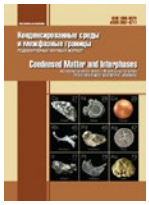

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Semiconductor metal oxide sensor for hydrogen sulphide operating under non-stationary temperature conditions

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Abstract

The aim of the work was to create a selective gas sensor for hydrogen sulphide. As a result of adding ammonia to the zinc acetate solution, centrifuging the obtained zinc hydroxide and subsequent calcination, a polydisperse zinc oxide powder with a grain size of 5–50 nm was obtained. The material was characterized using X-ray phase analysis and transmission electron microscopy. Subsequently, silver nitrate and terpeniol were added to the zinc oxide nanopowder to form a paste. The gas-sensitive material was obtained by applying the resulting paste on a special dielectric substrate and subsequent calcination, as a result of which the terpeniol burned out, and the silver nitrate turned into an oxide (the mass fraction of the silver was 3%). A non-stationary temperature mode for the operation of the sensor was selected, in which, after rapid heating of the sensor to 450 °C (2 seconds), slow (13 seconds) cooling to 100 °C occurred. Each subsequent heating-cooling cycle with a total period of 15 seconds began immediately after the end of the previous cycle. The use of an unsteady temperature mode in combination with the selection of the composition of the gas-sensitive layer made it possible to obtain a response of 200 for a hydrogen sulphide concentration of 1 ppm. Along with an increase in sensitivity, a significant increase in selectivity was also observed. The cross-sensitivity for the determination of hydrogen sulphide and other reducing gases (CO, NH_3, H_2) was more than three orders of magnitude. Thus, this sensor can be used to detect hydrogen sulphide even in the presence of interfering components. The use of highly selective sensors in the tasks of qualitative and quantitative analysis can significantly simplify the calibration in comparison with "electronic nose" devices. Devices based on highly selective sensors do not require the use of mathematical methods for processing multidimensional data arrays.

Keywords: Sensitivity; MOX sensor; Temperature modulation; Qualitative analysis; Quantitative analysis

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1. Introduction

Due to their high sensitivity, compactness, and low cost, semiconductor gas sensors are often used in the determination of toxic and flammable substances, however, the area of their possible use is limited by insufficient selectivity [1]. There are two approaches to the solution of this problem. The first of them is associated with the use of a matrix of low-selective sensors in multisensor "electronic nose" devices. In this case, mathematical processing of the obtained multidimensional data arrays can lead to the solution of problems of qualitative and quantitative analysis. The disadvantages of this approach are the complexity and laboriousness of device calibration, the laboriousness of recalibration when replacing even one sensor, the difficulty of mathematical processing, which requires significant computing resources. The second approach involves the creation of selective sensors, the cross-sensitivity of which to interfering components is rather low.

It is known that the determination of hydrogen sulphide by semiconductor metal oxide sensors is characterized by a higher selectivity compared to the determination of other gases. This is due to the fact that the sorption of hydrogen sulphide on the surface of metal oxides can lead to the reversible transformation of some oxides into sulphides with high electrical conductivity and/or a different conductivity type, and this process can make an additional significant contribution to the sensor response. For example, the addition of copper oxide (+2) leads to a change in the composition of the gas-sensitive layer during the sorption of hydrogen sulphide [2, 3], the transformation of semiconductors with the *p*-type conductivity, copper oxide, into a sulphide with high electrical conductivity.

