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DEVELOPMENT OF SELECTIVE SEMICONDUCTOR SENSORS OF HYDROGEN SULFIDE, AMMONIA, AND METHANE USING NANOMATERIALS OBTAINED BY THE SOL-GEL PROCESS

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ABSTRACT

In a wide range of changes in the concentration of the initial components, the influence of the components of the initial substances on the patterns of formation of a gas-sensitive material was studied. It was found that the initial solution has the highest stability (18.5 days) at the ratio of contents: TEOS: water: ethanol: HCI=1:20: 30: 0.05. As a result of the study of the regularities of sol-gel synthesis of semiconductor gas-sensitive materials based on tetraethoxysilane and metal oxides Zn, Ti, and W, the following highly efficient gas-sensitive materials were selected, and the optimal operating temperature for the sensitive elements of semiconductor sensors H_2S, NH_3, and CH_4: H_2S ($t_{opt.}$=350°C; 95WO_3+5CuO), NH_3 ($t_{opt.}$=350 °C; 95TiO_2+5Fe_2O_3), CH_4 ($t_{opt.}$= 400°C; 90ZnO+10CoO). The results obtained were used in the development of thin-film semiconductor ssensors for H_2S, NH_3, and CH_4 with a substrate based on a spiral of a glazed platinum microwire. The metrological parameters of sensors based on gas-sensitive materials synthesized with and without a template (polyethylene glycol) were studied during the experiments. It has been found that the sensitivity of a metal oxide composite film obtained in the presence of a template in the determination of H_2S, NH_3, and CH_4 is higher than that of a film obtained without a template.

Keywords: Sol-Gel, Gas-Sensitive Film, Titanium, Cadmium Oxide, Semiconductor Sensor, and Methane.

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INTRODUCTION

To date, the original solution to the problem of monitoring atmospheric air is the use of selective sensors based on the semiconductor method.[1,2] The main advantages of the semiconductor method and sensors based on it are ease of operation, portability, significant service life, high accuracy, and speed.[3-5] The cheapest and most convenient method for obtaining semiconductor gas-sensitive materials (GSM) is the sol-gel technology method.[6-7] This method is capable of mixing components at the molecular level and obtaining materials with the required porosity.[8] The aim of this work is to study the regularities of the processes of formation of sensor elements based on thin films of the composition SiO_x: Me_xO_y (where Me_xO_y: ZnO, TiO_2, WO_3) using the sol-gel technology. Development of selective semiconductor gas sensors that determine concentrations of ammonia, hydrogen sulfide, and methane using nanomaterials obtained using a sol-gel process.

EXPERIMENTAL

The most important parameters of the synthesis of GSM are the concentrations of the starting substances, temperature, pH, and the method of mixing the components of the system. In this regard, in the course of experiments, the influence of these factors on the properties of a solution based on TEOS with and without dopant was studied. When optimizing the technology of sol-gel synthesis of GSM, the molar ratios of the initial components varied within the following limits: TEOS: water: alcohol: hydrochloric acid = (1-4) :(1-40): (1-45):(0,01-0,3). Ethyl alcohol was used as an organic solvent, which is a good solvent for TEOS and salts of most metals. As a result of the experiments, the optimal ratio of components: TEOS: H_2O: alcohol: HCI=1:20: 30: 0.05 was chosen to ensure the high stability of the initial solution. The introduction of a dopant (Ti, Zn, and W oxides) to the silicate matrix makes it

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possible to obtain highly sensitive and selective gas-sensitive nanocomposites. $TiCl_4$, $ZnCl_2$, and K_2WO_4 were used as a source of metal oxide. The influence of the dopant composition on the characteristics has been studied and it has been shown that the viscosity of solutions with an alloying additive (2.6-3.8 cPa) is higher than that of a solution (2.1 cPa) without additives. Also, a solution with a dopant in the range of 20-60°C is characterized by less stability. The film was formed by drying at temperatures from 20 to 120 °C. (for 60 minutes) and annealing at 370, 450, and 550°C. The optimal time for heat treatment of films based on the studied oxides is usually 15-30 minutes (at each temperature). Further increase in the heat treatment time leads to some sintering of the films and a decrease in their porosity. Thus, it has been established that the property of the gas-sensitive material varies depending on the composition of the components of the initial solution.

