A Catalytic Carrier Gas Sensor Based on a Nanotube Array

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ABSTRACT

To effectively monitor methane in coal mine environments, a new type of catalytic carrier gas sensor based on a nanotube array was designed and fabricated. The sensor consists of a catalytic carrier based on a nanotube array, a sensitive Pt electrode, leading wires made from Ag/Pd alloy, a standard two-pin tube shell, powder metallurgy sheets and other components. The metallurgical copper powder sheets make the sensor explosion-proof. The desired catalytic carrier based on an Al₂O₃ nanotube array was prepared by chemical deposition on a nanoporous carrier film. The sensitive Pt electrode was prepared by a thick-film printing process via impregnation with a chloroplatinic acid and palladium chloride solution to form the noble metal catalyst. The results show that for methane concentrations in the range of 0% to 3%, the measured output is approximately 73.5 mV, the response time is 6 seconds, and the recovery time is 5 seconds. When the CH₄ concentration is in the range of 0~3.81%, the response voltage of the sensor and the concentration of CH₄ exhibit a good linear relationship. The stability of the sensor was examined in a 2% CH₄ environment, and the stability of the sensor drifted 0.15% after 60 days.¹

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INTRODUCTION

Coal mining is one of the most dangerous industrial processes [1-2]. Flammable and explosive gases are easily produced during the process of collecting coal, and methane is considered to be one of the most dangerous of these gases. An effective method for monitoring methane is using gas sensors to detect the presence and concentration of methane to provide scientific data to limit the risk [3-5].

Most sensors applied in the coal mining industry are based on the principle of detecting gas by catalytic combustion. The structure of a traditional catalytic methane sensor consists of “uniform pearl-like spheres”, and this sensor is fabricated manually by coating an Al$_2$O$_3$ powder slurry on a carrier to form a catalyst [6]. In addition, the sensor is also coated with noble metal catalysts and sintered at high temperature [7]. The fabrication process of a traditional sensor has several advantages, such as the use of simple manufacturing equipment, few required technology investments, and easy to spread slurry. However, manual preparation of the sensor is not suitable for batch manufacturing, which is required for widespread production.

At present, a silicon-based micro-electro-mechanical systems (MEMS) catalytic sensor is available, but because the thermal matching of the substrate and carrier materials is poor, the stability of the sensor rapidly decreases during application.

In this paper, a new gas sensor in which the structure of the catalytic carrier based on a nanotube array is described.

The sensor is made from the in situ growth of porous Al$_2$O$_3$ ceramics as a template material, and nanotube arrays are formed in the porous carrier by chemical implantation and synthesis. The functional composite carrier is used to produce a catalytic gas sensor that could be easily mass produced.

EXPERIMENTAL SECTION

Sensitivity Mechanism of the Catalytic Methane-detecting Sensor

The procedure for detecting methane employs a catalytic gas-solid interfacial reaction on the sensitive element surface of the solid catalyst. To allow the catalytic reaction to continue, the product should dissociate from the catalyst surface overtime.

Pt and Pd are good catalysts for hydrodeoxygenation, as they allow methane gas to adsorb and dissociate through dissociative chemisorption, as follows:

$$
\text{CH}_4 + 2\text{M} \rightarrow \text{CH}_3\text{M} + \text{HM}
$$

(1)
In this reaction, M represents a metal atom on the catalyst surface. Methane is a saturated hydrocarbon, and its adsorption time on the catalyst surface is very short, making its oxidation difficult.

In the process of CH₄ catalytic combustion, oxidation of the catalyst surface and free radical reactions occur simultaneously. CH₄ and O₂ first adsorb on the catalyst surface, which lowers the activation energy of the reaction. During the resulting catalytic reaction, methane can react with the adsorbed oxygen directly or as a methyl or methylene radical, generating CO₂ and H₂O, or methane can generate HCHO and HCOOH via chemisorption or the desorption and adsorption of oxygen on the noble metal surface to produce CO₂ and H₂O. Once the intermediate HCHO species dissociates, it rapidly decomposes into CO and H₂. The oxidation reactions of methane are as follows:

\[
\begin{align*}
CH_4 + \frac{1}{2}O_2 \xrightarrow{\text{Pt/Pd}/\Delta} & CH_3OH + 129.8\text{KJ} \\
CH_3OH + \frac{1}{2}O_2 \xrightarrow{\text{Pt/Pd}/\Delta} & CH_2O + H_2O + 147.5\text{KJ} \\
CH_2O + \frac{1}{2}O_2 \xrightarrow{\text{Pt/Pd}/\Delta} & HCOOH + 275.4\text{KJ} \\
HCOOH + \frac{1}{2}O_2 \xrightarrow{\text{Pt/Pd}/\Delta} & CO_2 + H_2O + 242.8\text{KJ}
\end{align*}
\]

The overall reaction is as follows:

\[
CH_4 + 2O_2 \xrightarrow{\text{Pt/Pd}/\Delta} CO_2 + 2H_2O + 795.5\text{KJ}
\] (3)

The reaction process releases heat, which will cause the temperature and resistance of the sensitive element to increase. Under the explosive concentration limit, the amount of heat generated from burning the combustible gas mixture per unit volume is approximately constant. The change in resistance caused by the heat generated in the combustion of methane gas is as follows:

\[
CH_4 + 2O_2 \xrightarrow{\text{Pt/Pd}/\Delta} CO_2 + 2H_2O + 795.5\text{KJ}
\] (4)

The parameter \( \rho \) in the formula is the temperature coefficient of the resistance component to be measured, \( \Delta T \) is the temperature change caused by combustion, \( \Delta H \) is the thermal capacity of the sensitive element, Q is the burning heat per unit mass of combustible gas, and \( \alpha \) is a constant determined by the catalytic properties of the component to be measured. The values of \( \rho \), C, and \( \alpha \) depend on the material, shape, surface treatment and structure of the
component to be tested. \( x \) is the content of methane measured, and \( Q \) varies for different types of combustible gases. The reference element does not undergo a combustion reaction. Therefore, the Wheatstone bridge is unbalanced, and the output signal is proportionally related to the concentration of methane being detected, thereby realising the measurement of the methane content in air.

