RESPONSE TIME AND RECOVERY TIME OF A SEMICONDUCTOR SENSOR FOR DETECTING METHANE AND NATURAL GAS

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Abstract: The response and recovery times of gas sensors provide insights into their dynamic behavior and are determined through experimental methods. The response time refers to the period needed for the sensor to reach 90% of its final signal value after exposure to a sudden change in gas concentration. This is often labeled as τ_{09} or τ_response. Conversely, the recovery time, denoted as τ_{01} or τ_recovery, is the time taken for the sensor to return to 10% of its initial baseline value after the gas is removed and clean air is introduced.

Keywords: Nanocomposite metal oxides, Gas sensors, Methane detection, Natural gas sensing, Semiconductor sensors, SnO_2, ZnO, WO_3 Sol-gel synthesis.

ВРЕМЯ ОТКЛИКА И ВРЕМЯ ВОССТАНОВЛЕНИЯ ПОЛУПРОВОДНИКОВОГО ДАТЧИКА ДЛЯ ОБНАРУЖЕНИЯ МЕТАНА И ПРИРОДНОГО ГАЗА

Аннотация: Время отклика и время восстановления газовых датчиков дают представление об их динамическом поведении и определяются экспериментальными методами. Время отклика относится к периоду, необходимому для того, чтобы датчик достиг 90% от своего конечного значения сигнала после воздействия внезапного изменения концентрации газа. Это часто обозначается как τ_{09} или τ_response. Наоборот, время восстановления, обозначаемое как τ_{01} или τ_recovery, представляет собой время, необходимое для того, чтобы датчик вернулся к 10% от своего начального базового значения после удаления газа и введения чистого воздуха.

Ключевые слова: Нанокомпозитные оксиды металлов, Газовые датчики, Обнаружение метана, Зондирование природного газа, Полупроводниковые датчики, SnO_2, ZnO, WO_3 Синтез золь-гель.

INTRODUCTION

In this study, the methane detection speed of the sensor was thoroughly analyzed at a working temperature of 375°C. The sensor's response time is influenced by several factors: physical and chemical reactions on the adsorption layer, gas diffusion through the sensitive film, and the rate at which the surrounding gas environment changes. To enhance response speed, the influence of the latter two factors should be minimized.

METHODS

In practical applications such as environmental monitoring and industrial emissions control, where gas concentrations are typically measured at intervals of 10 seconds or more, sensors with time constants ranging from several seconds to minutes are generally sufficient.

Experimental testing of methane sensors using metal oxides at 375 °C revealed the following: sensors based on SiO_2-ZnO-CoO composites demonstrated quick reaction times of 15–18 seconds and recovery times between 23–27 seconds. A notable exception was the SiO_2-ZnO sensor lacking cobalt oxide, which showed a slower response of approximately 28–30 seconds and a recovery duration exceeding one minute due to the absence of a catalytic enhancement layer.

Table 1. Response time and recovery time of the methane sensor (experiment temperature 375 °C, methane concentration in the mixture 500 mg/m^3)*.

№	Composition of gas-sensitive material	Sensor response time (τтк or τ09), sec	Sensor recovery time (τвос or τ01), sec
1	SiO_2-ZnO	30	66
2	SiO_2-ZnO-1.0%CoO	18	27
3	SiO_2-ZnO-5.0%CoO	17	25
4	SiO_2-ZnO-10%CoO	15	23

The methane sensitivity of sensors operating on the principle of conductivity variation in the gas-sensitive material (HFM) was evaluated using response curves obtained at a constant temperature of 375 °C when the sensor was exposed to a known concentration of the gas.

Figure 1 illustrates the time-dependent resistance change observed for the SiO_2-ZnO-10%CoO sample upon exposure to methane. The behavior of the resistance over time, as depicted in the figure, aligns with theoretical models describing the response mechanism of gas-sensitive layers to reducing gases. Specifically, the response includes a phase where resistance decreases during gas exposure and a recovery phase when the gas is no longer present.

