ISSN-1996-918X

Pak. J. Anal. Environ. Chem. Vol. 24, No. 2 (2023) 125 – 134

http://doi.org/10.21743/pjaec/2023.12.01

Gas-Sensitive Material for Semiconductor Hydrogen Sulfide Sensor

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Received 15 Sepember 2022, Revised 15 June 2023, Accepted 15 August 2023

Abstract

In this work, the synthesis of porous silica gas-sensitive materials for semiconductor sensors of hydrogen sulfide is presented. As a result of studying the activity and selectivity of individual and binary oxides in the oxidation of combustible gases, the composition of the catalyst (10CuO + 90WO_3) for the gas-sensitive element of the H_2S sensor was selected. The selected catalysts ensure high semiconductor sensor (SCS) selectivity in a wide range of temperatures and H_2S concentrations. The optimal ratio of the initial components for the synthesis of silica gas-sensitive materials for a semiconductor hydrogen sulfide sensor has been selected. It has been established that the period of maturation of the film-forming solution based on tetraethoxysilane (TEOS) is 6.5 hours, the period that ensures the production of gas-sensitive films is 18.5 days, and the aging period is 3.5 days. It was found that an increase in the process temperature from 20 to 40°C with a slight change in the viscosity of the solution leads to a sharp reduction in the stability time of the solution from 18.5 to 7.5 days.

Keywords. Sensor, Porous gas-sensitive material, Hydrogen sulfide, Selectivity, Tungsten oxide, Copper oxide.

Introduction

Porous silica materials are widely used in various fields of industry [1, 2]. The direction and efficiency of the use of porous silica materials are determined by their textural characteristics: specific surface, pore volume, and distribution of pore volume by size, so the regulation of the corresponding indicators is important [3-5]. Today, the use of modern innovative technologies to further increase efficiency, and the development of porous materials for gas-sensitive films, sorbents, catalysts, and drug delivery systems is one of the most urgent problems for the whole world [6–8]. Hydrogen sulfide (H_2S) is a widespread toxic air pollutant, the content of which is controlled using various sensors [9–11]. To date, effective gas-sensitive materials and chemical sensors based on them for monitoring H_2S are being developed [12, 13]. Therefore, the sol-gel synthesis of porous gas sensing materials (GSMs) using templates is of great importance.

With the development of various sectors of the economy, especially energy and industry, the requirements for environmental monitoring of atmospheric air are becoming more stringent on a global scale [14, 15]. In this regard, the improvement of existing methods and devices, the development of new highly sensitive semiconductor sensors, the scientific substantiation of the processes for

obtaining selective gas-sensitive materials in the presence of templates, etc. are imperative. Of particular importance is the development of selective sensitive elements of semiconductor sensors for combustible gases, in particular, H_2S [16-18]. An analytical review of the literature data showed that the number of works devoted to ensuring the selectivity of the semiconductor determination of such eco-toxicants as H_2S in gases is limited.

The most toxic and explosive combustible gases include H_2S, methane (natural gas), ammonia, etc. Existing papers on the determination of H_2S are limited mainly to providing monitoring of pre-explosive concentrations. Considering the above, one of the urgent problems in ensuring environmental safety remains the development of active and selective catalysts and the development on their basis of more advanced and modern semiconductor sensors (SCS) for the determination of combustible gases [19, 20].

The ever-increasing use of natural gas requires the control of its content in the atmospheric air. Although semiconductor sensors based on metal oxides such as TiO_2 [21], ZnO [22], Fe_2O_3 [23], CdO [24], SnO_2 [25], and NiO [26] are widely used to control leakage and accumulation of natural gas in closed premises over the past few years. Oxide-based sensors often work on an interface between n-type and p-type semiconductors [27, 28]. It has been established that the existing sensors based on individual metal oxides are characterized by sensitivity, selectivity, etc. about hazardous gases, especially natural gas and sulfur compounds, at low temperatures [29].