The most common material for hydrogen sulphide sensors is tin dioxide with the addition of copper oxide (+2). High sensitivity and selectivity were shown, in particular, for SnO_2 nanofibers coated with CuO obtained by electrospinning [4, 5]. Sensors for H_2S based on SnO_2 nanowires coated with CuO nanoparticles were obtained [6, 7], the mechanism of the sensory response of thin films SnO_2:CuO obtained by thermal sputtering to hydrogen sulphide was investigated [8]. A gas-sensitive material based on hollow nanospheres coated with CuO was successfully used for the determination of hydrogen sulphide in medical diagnostics. [9] The multilayer SnO_2–CuO structure showed a response of more than four orders of magnitude to 20 ppm H_2S combined with a low response time [10]. The influence of the interdiffusion of SnO_2 and CuO nanoparticles on the sensory properties to hydrogen sulphide was considered [11]. The sensory properties of thin-layer nanostructures based on CuO/SnO_2 were also investigated [12]. However, the most common method for obtaining SnO_2/CuO nanocomposites is the sol-gel process [13].

Along with the addition of copper oxide, sensors with the addition of silver are used for the determination of hydrogen sulphide. As well as copper oxide, silver oxide is able to reversibly transform into silver sulphide with high electrical conductivity. The transition of silver oxide into sulphide makes a large contribution to the analytical signal of the sensor [14, 15]. The addition of silver to nanocrystalline SnO_2 increases the response to hydrogen sulphide [16–18].

Pure SnO_2 [19] and SnO_2 with the addition of platinum [20] or fullerenes [21] were used for the determination of hydrogen sulphide.

In some cases, copper oxide was not an additive to other metal oxide materials, but the basis of the sensor, for example, a highly sensitive sensor was obtained based on palladium-doped "nanoflowers" from CuO [22]. The sensory properties of unsintered copper oxide (+2) nanowires were investigated [23].

For the determination of hydrogen sulphide, such traditional materials as, for example, zinc oxide without special additives have been successfully used [24]. The addition of copper oxide (+2) to zinc oxide usually increases the sensitivity to hydrogen sulphide [25–29]. Examples illustrating the influence of the composition of the gas-sensitive layer on the magnitude of response of the sensor to hydrogen sulphide are shown in Table 1.

It is known that the transition from ordinary stationary temperature modes to non-stationary modes often leads to a very significant increase in the sensitivity [22, 32, 33]. As we demonstrated in our study, the use of non-stationary temperature modes also contributes to an increase in the selectivity of the analysis of hydrogen sulphide.

Table 1. The properties of different sensor materials in relation to hydrogen sulphide

Sensor material	Receiving method	Concentration H_2S (ppm)	Response	Working temperature (°C)	Ref.
SnO_2	Impregnation of biomatrix with precursor solution followed by annealing	1	~ 5	92	[19]
SnO_2/CuO nanofibers	Electrospinning	1	23	200	[5]
SnO_2/CuO	Ultrasonic spray pyrolysis	1	78	300	[9]
CuO/Pd	Precipitation from solution (sol-gel process)	1	63.8	80/300 (pulse mode)	[22]
ZnO/Ag	Precipitation from solution (sol-gel process)	1	193	100/450 (pulse mode)	This work
Fe_2O_3	Thermal oxidation of iron film	10	~ 5	250	[30]
$CaCu_3Ti_4O_{12}$/Ag	Precipitation from solution (sol-gel process)	10	~ 100	250	[31]
ZnO/Ag	Precipitation from solution (sol-gel process)	10	905	100/450 (pulse mode)	This work

2. Experimental

2.1. Synthesis and characterisation of gas sensitive material

An aqueous solution of ammonia (w = 25%) was added dropwise to an aqueous solution of zinc acetate (chemically pure grade) acidified with acetic acid (pH = 5) to pH = 8 for the formation of sol and peptization of the resulting zinc oxide hydrate suspension:

$$Zn(CH_3COO)_2 + 2NH_3 + 2H_2O \rightarrow \rightarrow Zn(OH)_2\downarrow + 2CH_3COONH_4. \quad (1)$$

Ammonia was added with continuous stirring, the reaction mixture was cooled to a temperature of 20 °C. The resulting zinc hydroxide sol was precipitated by centrifugation, dried at 80 °C for 8 h, and calcined, resulting in the formation of zinc oxide nanoparticles:

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (2)$$

Calcination was performed for 8 hours at temperatures of 300 °C (sample 1), 400 °C (sample 2), 500 °C (sample 3), 600 °C (sample 4). The composition and structure of zinc oxide powder were investigated using transmission electron microscopy (Fig. 1) and X-ray phase analysis (Fig. 2). The main phase for all ZnO samples has a hexagonal syngony, while individual reflections of samples 3 and 4 may belong to the ZnO phase of the cubic modification.

