DESIGN AND OPERATING PRINCIPLE OF A SEMICONDUCTOR SENSOR FOR METHANE AND NATURAL GAS

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Abstract. Methane and natural gas detection is critical for safety in industrial, residential, and environmental applications. Semiconductor-based gas sensors offer a cost-effective, sensitive, and compact solution for real-time monitoring of these gases. This paper presents the design and operational principles of a typical semiconductor sensor tailored for methane and natural gas detection. The sensor utilizes a metal oxide semiconductor (MOS), commonly tin dioxide (SnO_2), whose electrical resistance changes in the presence of reducing gases like methane. The working principle, materials selection, sensor structure, and calibration methods are discussed. Experimental considerations, sensitivity optimization, and limitations are also explored.

Keywords. Methane sensor, Natural gas detection, Semiconductor sensor, Metal oxide sensor, SnO_2, Gas sensing, MOS sensor, Chemiresistive sensor

Аннотация. Обнаружение метана и природных газов имеет решающее значение для обеспечения безопасности в промышленности, жилых помещениях и окружающей среде. Газовые датчики на полупроводниковой основе представляют собой экономичное, чувствительное и компактное решение для мониторинга этих газов в режиме реального времени. В данной статье представлены конструкция и принципы работы типичного полупроводникового датчика, предназначенного для обнаружения метана и природного газа. В датчике используется полупроводник из оксида металла (MOS), обычно диоксид олова (sno_2), электрическое сопротивление которого изменяется в присутствии восстановительных газов, таких как метан. Обсуждаются принцип работы, выбор материалов, структура датчика и методы калибровки. Также рассматриваются экспериментальные соображения, оптимизация чувствительности и ограничения.

ISSN 3030-3907

Ключевые слова. Датчик метана, Обнаружение природного газа, Полупроводниковый датчик, Датчик оксида металла, sno₂, Обнаружение газа, MOS-датчик, Химиорезистивный датчик

Annotatsiya. Metan va tabiiy gazni aniqlash sanoat, turar-joy va atrof-muhit sohalarida xavfsizlik uchun juda muhimdir. Yarimo'tkazgichga asoslangan gaz sensorlari ushbu gazlarni real vaqtda kuzatish uchun tejamkor, sezgir va ixcham echimni taklif etadi. Ushbu maqolada metan va tabiiy gazni aniqlash uchun moslashtirilgan odatdagi yarimo'tkazgich sensorining dizayni va ishlash tamoyillari keltirilgan. Sensor metall oksidli yarimo'tkazgichdan (MOS), odatda qalay dioksiddan (SnO_2) foydalanadi, uning elektr qarshiligi metan kabi kamaytiruvchi gazlar mavjudligida o'zgaradi. Ishlash printsipi, materiallarni tanlash, sensor tuzilishi va kalibrlash usullari muhokama qilinadi. Eksperimental mulohazalar, sezgirlikni optimallashtirish va cheklovlar ham o'rganiladi.

Kalit so'zlar. Metan sensori, tabiiy gazni aniqlash, yarimo'tkazgich sensori, metall oksidi sensori, SnO_2, gazni sezish, MOS sensori, kimyoviy Sensor

Introduction

Methane (CH_4), the main component of natural gas, is a highly combustible and potent greenhouse gas. Undetected leaks can lead to catastrophic explosions or environmental hazards. Traditional gas detection methods, while accurate, are often bulky, expensive, or slow. Semiconductor gas sensors have emerged as an efficient alternative due to their small size, low cost, fast response time, and ease of integration into digital monitoring systems.

Among the semiconductor sensors, metal oxide sensors (MOS) are widely used for methane detection. These sensors operate based on the change in electrical resistance of a sensing material when exposed to methane or other combustible gases. This paper focuses on the design and working principle of such a semiconductor sensor, emphasizing material choice, sensor fabrication, and performance parameters.