It was reported that nanocomposite film based on titanium dioxide was developed for NH_3 and CO sensors, which is based on the fact that an increase in the gas concentration inside the chamber causes an increase in the resistance of the composite film [30]. The authors developed a composite sensor for the detection of low concentrations of gaseous ammonia [31]. ZnO and TiO_2 doped with polyaniline (PANI) are the most preferred and widely used materials for the detection of gases H_2, NH_3, etc. [32, 33]. To date, sensors have been developed to detect combustible gases in the environment, including polymers, carbon-based materials, and metal oxides [34–38]. The principle of operation of a SCS is based on a change in the electrical conductivity of the gas-sensitive material of the sensor, depending on the composition of the gaseous medium where the sensor is enclosed [39-41]. The aim of the study was the choice of active and selective catalysts for gas-sensitive materials, as well as the development of selective semiconductor gas sensors for H_2S based.

Materials and Methods

In this work, SCS with GSM based on SiO_2 doped with WO_3 and CuO obtained using the sol-gel technology was exploited, and their sensing properties for H_2S concentration were determined. During the experiments, a sol-gel synthesis of porous materials was carried out using templates. A catalyst for a selective semiconductor sensor for hydrogen sulfide (SCS-H_2S) and a technology for assembling a SCS with an inert substrate based on a wire spiral of vitrified platinum microwire has been developed. Standard gas mixtures (SGM) H_2S with air were prepared and metrologically certified.

During this research, the synthesis of thin gas-sensitive SiO_2:WO_3 films with the use of a polyethylene glycol (PEG) template and without a template was carried out by the sol-gel technology. The advantage of WO_3 over other oxides is its chemical resistance

and ease of film production. However, in the scientific and technical literature, the number of studies on optimizing the conditions for the polycondensation of TEOS in the presence of tungsten salts is very limited. Therefore, such studies and the development on their basis of recommendations for the synthesis of multifunctional doped silicate coatings, which are in demand in sensors, are very important.
When optimizing the technology of sol-gel synthesis of gas-sensitive films for a H_2S sensor, PEG was used as a template. The molar ratios of the initial components varied in the following intervals: $Si(OC_2H_5)_4$: H_2O: C_2H_5OH: HCl = (1 to 4): (1 to 40): (1 to 45): (0.01 to 0.3).

Ethanol was used as a solvent in the experiments. The effect of the solvent on the stability of the film-forming solution was studied in the range $Si(OC_2H_5)_4$:H_2O: C_2H_5OH=1: 45. Various methods are known for applying gas-sensitive films. In experiments on obtaining GSM for SCS of H_2S based on tungsten oxide the dip coating method was used. According to the method, modified sols were applied by dipping onto the surface of springs made of vitrified microwire, preliminarily treated in alcohol and distilled water. Films were obtained by drying in the range: of 20, 30 and 40°C (20 min at each temperature) and heat treatment up to 600°C. The dip coating process after drying the samples was repeated several times (4 to 6 depending on the requirements). As a result, a GSM providing high sensitivity to hydrogen sulfide was obtained.

Results and Discussion

When the adsorbing H_2S molecules interact with surface oxygen ions the following reaction takes place on the surface of WO_3 material:

$$H_2S(g)+3O^- \rightarrow SO_2(g)+H_2O(g)+3e^- \quad (1)$$

As a result, the electron passes into the conduction band of WO_3, thereby increasing the conductivity of WO_3. The sensor response to H_2S was determined from the ratio: $S=\Delta R/R_{air}$, (2), where:$\Delta R=(R_{air}–R_{gas})$, R_{air}–sensor resistance in air, and R_{gas}–sensor resistance in the presence of gas.

