide concentrations [29]. As well, zinc oxide nanostructures such as flower-structures nanorods can be applied at room temperature for the measurement of H₂S [30]. Of course, the main disadvantage of room temperature sensors is extremely long recovery—several hours—making the sensor almost useless.

CuO additives to ZnO lead to an increase in ZnO-based material response to H₂S. This is virtually related with the same effect observed for SnO₂ sensors, that is, the formation and disappearance of the p-n junction without and with the presence of H₂S in the atmosphere, respectively [31–33].

Of course, the authors of [34] could not help but try how the now very popular gas-sensitive material based on reduced graphene oxide (RGO) works. The response of the composite consisting of CuO decorated ZnO covered with RGO is very small, however, the concentration of 100 ppm leads to a well-pronounced response of about 0.9% at 100 ppm of H₂S. Another popular approach is the application of metal–organic framework as a template for the synthesis of material with high surface area [35]. The application of this approach leads to material with strong response to H₂S and very promising selectivity of the sensor based on CuO/ZnO. However, to obtain reasonable recovery time, it is necessary to heat the sensor up to ~ 300 °C after each measurement.

The SnO₂/ZnO heterojunction increases the sensitivity to hydrogen sulfide [36]. The addition of Au to the SnO₂/ZnO heterojunction leads to an even greater increase in sensitivity [37]. High sensitivity to hydrogen sulfide was also found in sensors based on the (Sr_{0.6}Bi_{0.305})₂Bi₂O₇/ZnO heterostructure [38].

There were also trials to add copper (II) oxide to indium oxide. In this case, a very strong response to hydrogen sulfide was demonstrated [39]. In this work, the metal–organic framework was also used as a template for the synthesis of nano-sized particles of sensing composite. The response of this sensor to 5 ppm of H₂S at 150 °C was of about 10^5 , however, to obtain reasonable recovery time, it was necessary to heat the sensing material up to 400 °C to accelerate the desorption [40].

Iron (III) oxide is, in principle, promising material for the sensors of hydrogen sulfide. The main advantage of this material is than the iron sulfide—in contrast to tin sulfide, for example—reacts with oxygen, assuring the reversibility of sensing responsible reaction of the formation of the appropriate sulfide [41]. These thin films of nanoparticle-based sensors consisting of Au-modified Fe₂O₃ demonstrate the response of about 5 at H₂S concentration of 5 ppm. The problem of this sensor is a very long recovery time of several hours. Hydrogen sulfide gas-sensing properties of metal–organic framework-derived α -Fe₂O₃ hollow nanospheres decorated with MoSe₂ nanoflowers [42].

An advantage of H₂S sensors based on tungsten oxide nanostructures, nanoparticles, nanoplatelets and nanowires of WO₃ is the short recovery time of the sensor based on this material [43]. However, the selectivity of this material, known by its good sensing properties in the detection of oxidizing gases (NO_x, Ozon, etc.), is not perfect. WO₃ nanoparticles can be distributed in natural polymer chitosan [44]. Such composite material demonstrates the response to H₂S at a low temperature. One of important applications of WO₃-based sensors having low sensitivity to humidity is the analysis of human breath [45]: hydrogen sulfide is an important marker of halitosis accompanying many diseases, such as tonsillitis.

H₂S gas sensors based on WO₃-coated SnO₂ nanowires were fabricated through a two-step process. At the optimal working temperature of 200 °C, the sensor had a sensitivity of

177 toward 1 ppm H₂S with good selectivity over the contamination of NO₂, NH₃, H₂ and CO gases [46].

The results obtained with different sensing materials are summarized in Table 1.

Table 1. Gas-sensing properties of different nanostructures prepared by several synthetic methods toward various gases, particularly H₂S.