RESULTS AND DISCUSSION

As a result of the study of the regularities of the oxidation of combustible gases by air oxygen in the presence of binary mixtures of metal oxides in a wide range of different parameters, the following highly efficient gas-sensitive materials were selected, and the optimal operating temperature for the sensitive elements of semiconductor sensors H_2S, NH_3 and CH_4: H_2S ($t_{opt.}$=350°C; $95WO_3+5CuO$), NH_3 ($t_{opt.}$=350°C; $95TiO_2+5Fe_2O_3$), CH_4 ($t_{opt.}$=400°C; 90ZnO+10CoO). The results obtained were used in the development of thin-film semiconductor sensors for H_2S, NH_3, and CH_4 based on a platinum microwire. During the experiments, the metrological characteristics of hydrogen sulfide, ammonia, and methane sensors with sensitive elements based on (in %): $95WO_3+5SiO_2$, $95TiO_2+5Fe_2O_3$, 90ZnO+10CoO were studied. In the developed SCS, the change in the temperature of the gas-sensitive semiconductor layer is ensured by a corresponding change in the voltage of the sensor heater. The dependence of the sensor sensitivity on the supply voltage values was studied in the range of 1.0–3.0 V. In the experiments, the comparative characteristics of GSM synthesized in the presence of a template polyethylene glycol (PEG) and without PEG were studied. The results obtained are shown in Fig.-1.

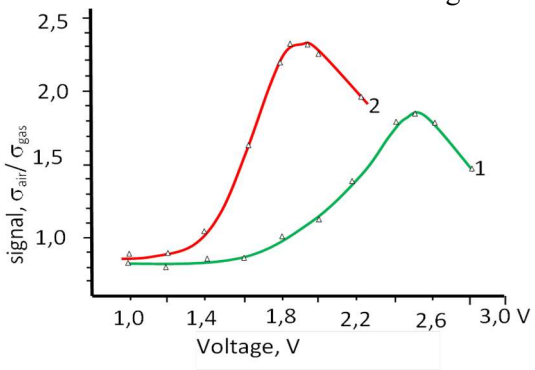

Fig.-1: The Dependence of the Signal on the Voltage: 1-(SiO_2/WO_3+10% SiO_2); 2-(SiO_2/WO_3+10%SiO_2 + PEG)

From Fig.-1 it follows that the voltage providing the highest values of the SCS signal is H_2S for a film containing SiO_2/WO_3+10% SiO_2+PEG 1.8-1.9 V, and this is much less than the film supply, containing SiO_2/WO_3+10% SiO_2 (2.4-2.5 V), i.e., without PEG. A film based on WO_3 and CuO synthesized in the presence of PEG provides a 1.3-fold decrease in the optimal voltage value (V) of the H_2S sensor compared to that without a template and a simultaneous increase in the SCS signal value by 1.6 times. The deviation of the sensor supply voltage from the optimal one is accompanied by a decrease in the sensor signal. At high temperatures, large temperature gradients occur, which leads to degradation processes and sensor failure. The results of determining the selectivity of SCS-NH_3 based on SiO_2/TiO_2+10%$Fe_2O_3$and SiO_2/TiO_2+10%Fe_2O_3+PEG are shown in Fig.-2.

Experimental data show that the highest selectivity in detecting NH_3 in the presence of CO, H_2, and CH_4 corresponds to a sensor based on SiO_2/TiO_2+10%Fe_2O_3 + PEG (Fig.-2). During the experiments, the metrological parameters of a semiconductor sensor containing $SiO_2/(WO_3+CuO)$+PEG and $SiO_2/(WO_3+CuO)$ were studied to control the amount of H_2S in atmospheric air and process gases.

The time required to reach the 90% signal, i.e., the time the sensor is ready for operation, should not exceed 5 seconds. The results of determining the dynamic characteristics of the H_2S semiconductor sensor are shown in Fig.-3.

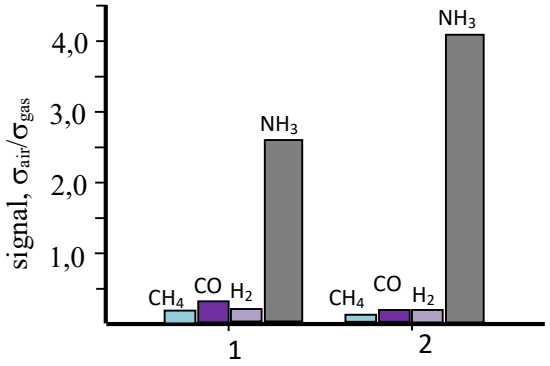

Fig.-2: Results of Determination of Selectivity of Sensors Based on TiO_2 and Fe_2O_3 Detecting NH_3.1-SiO_2/TiO_2+10%Fe_2O_3, 2-SiO_2/TiO_2+10% Fe_2O_3+PEG