METHODS

1. Sensor Material and Structure

The most commonly used sensing material is tin dioxide (SnO_2), chosen for its high sensitivity to reducing gases like methane. The sensor typically consists of:

A ceramic substrate (e.g., alumina)

A thin film or thick film of SnO_2

Interdigitated electrodes (usually platinum or gold)

A built-in microheater to maintain the optimal operating temperature (typically 200–400°C)

ISSN 3030-3907

Utilizing a semiconductor layer composed of zinc oxide and cobalt oxide—where the CoO concentration does not exceed 10%—has proven effective for methane detection applications [118,119]. The methane sensors developed in this research feature a spiral structure built on a platinum microwire coated with glass, which is subsequently covered with a gas-sensitive film consisting of zinc and cobalt oxides. The platinum core, housed within a glass tube, acts as the heating element, a critical component since the surface chemical reactions associated with gas detection are temperature-dependent.

The gas-sensitive material and catalytic layer are deposited onto the sensor electrode using a sol-gel technique. The sensor operates by detecting changes in the electrical characteristics of the semiconductor layer, which vary according to the composition of the surrounding gas atmosphere. The resistance—or, equivalently, the conductivity—of the sensor shifts in response to different methane concentrations.

During the investigation, various performance metrics of the sensors were examined, including sensitivity, response time, and recovery time across a range of temperatures. Measurements primarily focused on the resistance (Rs) of the sensing material applied to an insulating substrate. In the presence of a reducing gas such as methane, the resistance of the layer drops considerably compared to its baseline in clean air. The response behavior generally follows an exponential model described by the equation:

Here, C represents the concentration of methane in the gas mix, and K and α are constants characterizing the sensor response.

To better understand the semiconducting behavior, it's useful to analyze a plot of the logarithm of conductivity against the inverse of temperature (1/T) over a broad thermal range. Sensor sensitivity is often represented by a dimensionless parameter S, also referred to as the "sensor response" in various scientific sources. This is defined as:

$$S = R_{air} / R_{gas} = \sigma_{gas} / \sigma_{air}$$

where R_{air} and σ_{air} are the resistance and conductivity in clean air, and R_{gas} and σ_{gas} are the values under methane exposure.

An alternative formulation for sensitivity is:

$$S = (\sigma_{gas} - \sigma_0) / \sigma_0 \qquad \textit{(Equation 4.3)}$$

In this expression, σ_0 is the conductivity in air without the presence of gas, while σ_gas is the conductivity under methane exposure.

The research ultimately led to the creation of a methane sensor that demonstrates both high selectivity and strong sensitivity. It is suitable for

ISSN 3030-3907

environmental monitoring and industrial process control, and can be integrated into gas analyzers and methane leak detection alarms.

Methane has its own temperature dependences of the rates of adsorption, reaction, and desorption on the surface of the semiconductor layer. The change in resistance of the gas-sensitive layer of the methane sensor at a given temperature change rate must be unique for each composition of the gas-sensitive material. In methane sensors, the change in temperature of the gas-sensitive semiconductor layer is ensured by a corresponding change in the heater voltage [120].

The results of determining the dependence of the power consumed by the heater on the operating temperature of the PPS-CH_4 sensor are shown in Fig. 4.2.

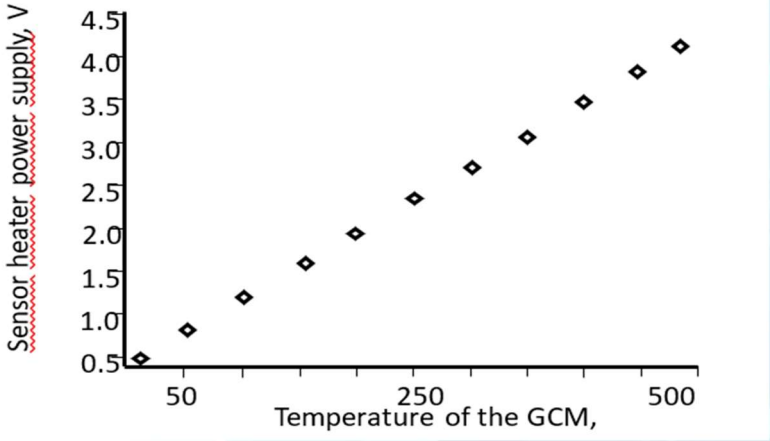


Fig.4.2. Dependence of the temperature of the GCM on the supply voltage of the PPS-SN4 heater

According to the data presented in Fig. 4.2, the power consumption of the PPS-CH4 sensor shows a linear relationship with the operating temperature across the studied range. The sensor's construction ensures a minimal temperature gradient between the heating element and the gas-sensitive layer, which supports precise temperature control during operation.