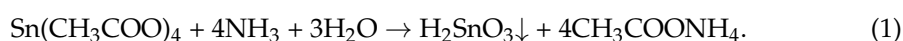
Sensing Material	Technique Used	Gas Conc. (ppm)	Response	Operating Temp (°C)	Ref.
SnO ₂	mesoporous hierarchical architectures derived from waste scallion root	1	~5	92	[23]
SnO ₂ /CuO nanofibers	electrospinning	1	23	200	[6]
SnO ₂ /CuO	ultrasonic spray pyrolysis	1	78	300	[10]
CuO/Pd	precipitation from solution (sol-gel)	1	63.8	80/300 (pulse)	[26]
SnO ₂ /Ag	precipitation from solution (sol-gel)	1	1.23×10^3	100/450 (pulse)	this work
Fe ₂ O ₃	thermal oxidation of Fe films	10	~5	250	[41]
CaCu ₃ Ti ₄ O ₁₂ /Ag	precipitation from solution (sol-gel)	10	~100	250	[22]
SnO ₂ /CuO nanofibers	electrospinning	10	1.98×10^4	300	[5]
SnO ₂ /Ag	precipitation from solution (sol-gel)	10	7.3×10^5	100/450 (pulse)	this work

The transition from stationary to non-stationary temperature regimes often leads to a very significant increase in the sensitivity of MOX sensors [25,38]. In [47], we also showed that non-stationary temperature regimes increase the selectivity of MOX sensors to hydrogen sulfide. The target of this work was the demonstration of similar effect for the determination of hydrogen sulfide. For this, we used tin dioxide nano-material decorated with Ag. Silver nanoparticles can be oxidized at an elevated temperature and then, at a much lower temperature, can be used as soft oxidizer of H₂S, while other reducing gases cannot be oxidized by AgO_x at this relatively low temperature. Therefore, the application of non-stationary regimes of sensor operation leads not only to an increase in sensor sensitivity, but also to improvements of its selectivity toward hydrogen sulfide.

2. Materials and Methods

2.1. Sensor Fabrication

The gas-sensitive layer of the metal oxide sensor was formed from a very fine tin dioxide powder. To synthesize this powder, we added dropwise a cooled concentrated solution of ammonia to a cooled solution of tin acetate (+4) in glacial acetic acid:



Tin acid was separated by centrifugation, washed with deionized water, dried and calcined to 773 K. As a result of these operations, we obtained a very fine tin dioxide powder [47]:



The composition and nanostructure of SnO₂ powder have been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) [47], X-ray photoelectron spectroscopy (XPS) and X-ray near-edge absorption spectroscopy (XANES) [48].

An aqueous solution of silver nitrate was added to the tin dioxide powder, dried and heated to 573 K. The resulting powder, consisting of a mixture of tin dioxide with a dopant, was mixed with a viscous filler to obtain a paste. The resulting paste was applied as thin as possible on a dielectric substrate composed of aluminum oxide with platinum electrodes and an RuO_2 heater [49]. After that, the dielectric substrate was dried at 363 K and heated to 1023 K. As a result, a gas-sensitive layer of a highly dispersed brittle gel was formed on the substrate. The palladium complex compound decomposed to a mixture of oxides containing up to 3% silver by weight.

The resulting material was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). It was found that the grain size of the SnO_2 nanopowder according to transmission electron microscopy is approximately 5 nm, and the crystallite size according to X-ray diffraction is approximately 2–3 nm, a polycrystalline grain structure [47]. This is confirmed by the results of studies using X-ray photoelectron spectroscopy (XPS) and X-ray near-edge absorption spectroscopy (XANES) [48].

The dielectric substrate coated with a gas-sensitive layer was soldered to the TO-8 metal case (Figure 1).