Subsequently, the zinc oxide powder was treated with a solution of silver nitrate, dried, and then terpeniol was added to the powder as a bonding agent. The resulting paste was applied to a dielectric substrate made of aluminium oxide with special platinum electrodes for measuring electrical conductivity and with a platinum heater. The substrate with the applied paste was calcined to a temperature of 750 °C, as a result bonding agent burned out, and a ZnO gel with the addition of silver was formed.

2.2. Measurement of sensory characteristics

For the investigation of the sensory properties of the obtained materials, calibration gas mixtures “hydrogen sulphide in synthetic air”

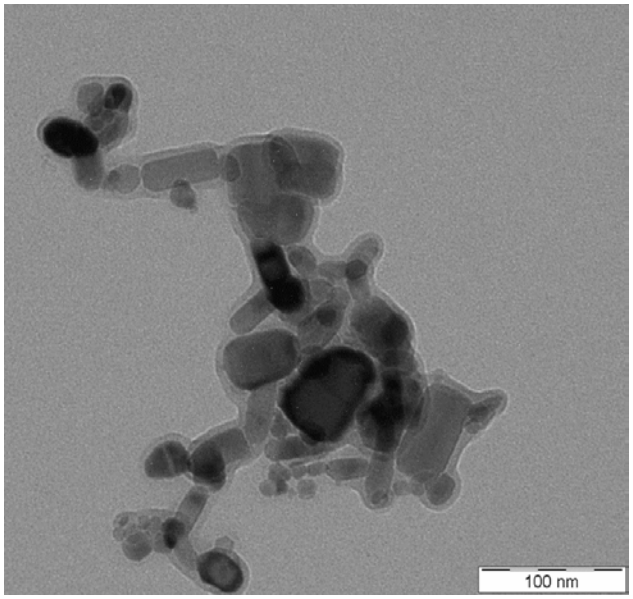

Fig. 1. Transmission electron microscopy image of a zinc oxide nanopowder

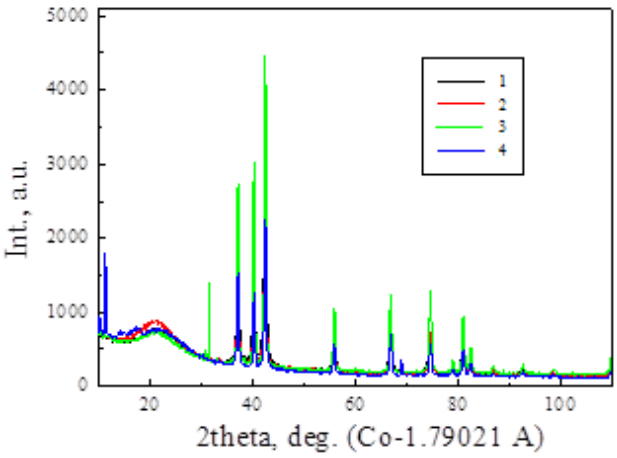

Fig. 2. X-ray diffraction. Sample *1* of zinc oxide nanopowder was calcined at 300 °C, sample *2* – at 400 °C, sample *3* – at 500 °C, sample *4* – at 600 °C

with concentrations of 10 and 200 ppm, diluted with synthetic air were used. The total flow rate was 250 ml/min. The sensor in a TO-8 metal case was placed in a stainless-steel chamber. The temperature of the sensor was set using a special electronic device based on the temperature coefficient of resistance of the heater known from preliminary measurements.