The sensitivity of metal oxide to gases is associated with the interaction of gaseous components with adsorbed oxygen ions (O^{2-}, O^-, O_2^-) on the surface. Initially, when the metal oxide nanomaterial is exposed to air, the adsorbed oxygen captures electrons from the conduction band:

As a result, a depleted zone is formed, which increases the resistance of the nanomaterial. It should be noted that the type of adsorbed O_2 particles strongly depends on temperature. At lower temperatures, ionized O_2^- molecules predominate. At high temperatures, the main ions are O^- and O^{2-}. A high concentration of O^{2-} ions on the surface of WO_3 at room temperature contributes to a greater efficiency of the interaction between O_2^- and H_2S and, as a result, to a higher sensitivity of the sensor. The electrons enter the conduction band and the current flowing through the gas-sensitive layer increases. The reaction between H_2S and O_2 is accompanied by the release of energy, so SO_2 and H_2O molecules quickly desorb from the surface. A high concentration of O_2^- ions on the film surface promotes efficient interaction between O_2 and H_2S and, thus, a greater sensor response. In experiments to confirm the selectivity of the determination of hydrogen sulfide in the presence of H_2, CO, CH_4 and NH_3 at 350°C, the activity of the following metal oxides was studied: Fe, Co, Ni, Mn, Cr, Cu, W, Mo, V, and Bi. As a result, it was found that during the oxidation of H_2S, WO_3, CuO, Fe_2O_3, and MnO_2 have shown the highest activity (Table 1).

In the studied oxides, WO_3 and CuO are the most active and selective. 100%

conversion of H_2S at 350°C is provided in the presence of WO_3. However, the presence of WO_3 does not ensure the selectivity of H_2S oxidation. In the studied catalysts, CuO turned out to be the most selective. Therefore, further research was carried out in the presence of binary mixtures of the most active (WO_3,) and selective (Cu) metal oxides. The experiments were carried out at various ratios of WO_3 and CuO at 350 °C. (Table 2.).

Table 1. **Results of studying the activity of metal oxides during the oxidation of gases (temperature 350°C, n=5, P=0.95).**

Catalyst	Degree of conversion $(x + \Delta x)$				
	H_2S	NH_3	CH_4	H_2	CO
Fe_2O_3	80.0±0.3	100.0±0.9	11.8±0.1	82.5±0.7	51.5±0.4
CoO	61.0±1.0	82.5±1.5	68.7±0.4	98.0±0.8	85.0±0.9
NiO	34.0±0.3	60.0±1.0	33.4±0.4	66.0±0.5	67.0±0.8
MnO_2	69.0±0.5	88.0±1.0	49.8±0.6	10.00±1.3	100.0±1.0
Cr_2O_3	62.0±0.5	62.1±1.0	29.5±0.3	64.0±0.5	80.0±0.9
CuO	92.0±1.2	28.4±0.5	16.6±0.4	18.0±0.9	19.5±0.3
WO_3	100.0±1.4	56.0±0.4	42.0±0.4	98.0±1.1	41.1±0.5
MoO_3	48.3±0.3	33.5±0.3	19.7±0.1	30.4±0.2	25.0±0.2
V_2O_5	36.0±0.4	56.0±0.5	7.8±0.1	35.5±0.4	36.0±0.5
Bi_2O_3	32.0±0.3	23.0±0.1	31.4±0.3	57.0±0.6	31.0±0.4

Table 2. **Influence of WO_3-CuO ratio on their activity and selectivity (content, % vol.: C_{H2S}-2.20, C_{NH3}-2.20, C_{SO2}-2.20, C_{H2}-2.20, C_{CO}-2.45, C_{CH4}-2.50).**