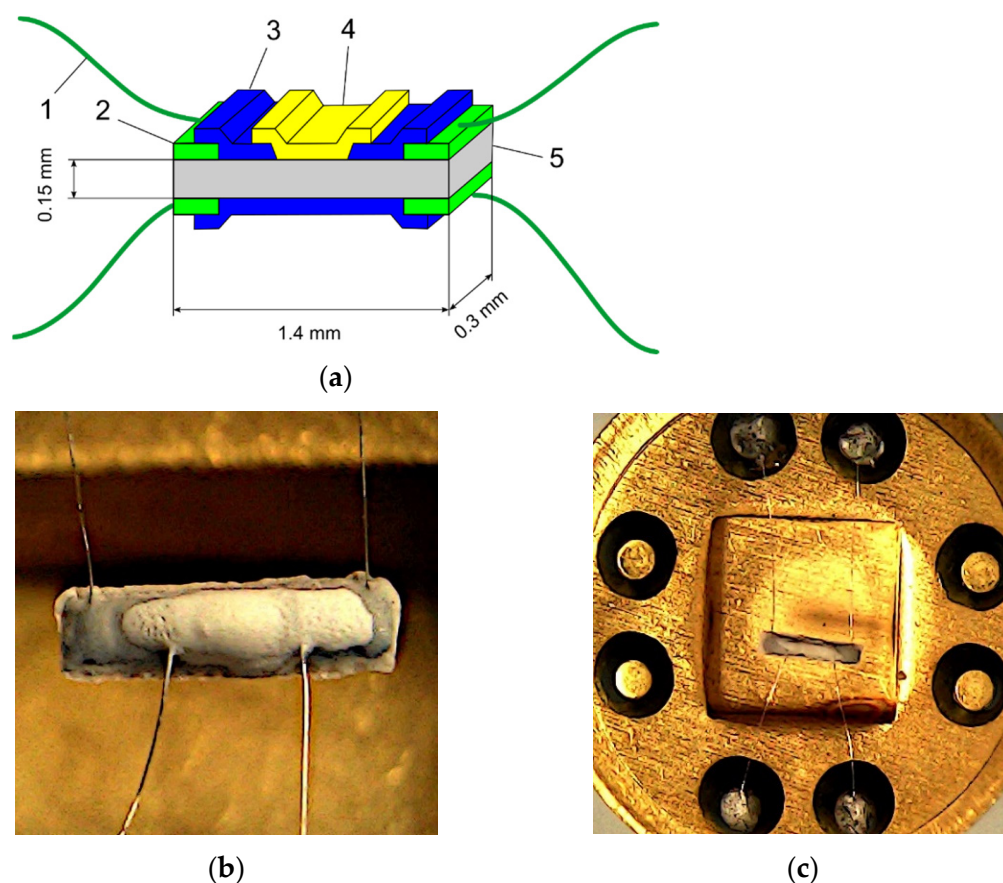


Figure 1. Schematic diagram with the main dimensions (a) and photographs of the $\text{SnO}_2\text{-Ag}$ sensor in a TO-8 metal case (b,c): 1, 2—platinum wire and bonding pads; 3— RuO_2 heater and barrier layers; 4—gas-sensitive layer; 5— Al_2O_3 substrate.

2.2. Sensor Measurements

To study the sensors, we used calibration gas mixtures “hydrogen sulfide in synthetic air” with hydrogen sulfide concentrations of 10 ppm and 200 ppm, “carbon monoxide in synthetic air” with carbon monoxide concentrations of 200 ppm, “hydrogen in synthetic air” with hydrogen concentrations of 200 ppm and “ammonia in synthetic air” with ammonia concentrations of 200 ppm. These mixtures were diluted with dry synthetic air, which was

a mixture of 21% pure oxygen and 79% pure nitrogen. The volumetric gas flow rate during the experiments was kept at a constant level of 250 mL/min.

The MOX sensor was placed in a test chamber made of stainless steel, and its temperature was modulated using an RuO₂ heater on the sensor substrate. For experimental investigation of the sensor characteristics, the team of authors developed a special device that allows not only measuring the resistance of the gas-sensitive layer of the sensor with a frequency of up to 40 Hz, but also controlling its temperature mode. Information about the resistance of the sensor with a given sampling rate was transmitted to a computer and recorded as a text file.

When operating in stationary mode, the sensor temperature was maintained at 573 K, and when operating in a non-stationary mode, the measurement cycle lasted 15 s, of which 2 s, the sensor was heated to 723 K, and the remaining 13 s were cooled to 373 K (Figure 2).