The ideal temperature for heating the gas-sensitive layer is determined based on the point where the sensor demonstrates peak sensitivity to methane. This parameter was evaluated using a dynamic method within the 200–500 °C range, with temperature increments of 50 °C. The procedure for testing the temperature-dependent sensitivity included the following steps:

1. The test chamber was set to a specific temperature, and measurements began once thermal equilibrium was reached.
2. A steady flow of ambient air was introduced, and the resistance of the nanostructured sensor film was recorded at this temperature.
3. Methane was then introduced by switching the airflow to a calibrated gas mixture. After allowing the sensor's resistance to stabilize, the measurement was recorded.

ISSN 3030-3907

4. To initiate recovery, the methane flow was stopped, air flow resumed, and the time required for the sensor resistance to return to within ±10% of its initial value was measured.

Results from these tests, summarized in Table 4.3 (Appendix 22), show that resistance (and thus conductivity) of the sensors based on ZnO and CoO does not vary uniformly with temperature. As the heater temperature increases up to around 370–380 °C, resistance decreases for all compositions of the gas-sensitive material. Beyond this point, however, the resistance begins to rise again.

Further analysis, shown in Fig. 4.3 (Appendix 23), confirms that the highest sensitivity to methane occurs at 375 °C for sensors composed of SiO_2/ZnO films with cobalt oxide additives. Sensitivity drops when the sensor operates outside this temperature range. At lower temperatures, incomplete desorption of reaction products limits regeneration of the active sites for methane and oxygen. At higher temperatures, reduced adsorption efficiency of both oxygen and methane impairs sensor response. Furthermore, excessive heating introduces large thermal gradients that can lead to material degradation and eventual sensor failure [121; pp. 54–56].

The study also found that increasing the CoO content in SiO_2/ZnO-based sensors enhances the signal strength at the optimal temperature. The best performance was achieved with a 10% CoO composition, where the sensor delivered the strongest response to a given methane concentration. Experiments confirmed that maintaining a heater voltage of 2.1 V reliably ensures the sensor surface reaches the optimal temperature of 375 °C, which was subsequently used in all further testing.

Variations in conductivity behavior with temperature across different gas-sensitive compositions are attributed to differences in gas adsorption characteristics and the mechanisms of surface interactions. These differences offer opportunities for selective methane detection in environments containing multiple gases.

In summary, the experimental findings demonstrate that the optimal operating temperature for achieving maximum methane sensitivity in sensors based on zinc and cobalt oxide films is 375 °C. At this temperature, sensitivity improves with increasing CoO content, with the best performance observed in SiO_2/ZnO-10%CoO compositions. A consistent heater voltage of 2.1 V is sufficient to maintain this temperature across the gas-sensitive layer.

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

ISSN 3030-3907

time taken for the sensor to return to 10% of its initial baseline value after the gas is removed and clean air is introduced.

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.

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 4.4 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.

ISSN 3030-3907

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.

CONCLUSION

Semiconductor gas sensors based on SnO_2 provide a reliable and efficient method for detecting methane and natural gas. Their design hinges on the chemiresistive property of metal oxides and the dynamic surface interactions with gas molecules. Although they offer many advantages, such as fast response and low cost, their performance can be influenced by environmental factors and cross-sensitivity to other gases. Future improvements include enhancing selectivity, lowering operating temperature, and integrating with IoT platforms for smart gas monitoring systems.

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ISSN 3030-3907