Catalyst composition, wt %	H_2S	NH_3	SO_2	H_2	CO	CH_4
The temperature of the oxidation process–300 °C						
1CuO+99 WO_3	69.2	6.3	12.1	5.5	3.7	1.6
5CuO+95 WO_3	83.1	4.7	5.1	6.5	4.6	0.6
10CuO+90 WO_3	90.5	4.4	3.2	7.4	6.5	0.6
The temperature of the oxidation process–325 °C						
1CuO+99 WO_3	75.0	6.8	13.1	6.0	4.0	1.7
5CuO+95 WO_3	90.0	5.1	5.5	7.0	5.0	0.7
10CuO+90 WO_3	98.0	4.8	3.5	8.0	7.0	0.7
The temperature of the oxidation process–350 °C						
1CuO+99 WO_3	81	7.3	14.0	6.5	4.3	1.8
5CuO+95 WO_3	97.2	5.5	5.9	7.6	5.4	0.8
10CuO+90 WO_3	100	5.2	3.8	8.6	7.6	0.8
The temperature of the oxidation process–400 °C						
1CuO+99 WO_3	92.6	8.4	16.2	7.4	4.9	2.1
5CuO+95 WO_3	100.0	6.3	6.8	8.6	6.2	0.9
10CuO+90 WO_3	100.0	5.9	4.3	9.9	8.6	0.8

The results of the experiments indicate the possibility of using 10CuO + 90WO_3 as a gas-sensitive layer of selective SCS-H_2S.

Thus, in the experiments, the catalytic characteristics of individual metal oxides and their mixtures were studied. The composition of the active and selective GSM of a SCSr for H_2S has been established. This composition of the gas-sensitive material provides high selectivity in a wide range of H_2S concentrations of external parameters (humidity, temperature and pressure). The GSMs used in the development of the H_2S sensor were made based on tungsten and copper oxides.

The features of sol-gel systems that are most interesting for sensors are that TEOS-based sols can be doped with inorganic compounds, i.e. salts. During the final formation of the material, these dopants mix the silicate matrix of the formed nanocomposite, giving it the necessary gas-sensitive properties. In the course of the experiments, the processes of structure formation in sols based on TEOS in the presence of a dopant based on K_2WO_4 were considered in detail. Experiments have shown that K_2WO_4 added to the initial reaction mixture provides an increase in its viscosity and a decrease in the shelf life. With an increase in the content of K_2WO_4, the viscosity of the solution increases. The dependence curve of the change in the viscosity of the solution at the optimal ratio of its components (TEOS: ethanol: H_2O : HC1 = 1:30 : 20 : 0.05) is shown in Fig. 1.

As can be seen from Fig. 1, in the selected ratios of the initial components, the maturation period of the film-forming solution based on TEOS is 6.5 hours (section an in Fig. 1), the period providing the production of gas-sensitive films (section b in Fig. 1) is 18.5 days and an aging period (section c) equal to 3.5 days, during which the film-forming

solution passes from a liquid to a solid state. With an increase in the temperature of the solution in the sol-gel synthesis of gas-sensitive material in the range of 20-40 °C, a decrease in the stability of the solution (from 18.5 to 7.5 days) is observed for 11 days.

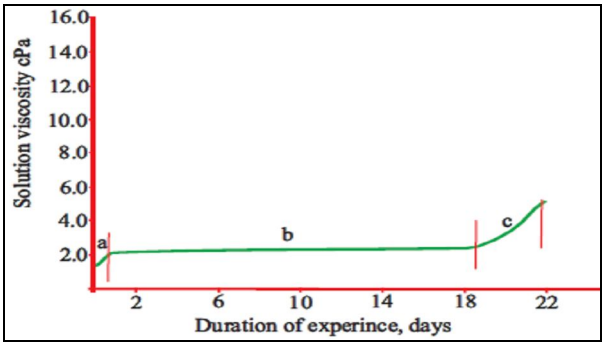

Figure 1. **Dependence of solution viscosity on time. (content in solution: TEOS: H_2O : ethanol : HC1 = 1: 30 : 20 : 0.05 mol)**

The experimental results showed that an increase in the ratio of TEOS: ethanol in solution from 1:1 to 1:45 is accompanied by a decrease in its density (ρ) from 0.9783 to 0.8350, i.e. 1,172 times. In the studied range of TEOS: ethanol, the period of solution stability is 4-18.5 days. In this case, the highest stability of the solution corresponds to TEOS: ethanol equal to 1:30. At this ratio, the viscosity of the solution remains stable for 450 hours, which makes it possible to use it for the manufacture of a hydrogen sulfide sensor.