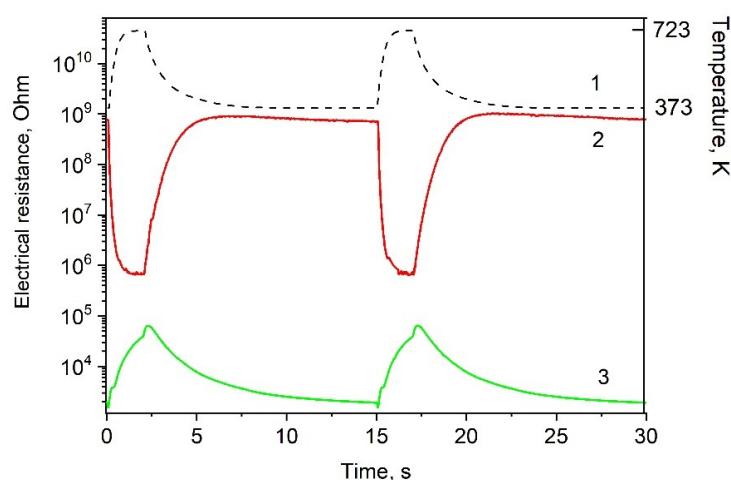


Figure 2. Changes in absolute temperature (1) and electrical resistance of the SnO₂-Ag sensor at 50 ppm carbon monoxide (2) and 50 ppm hydrogen sulfide (3) in air over two measuring cycles.

The first 10 measurement cycles obtained in the non-stationary mode were not used for subsequent processing so the instrument readings could stabilize. To characterize each concentration of the studied gas system, we recorded from 30 to 50 measuring cycles. For quantitative analysis, we used only one point in each measurement cycle, the point corresponding to the moment 14.95 s after the beginning of the cycle (Figure 3).

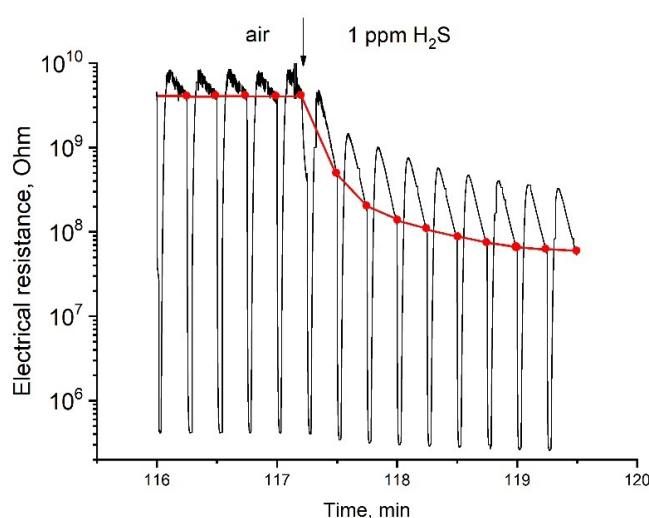


Figure 3. An example of changes in electrical resistance of the SnO₂-Ag sensor over 14 measuring cycles. Red circles correspond to the points at 14.95 s after the beginning of each cycle.

In addition, we determined the sensor response at a constant sensor temperature equal to 573 K. This temperature is optimal for the determination of H_2S in constant temperature operation mode. Sensor response S was calculated as the ratio of the electric sensor resistance R_0 in the clean air to the sensor resistance R_g in the gas mixture under study:

$$S = R_0/R_g. \quad (3)$$

In the non-stationary mode, the sensor resistance was sampled at a frequency of 38.4 Hz during a 15 s measurement cycle, which generated a sample of 576 values in the range from 10^3 to 10^{10} Ohms.

3. Results

Figure 4 shows the resistance of the sensor based on $\text{SnO}_2\text{-Ag}$ in synthetic air and at different concentrations of H_2S as a function of time and, therefore, gas concentration. For the non-stationary regime (red line), the line consists of the points at the end of each measurement cycle, as shown in Figure 3.