The electrical resistance of the gas-sensitive layer was determined using a special electronic device with a frequency of up to 40 Hz and recorded as a computer file. The duration of each measurement cycle was 15 seconds, of which heating from 100 to 450 °C was performed for 2 seconds, and the cooling from 450 to 100 °C was performed for the following 13 seconds. The heating-cooling cycles followed each other without interruption. The measurement results obtained in the first five cycles were discarded. For quantitative analysis, only one out of the 575 points of the cycle was used, corresponding to a time of 14.95 seconds after the start of the cycle.

The response S was calculated as the ratio of electrical resistance R_0 in air to electrical resistance R_g in the investigated gaseous medium:

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

3. Results and discussion

The dependence of the electrical resistance of the ZnO-Ag sensor on time during one measurement cycle for different hydrogen sulphide concentrations is shown in Fig. 3. As can be seen from Fig. 3, an increase in the concentration of hydrogen sulphide led not only to a significant increase in the response, but the shape of the curves also changed.

The calibration dependence for determination of hydrogen sulphide concentration with a ZnO-Ag sensor in non-stationary temperature mode is shown in Fig. 4. The transition from a constant temperature to a non-stationary mode led not only to an increase in the response to hydrogen sulphide, but also increased the selectivity of the analysis. The cross-sensitivities of SnO_2-Ag sensor to hydrogen sulphide/carbon monoxide, hydrogen sulphide/hydrogen, hydrogen sulphide/ammonia are shown in Table 2. As can be seen from Table 2, a ZnO-Ag sensor operating in non-stationary mode can be considered highly selective, since its responses to the same concentration of hydrogen sulphide and other

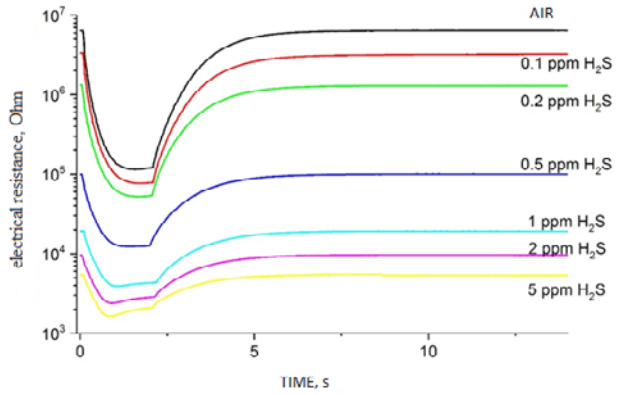

Fig. 3. Electrical resistance of ZnO-Ag sensor in hydrogen sulphide as a function of H_2S concentration under non-stationary temperature condition during one measurement cycle

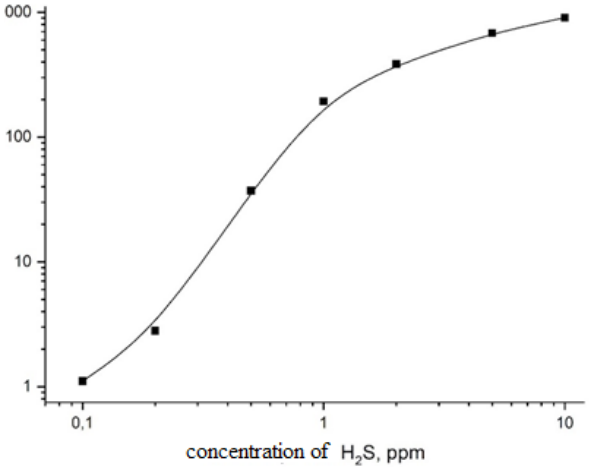

Fig. 4. Calibration curve of the sensor ZnO-Ag at the determination of hydrogen sulphide concentrations

Table 2. Responses of sensor ZnO + Ag

Response to 10 ppm H_2S	Response to 10 ppm CO	Response to 10 ppm NH_3	Response to 10 ppm H_2
905	0.21	0.44	0.87

reducing gases differ by more than 3 orders of magnitude.