The study of the influence of humidity on the properties (electrical conductivity, specific density, stability, and viscosity) of the sol during the synthesis of gas-sensitive films was carried out on an ethanol solution at a molar ratio of TEOS : H_2O from 1:1 to 1:40. Based on the obtained results, taking into account the stability of the solution and the solubility of film-forming and dopant additives (W and Cu metal salts), the H_2O/TEOS = 20 ratios were chosen as optimal, which ensures sufficiently high stability of the solution (445) and uniformity of solutions with a dopant (tungsten and copper metal salts.

The change in the stability of the sol depending on the content of TEOS in the solution was studied in the range of concentration from 1 to 4 mol. With an increase in the amount of TEOS in the reaction systems from 1 to 4 mol, the period of stability of the sol sharply decreases (from 18.5 to 6.5 days, i.e., by 2.85 times). The use of low concentrations of TEOS makes it possible to obtain a homogeneous gel with a long stability period and no signs of sedimentation. The molar ratios of the initial $Si(OC_2H_5)_4$:HCl varied in the range of 0.01-0.3. As the results of the experiments showed, the most optimal ratio for obtaining gas-sensitive films is the ratio TEOS : HC1 = 0.05, which provides 450-hour stability of the solution.

Differential-thermal analysis (DTA) and thermogravimetric analysis (TG) were used for thermoanalytical evaluation of the decomposition of the components and structure-controlling agent (Template) PEG under the influence of temperature in the obtained samples (Fig. 2).

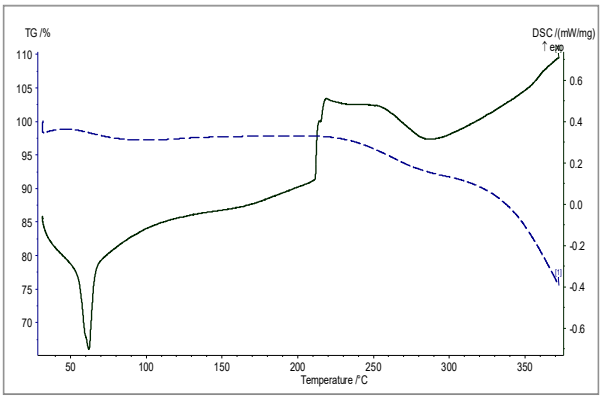

Figure 2. **Results of differential thermal analysis of TEOS-PEG GSM**

The presence of a distinct endothermic peak at 62.2 °C in the derivatogram of the sample indicates that the sample has a crystalline nature (confirming the probability of the polymer being highly ordered). At the temperature of 219 °C, an exothermic peak is

observed due to the breaking of polymer bonds, and above 250 °C, the decomposition process takes place. Adsorption isotherms of benzene vapors in the obtained samples were measured in a sensitive quartz spiral device of Mac-Ben. Based on the isotherms of benzene vapor adsorption in the samples, the monolayer capacity is, saturation volume Vs (or adsorption) and their relative surfaces S were determined using the BET theory equation, calculated from the important parameters of the samples (Table 3).

Table 3. **Structure-sorption parameters for adsorption of benzene vapors.**

Sample	Monolayer capacity a_m, mol/kg	Specific area, $S \cdot 10^{-3}$, m^2/kg	Saturation adsorption a_s, mol/kg
TEOS	0.13	32	0.37
TEOS+PEG-6000 (5%)	0.31	75	0.97
TEOS+PEG-6000 (20%)	1.65	398	3.3

Based on the mesopore volume saturation theory (MVST) equation, the adsorption volumes of mesopores (W_0), micropores $W_{me} = V_s - W_0$ (3) and the saturation adsorption volume (V_s) and the average radius of the pores (according to the formula $r_{mean} = \frac{2 \cdot V_s \cdot 10^4}{S}$ (4) were calculated. The obtained results are presented in Table 4.