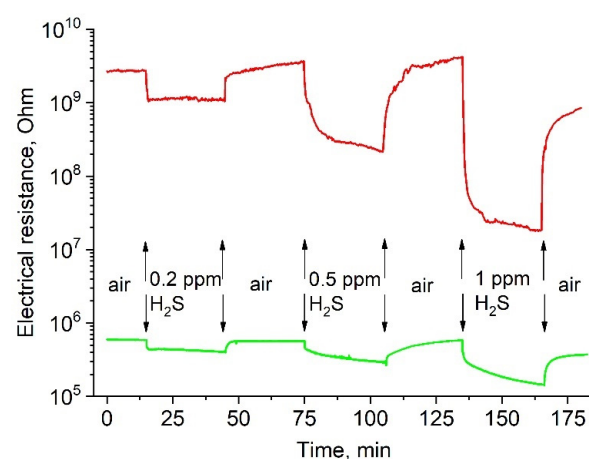


Figure 4. Electric resistance of the sensor $\text{SnO}_2\text{-Ag}$ in dry synthetic air at different concentrations of H_2S in the non-stationary regime (red line) and in the stationary regime at 573 K (green line).

Figure 5 shows the electric resistance of the sensor based on $\text{SnO}_2\text{-Ag}$ as a function of time during each measurement cycle for different concentrations of hydrogen sulfide. It is possible to see that an increase in H_2S concentration leads not only to a very strong increase in the sensor response, but also to very considerable change in the curve shape.

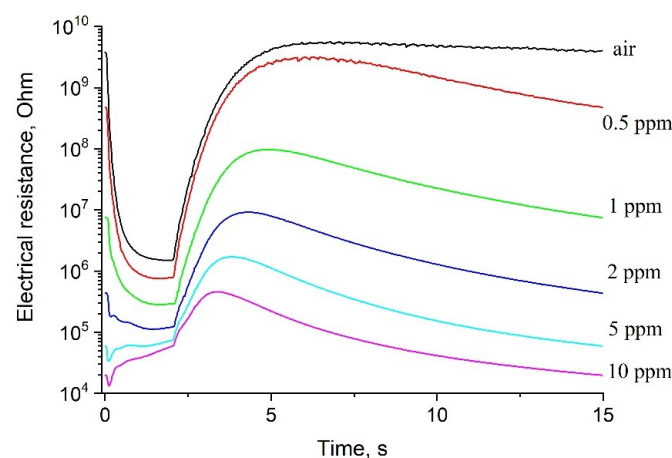


Figure 5. Electric resistance of the sensor based on $\text{SnO}_2\text{-Ag}$ at different concentrations of hydrogen sulfide for the sensor operating in the non-stationary regime. The figure represents the curves obtained during single measurement cycles.

Figure 6 represents the calibration curve, the resistance of the sensor based on $\text{SnO}_2\text{-Ag}$ as function of H_2S concentration. The red line corresponds to the non-stationary regime described above, and the green line to the measurements at a constant temperature equal to 573 K.

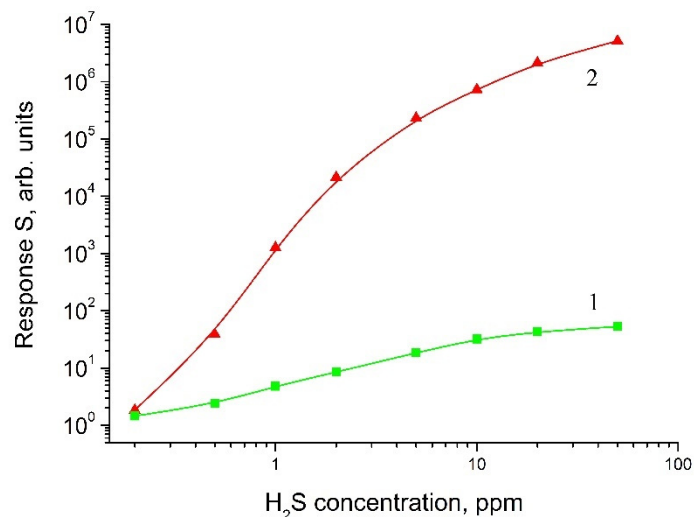


Figure 6. Resistance of the sensor based on $\text{SnO}_2\text{-Ag}$ as a function of H_2S concentration: line 1—measurements at constant temperature equal to 573 K, line 2—measurements performed in the non-stationary regime.