Experimental findings indicate that the minimum response time for sensors based on SiO_2-ZnO-CoO composites ranges from 15 to 18 seconds, while the recovery period varies between 23 and 27 seconds across all examined compositions of this type.

These results confirm the feasibility of using zinc-cobalt oxide-based gas-sensitive composite materials (GCMS) for rapid methane detection. This capability makes the developed sensors suitable for fire risk monitoring in enclosed ecological environments. Additionally, when the concentration of the test gas begins to drop, the time constant and duration of the transient response slightly increase.

RESULTS

The gas sensitivity property in semiconductor materials is demonstrated through changes in resistance (R) or electrical conductivity (σ) when the material is exposed to a gas with a known concentration. These changes in resistance or conductivity result from a series of successive surface physicochemical processes.

The adsorption processes occurring on the surface are linked to alterations in the electronic state of the surface and the near-surface atomic layers, which in turn affects the surface conductivity of the gas-sensitive material.

The methane sensitivity of the silicon oxide film, produced through the hydrolysis of Tetraethyl orthosilicate (TEOS), increases when zinc oxide is incorporated into its structure. The most sensitive methane sensors are achieved by using mixed oxides of silicon, zinc, and cobalt. Typically, one of the oxides, zinc oxide (ZnO), forms the majority of the composition, while cobalt oxide (CoO), added in small amounts or applied to the surface of the zinc oxide, enhances the gas-sensitive properties of the film and the overall performance of the sensor.

To create a composite gas-sensitive material, doping was performed during the sol-gel solution maturation stage by adding cobalt chloride at concentrations ranging from 1 to 10 wt. %

CoO. Cobalt oxide is known for its high catalytic activity in methane oxidation. After the films were applied to the substrate, heat treatment was conducted in an oxygen atmosphere. The results of the sensitivity tests for films based on ZnO doped with CoO in methane detection are presented in Table 2.

Table 2. Results of the study of the sensitivity of films based on SiO2/ZnO-CoO in determining methane (n=5, P=0.95)*.

№	Composition of the GCM	Methane content in the mixture, mg/m³	Sensor signal, 1/R kOhm-1		
			x+Δx	S	Sr
1	SiO_2/ZnO	1000	397±2	1.61	0.41
2	SiO_2/ZnO+1%CoO	1000	605±3	2.41	0.40
3	SiO_2/ZnO+5%CoO	1000	1441±5	4.02	0.28
4	SiO_2/ZnO+10%CoO	1000	2273±7	5.63	0.25

9.*Eshkobilova M.E., Abdurakhmanov I.E. Nasimov A.M. Some metrological characteristics of a semiconductor methane sensor./Scientific Bulletin of SSU. 2018. No. 1. P.

The experimental data indicates that incorporating 1 to 10% CoO into the HFM enhances its methane sensitivity. Specifically, adding 1% CoO to the SiO2/ZnO-based HFM increases the methane sensor's sensitivity by a factor of 1.5 (Table 4.5). As the CoO concentration in the HFM rises to 5% and 10%, the sensor's sensitivity to methane increases by 3.6 and 5.7 times, respectively. The most sensitive methane sensors are achieved when using a combination of zinc and cobalt oxides, particularly with a CoO content of 10% in the HFM.

CONCLUSION

In conclusion, the sensitivity of the silicon oxide film to methane improves with the incorporation of zinc and cobalt oxides into its structure. The highest sensitivity to methane is observed when mixed silicon, zinc, and cobalt oxides are used, with the CoO content in the GCM reaching 10%. Therefore, the study demonstrates that using sol-gel technology enables the creation of gas-sensitive films based on metal oxides. These films exhibit sensitivity to flammable and toxic gases, including methane. The semiconductor sensor elements developed from these films can be utilized in air quality monitoring systems, particularly for hazardous zones in industrial settings.

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