Table 4. **Results of determination of adsorption parameters of gas-inert films obtained in the presence of PEG.**

Sample	$W_0 \cdot 10^3$	$V_s \cdot 10^3$, m^3/kg	$W_{me} \cdot 10^3$	The mean radius of pores r_{mean}, Å
TEOS+PEG-6000 (5%)	0.078	0.086	0.008	23
TEOS+PEG-6000 (20%)	0.256	0.294	0.038	14.8

Based on the results presented in the table, we observe that the formation of a mesoporous film in the process of sol-gel synthesis with the presence of GSM as a template corresponds to the concentration of 5% of added PEG. To obtain highly sensitive sensors, it is necessary to control the parameters in different ways. Determination of elemental content, examination of film surface structure and quantitative elemental analysis of sample composition was performed on an XRD Empyrean PANalytical X-ray diffractometer and EVO MA 10 SEM on a Carl Zeiss scanning electron microscope. The images of the objects taken in SEM and the composition of the elements are presented in Fig. 3.

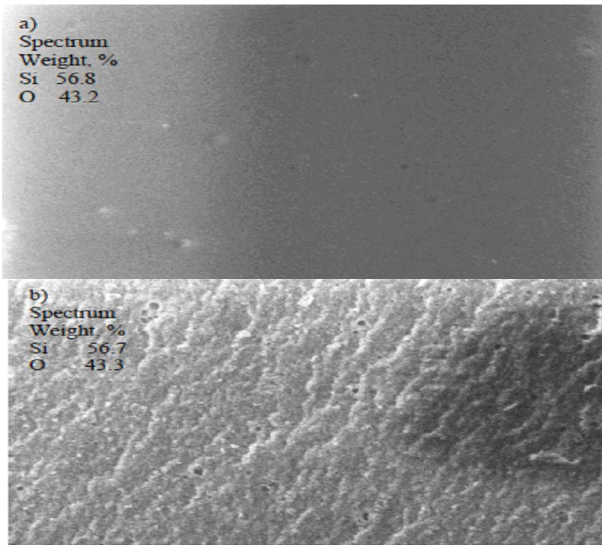

Figure 3. **Images of the surface of TEOS-based films (a) without a template and (b) with a template in the presence of a sol-gel technology**

As can be seen from the photos, the surfaces of TEOS-based films without a template (Fig. 3. a) and with the addition of a template (Fig. 3. b) are mutually different. Studies have shown that the structure of samples of films synthesized in the presence of PEG has a porous structure, unlike films obtained without a template. As a result of the quantitative analysis of the elemental composition of the studied samples, it was found that the films synthesized from the TEOS: C_2H_5OH : H_2O : HC1 mixture in the ratio of 1 : 30 : 20 : 0.01 without a template and with the presence of a template have the same quantitative composition.