The substitution of constant temperature measurements by the measurements in the non-stationary regime leads not only to an increase in sensor response to hydrogen sulfide, but also to a very considerable improvement in the selectivity of the analytical procedure. Figure 7 gives the data concerning the cross-sensitivity of the $\text{SnO}_2\text{-Ag}$ sensor in pairs $\text{H}_2\text{S}/\text{CO}$, $\text{H}_2\text{S}/\text{H}_2$ and $\text{H}_2\text{S}/\text{NH}_3$ measured for the concentrations of all gases equal to 50 ppm.

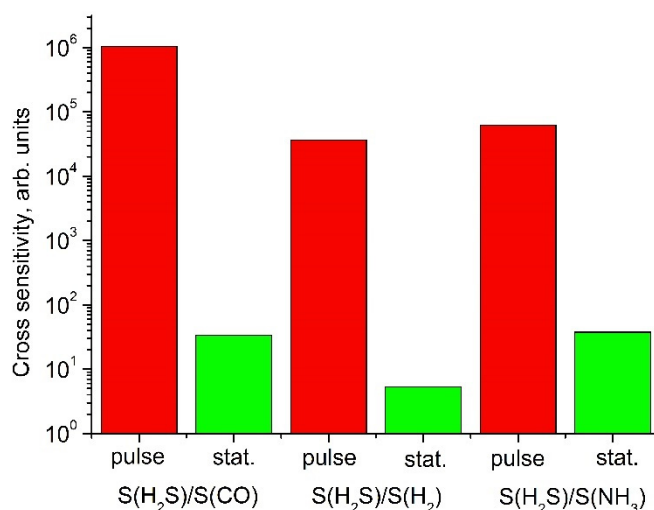
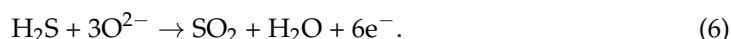
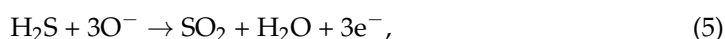
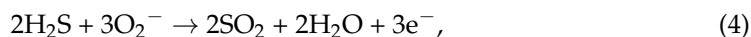


Figure 7. Cross sensitivity of $\text{SnO}_2\text{-Ag}$ based sensor at the determination of the concentrations of hydrogen sulfide, carbon monoxide, and ammonia gas. Green bars correspond to the measurements at constant temperature of the sensor equal to 573 K, and red bars to the measurements in the non-stationary regime.

Following the data presented in Figure 7, the $\text{SnO}_2\text{-Ag}$ sensor operating in a non-stationary regime is very selective, because the response to other reducing gases is lower than the response to target gas (hydrogen sulfide) by five to six orders of magnitude.

4. Discussion

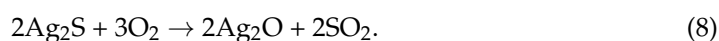
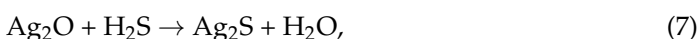
Interactions of metal oxide semiconductor sensors with hydrogen sulfide can occur using two fundamentally different mechanisms. The first is based on the redox interaction of hydrogen sulfide with a semiconductor, which leads to a donor response due to an increase in the concentration of charge carriers in an n-type semiconductor, to which, in particular, SnO₂ belongs. Various forms of chemisorbed oxygen play a significant role in this interaction:



At low temperatures (for example, at room temperature), chemisorbed oxygen is predominantly in the form O₂[−] and the main interaction proceeds through channel (4). At temperatures slightly above 200 °C, chemisorbed oxygen tends to transform into form O[−] and the main interaction shifts to channel (5) [50,51]. A further increase in temperature (400 °C; and above) leads to preferential interaction through channel (6).

However, the redox mechanism of sensory response is not conducive to selective analysis of hydrogen sulfide, since many reducing gases (for example, hydrogen, carbon monoxide, ammonia and others) interact with semiconductor material in similar ways, and this leads to similar sensory responses.

The second sensory response mechanism in the determination of hydrogen sulfide differs from the first, but also leads to a donor response in n-type semiconductors. Some metal oxides in the presence of hydrogen sulfide can be converted to metal sulfides with lower electrical resistance. The transformation of oxides into sulfides occurs as a result of a chemical reaction with hydrogen sulfide, which helps its selective detection. Oxides of various metals, including tin dioxide, are capable of transforming into sulfides, but this process is much easier for copper or silver oxides:



The reaction (7) is exothermic; therefore, at a relatively low temperature, the equilibrium in this process is shifted toward the formation of silver sulfide. At a high temperature, the endothermic reaction (5) of the formation of silver oxide dominates [18].