Under stationary temperature modes, the cross-sensitivity of the determination of hydrogen sulphide and other reducing gases (hydrogen, carbon monoxide, ammonia) was one and a half orders of magnitude; when switching to non-stationary mode, the cross-sensitivity exceeded three orders of magnitude (Table 2). One of the reasons for the increased sensitivity and selectivity in the determination of hydrogen sulphide is the time separation of the sorption of the gas analyte and the catalytic activity of the gas-sensitive layer. Pulsed temperature mode allows the catalyst to be activated before desorption of the gas analyte occurs [33]. This effect seems to play an important role, but it is not the only one effect. The sensor response largely depends on the total concentration of charge carriers. In the case of the same action of the gas analyte, the sensory response will be the higher, the fewer charge carriers were present in the semiconductor before the gas analyte was introduced. The unsteady temperature mode allows increasing the resistance of the metal oxide nanomaterial in the air due to the efficient sorption of oxygen. Various forms of chemisorbed oxygen play an important role in the interaction with hydrogen sulphide:

$$2H_2S + 3O_2^- \rightarrow 2SO_2 + 2H_2O + 3\bar{e}, \quad (4)$$

$$H_2S + 3O^- \rightarrow SO_2 + H_2O + 3\bar{e}, \quad (5)$$

$$H_2S + 3O^{2-} \rightarrow SO_2 + H_2O + 6\bar{e}. \quad (6)$$

At low temperatures (for example, at room temperature), chemisorbed oxygen is predominantly in the form O_2^-, therefore, the reaction channel (4) prevails. At temperatures slightly exceeding 200 °C, chemisorbed oxygen transforms into the form O^-, and channel (5) prevails. A further increase in temperature (400 °C and above) leads to the reaction through channel (6). However, the redox mechanism of the interaction of hydrogen sulphide with the semiconductor surface (4–6) does not allow the selective determination of reducing gases, since similar interaction mechanisms occur on the surface during the chemisorption of hydrogen, carbon monoxide, ammonia, ethanol, and so on.

Sensors based on metal oxides with silver additives exhibit some selectivity to hydrogen sulphide even when they operate with a stationary temperature. This is due to the processes of reversible transformation of silver oxide into sulphide, which has a low electrical resistance, and therefore this transition makes a significant contribution to the donor sensory response:

$$Ag_2O + H_2S \rightarrow Ag_2S + H_2O. \quad (7)$$

Process (7) is exothermic, and at low temperatures the equilibrium shifts towards the formation of silver sulphide. At high temperatures, an endothermic process (8) of the formation of silver oxide occurs [17]:

$$2Ag_2S + 3O_2 \rightarrow 2Ag_2O + 2SO_2. \quad (8)$$

4. Conclusions

In our study, we investigated the sensory characteristics of the material obtained by adding silver oxide (3% by weight) to the ZnO nanopowder in relation to hydrogen sulphide and other reducing gases (H_2, CO, NH_3). The sensor was obtained using the classic sol-gel technology. The main task of the study was comparison of the characteristics of the sensor in two modes: with a stationary temperature and with temperature modulation. It was shown that the use of a mode in which the sensor quickly heated up to 450 °C (2 seconds) and then cooled down to 100 °C (13 seconds), led not only to a significant increase in sensitivity, but also to a noticeable increase in selectivity. The cross-sensitivity in the determination of hydrogen sulphide and in the determination of other reducing gases (hydrogen, carbon monoxide, ammonia) was approximately three orders of magnitude, which makes this sensor highly selective.

Thus, a sensor based on ZnO–Ag when operating in a pulsed temperature mode has a high selectivity and can be used to determine hydrogen sulphide in the presence of interfering components, as well as in mixtures of hydrogen sulphide with other target gases.

Authors contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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