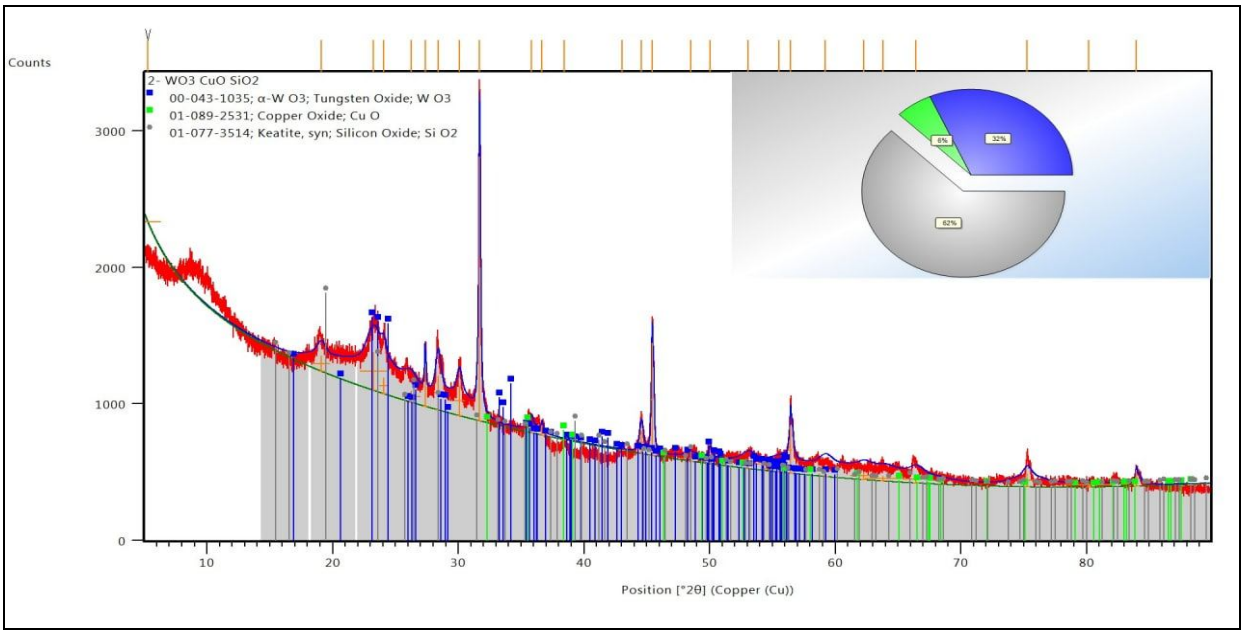

Figure 4. **X-ray diffraction pattern of a semiconductor film based on WO_3 and CuO.**

An X-ray diffraction pattern of a semiconductor film based on WO_3 and CuO, where the ratio CuO : WO_3 = 1 : 5 is shown in Fig. 4.

As can be seen from Fig. 4, the composition of the film obtained based on TEOS, K_2WO_4 and $Cu(NO_3)_2$ $3H_2O$ at a ratio of gas-sensitive components CuO : WO_3 =1: 5 in the presence of PEG contains SiO_2-62%, CuO-6% and WO_3 32%. The SEM results showed that the surface of this film is macroporous.

Conclusion

Thus, the regularities of the synthesis of porous gas-sensitive materials for semiconductor sensors of hydrogen sulfide have been studied. The influence of the composition and ratio of components and process conditions on the characteristics of the resulting gas-sensitive material and the course of the sol-gel process was studied. When developing the technology of sol-gel synthesis of gas-sensitive films for a H_2S sensor, PEG was used as a template. The molar ratios of the initial components varied within the following limits: $Si(OC_2H_5)_4$: H_2O : C_2H_5OH: HCl = (1 to 4) : (1 to 40) : (1 to 45) : (0.01 to 0.3). The optimal ratio of the initial components of the film-forming solution (TEOS : ethanol : H_2O : HC1 = 1 : 30 : 20 : 0.05) was adjusted to ensure the highest stability (18.5 days) of the film-forming solution. The composition and properties of the obtained films were studied by thermal analysis, scanning electron microscopy, X-ray diffraction analysis, and sorption methods. The results of studying the influence of various factors on the sol-gel process made it possible to develop approaches to controlling the process of obtaining GSM for SCS and to create a wide range of film-forming solutions. It is shown that the developed technology based on the sol-gel method makes it possible to form gas-sensitive films based on tungsten oxide, gas-sensitive to H_2S. Gas sensitive elements and semiconductor sensors developed on their basis as part of automatic gas analyzers and signaling devices can be used to control the content of H_2S in the air of closed ecological systems (closed industrial and domestic premises).

Conflict of Interest

Authors declare that they have no conflict of interest.

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