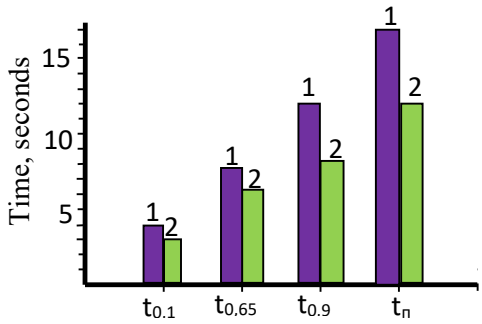

Fig.-3: Dynamic Parameters of the H_2S Semiconductor Sensor. 1-Gas Sensitive Material Obtained Without a Template, 2-With the Participation of a Template. ($t_{0.1}$ is the reaction start time, s; $t_{0.65}$ is the time to reach 65% of the signal, s; $t_{0.9}$ is the time to reach 90% of the signal, s; t_p is the time to reach 100% of the signal, s.)

The results of Fig.-3 confirm the possibility of using the developed sensors for the express detection of H_2S. The use of a porous film based on W, Cu, and PEG oxide as a GSM reduces the time of one analysis from 17 seconds (for SiO_2/WO_3+CuO) to 12 seconds (for SiO_2/WO_3+CuO+PEG). The study of the characteristics of an H_2S sensor based on a sensitive material obtained with and without a template has a direct dependence on the amount of H_2S in a wide (50–1000 mg/m^3) range. The signal of the H_2S sensor based on the gas-sensitive material containing SiO_2 /WO_3 +10%CuO+PEG was 1.77-1.80 times higher than the signal of the sensor based on SiO_2/WO_3 +10%CuO. The selectivity of the developed sensor towards H_2S was studied in the presence of various gases, the results of which can be seen in Table-1.

Table-1: The Results of Determining the Selectivity of an SCS for H_2S (n=5, p=0.95)

Composition of the gas mixture	$SiO_2/WO_3$10%CuO		$SiO_2/WO_3$10%CuO+ PEG	
	Hydrogen sulfide found, mg/m^3			
	$\bar{x}$ ±Δx	Sr·10^2	$\bar{x}$ ±Δx	Sr·10^2
H_2S-50± (the rest of the air)	53±3	1.5	51±5	1.1
H_2S-50±H_2-104± (the rest of the air)	52±2	1.2	52±4	1.2
H_2S-50±CO-120±(the rest of the air)	54±3	1.5	51±3	1.1
H_2S-50±CH_4-124±(the rest of the air)	53±4	1.3	52±4	1.2

The developed sensors allow for selectively detecting of H_2S in the studied concentration range. Due to the addition of H_2 and CH_4, the detection error of the H_2S sensor does not exceed 2.0% for a sensor containing SiO_2/WO_3+10%Cu and does not exceed 1.0% for a sensor containing SiO_2/WO_3+10%CuO+PEG.

CONCLUSION

The influence of the content and ratio of the components of film-forming solutions on the kinetics of the gelation process of the initial sol has been studied in a wide range of the concentration of the initial components. It has been established that solutions consisting of TEOS: H_2O: alcohol: HC1 at their ratio

equal to 1:20: 30: 0.05 have high stability (450 h). The introduction of Ti, Zn, and W oxides to the silicate matrix makes it possible to obtain highly sensitive and selective gas-sensitive nanocomposites for selective NH_3, H_2S, and CH_4 sensors. The regularities are investigated and optimal conditions for the sol-gel synthesis of gas-sensitive films for semiconductor sensors NH_3, H_2S, and CH_4 are established. Semiconductor sensors based on 5%Fe_2O_3-95%TiO_2, 5%CuO-95%WO_3, and 10%CoO-90%ZnO based on sol-gel technology provide high efficiency of NH_3, H_2S, and CH_4 determination and can be used to control environmental objects. It has been found that the sensitivity of the metal oxide composite film obtained in the presence of a template in the determination of H_2S, NH_3, and CH_4 is higher than that of the film obtained without a template. The possibility of developing highly sensitive and selective semiconductor sensors H_2S, NH_3, and CH_4 is shown by using template-polyethylene glycol and metal oxide composites with different activities in relation to the component is determined.

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