As shown in Figure 7, the SnO₂–Ag sensor has some hydrogen sulfide selectivity even when operated at stationary temperatures. This selectivity can be, however, dramatically improved by the application of a non-stationary regime of sensor operation. In this case, the response to hydrogen sulfide increases by several orders of magnitude, which, in turn, results in an adequate increase in sensor selectivity. Let us consider the reason for this dramatic increase in sensor selectivity in a non-stationary operation mode.

The measurement of gas concentration by a sensor working in a constant temperature mode is always a compromise related with the optimization of working temperature. If the temperature of the gas-sensitive layer increases, then the catalyst is activated, but the sorption of the analyte decreases, and if the temperature decreases, then the sorption of the analyte increases, but the rates of chemical reactions decrease. Another result of an increase in the working temperature is related with the losses in sensor selectivity, because the catalyst activated by the high temperature becomes active toward many reactions of gas oxidation.

An increase in sensor response and sensor selectivity, when the non-stationary temperature regime is applied, is related with the temporal segregation of the processes of catalyst activation at a high temperature and, on the other hand, the processes of analyte adsorption and its soft oxidation at a low temperature. Impulse temperature heating enables catalytic sensitive layer activation before the sensor-active chemical reaction takes place [47]. This

effect, surely, is important, but it is not the only process playing an important role in gas sensing.

The response of the sensor depends as well on the resistance of the sensing layer in air. In the case of a similar action of gas-analyte (the addition of the same numbers of charge carriers), the sensor response of the semiconductor would be stronger, if before this action, the background concentration of charge carriers in the semiconductor was lower. The results presented in Figure 4 show that the background value of sensor resistance is higher than the background resistance at constant temperature at 573 K by almost four orders of magnitude. In our opinion, the reason for the significant increase in the background resistance of the sensor upon modulation of temperature is the transition of chemisorbed oxygen from the O_2^- form to the O^- and O^{2-} forms during the heating phase and an increase in the sorption of oxygen in the O_2^- form on its surface during the cooling phase. Moreover, the O^- and O^{2-} forms remaining after the heating phase can remain on the sensor surface during the cooling phase.

An important problem in the detection of hydrogen sulfide is the poisoning of the gas-sensitive layer of the sensor associated with the activation of the reverse conversion of sulfide into oxide (8) [52]. After analyzing the data shown in Figure 4, we can conclude that at concentrations below 1 ppm of hydrogen sulfide, the background resistance quite confidently returns to its original values both at stationary temperature and temperature modulation. However, at concentrations of 1 ppm and higher, relaxation is difficult, as shown by the corresponding curves. Since reaction (8) proceeds better at high temperatures, the temperature modulation mode with periodic heating of the sensor to 450 °C demonstrates better performance compared to stationary low-temperature modes often used in the detection of hydrogen sulfide.

5. Conclusions

In this work, we investigated the sensory characteristics of a material based on SnO_2 nanopowder with the addition of 3% by weight Ag_2O to hydrogen sulfide and other reducing gases (H_2 , CO , NH_3). The sensor was manufactured using the classical sol-gel method. The main purpose of the work was to compare two modes of sensor operation: stationary temperature mode and temperature modulation mode. We have shown that the temperature modulation mode, which consisted of rapid heating of the sensor to 450 °C and gradual cooling to 100 °C, led both to an increase in the sensor's sensitivity to hydrogen sulfide and to a very significant increase in its selectivity. The latter is confirmed by a difference of five to six orders of magnitude in the cross-sensitivities of the sensor to other reducing gases (hydrogen, carbon monoxide and ammonia).

Thus, the sensor based on SnO_2 -Ag working in a non-stationary regime demonstrates high sensitivity and very high selectivity toward hydrogen sulfide compared to the sensor working at constant temperature; the sensor can be used for the detection of H_2S in the presence of interfering gases and in mixtures of hydrogen sulfide with other target gases.

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