**Carrier Material Preparation**

The porous Al\( _2 \)O\( _3 \) template was prepared by in situ growth using a three-electrode system composed of pure aluminium foil as the anode, gold foil as the cathode and aluminium foil as the reference electrode, and 10~50 AC voltage was utilised for the corrosion growth. The electrolyte was an oxalic acid solution containing sulfuric acid. A Pt resistance thermometer with an accuracy of 0.2°C was placed in the container to measure the electrolyte temperature. The reaction vessel was put in the refrigerator, the electrolyte temperature was controlled and adjusted, and the circulation of the electrolyte was forced by an electromagnetic pump. A 99.95% pure aluminium foil was cut into 50 mm × 50 mm sections as the substrate, annealed at a high temperature of 450 °C for 4 hours, polished in an electrochemical polishing solution, and cleaned with distilled water.

The aluminium foil was inserted into the electrolytic device and then oxidised through a one-step anodic sweep in 3.5% oxalic acid with an electrode voltage of 30 V and an electrolyte temperature of 25±1 °C for 1 hour. The aluminium substrate was then immersed in a solution of phosphoric acid and chromic acid in a 1:1 volume ratio at constant temperature to remove the primary oxide film, leaving only the metallic aluminium.

The two-step anodic oxidation process was carried out in 3.5% oxalic acid and phosphoric acid with electrode voltages of 32 V and 27 V and an electrolyte temperature of 15±1 °C for a period of 5 hours. A porous Al\( _2 \)O\( _3 \) film with a chip carrier structure was fabricated on the aluminium foil by photolithography and wet etching. The porous Al\( _2 \)O\( _3 \) chip carrier film was stripped by a depressurisation method and then distilled, washed and vacuum-dried to obtain the chip carrier.

The ordered porous Al\( _2 \)O\( _3 \) template was immersed in a mixed solution of Al(ON3)\( _3 \), Zr(ON3)\( _4 \) and Th(ON3)\( _4 \) and then vacuum-filtered and dried. After this process was repeated three times, the ordered porous Al\( _2 \)O\( _3 \) template was sintered at 600 °C and then washed in deionised water 3 to 4 times, dried again for 1 hour at a constant temperature of 150 °C, and calcined for 2 hours in a tube furnace at a temperature of 700 °C. Finally, an Al\( _2 \)O\( _3 \)/ZrO\( _2 \)/ThO\( _2 \) composite nanotube array carrier was obtained on the ordered porous Al\( _2 \)O\( _3 \) template.
Preparation of the Pd/Pt Composite Catalyst

Hydrochloric acid was used to prepare a 0.1 mol hydrochloric acid solution. Pure PdCl2 and H2PtO3 (0.5g each) were dissolved in the hydrochloric acid solution, which was heated to 70°C, mixed evenly and aged 24 hours. The nanotube array carrier was impregnated with the mixed catalyst solution for 3 minutes, dried in a 120 °C vacuum drying chamber for 20 minutes, and then calcinated for 2 hours. In the next step, the carrier was calcined in a tube furnace at 400 °C for 2 hours, slowly heated to 600 °C, and held at that temperature for 1 hour. Then, the carrier was washed with distilled water to a neutral PH and then with anhydrous alcohol and subsequently dried at 70°C in a drying oven at constant temperature for 20 minutes. Finally, a Pd/Pt carrier catalyst with a load capacity of approximately 2.5% was obtained.

To verify the necessity of the nanotube array for producing an excellent catalytic carrier, we performed the following experiments with a granular alumina carrier prepared using the same impregnation method under the same conditions as those above to give a Pd/Pt catalyst loading of approximately 2.5%.

Sensor Chip Design

The chip was designed with a square structure convenient for wafer segmentation. The size of the carrier chip was 2.3 mm × 1.5 mm, and its thickness was 0.06 mm. The electrode in the chip consisted of a Pt slurry with an effective sensitive area of 1.2 mm × 1.0 mm. The width and thickness of the electrode line were 0.1 mm and 0.0020~0.0025 mm, respectively. The lead material was 99.9% pure Pt wire with a diameter of 0.06 mm. The chip structure is shown in Figure 1.

![Figure 1. Schematic diagram of the sensitive chip of the sensor, (a) design of the chip layout; (b) design of the chip structure.](image-url)
Fabrication and Measurement of the Gas Sensors

The main processes involved in the manufacture of the gas sensor include chip microfabrication, chemical implantation of the modified microporous Al2O3/ZrO2 carrier, printing of the Pt heating electrode, high-temperature sintering, high-temperature decomposition, leaching of the catalyst, welding of the Pt metal lead, assembly, packaging, ageing, screening, matching, and testing. Sensitive chip manufacturing process flow chart shown in Figure 2.

The key processes for chip manufacturing include the following three aspects:

Chip micromachining We adopted photolithography and wet etching for this process, in which the wet etching agent was dilute phosphoric acid in buffer.

Microporous chemical injection We adopted a mixed solution consisting of Al(ON3)3, Zr(ON3)4 and Th(ON3)4 and impregnated it in the ordered porous Al2O3 template; the Al2O3/ZrO2/ThO2 nanotube composite carrier was then formed after heat treatment.

Pt electrode printing We used 2312-Atype-3 Pt electrode paste from ESL Company (United States) in this process. To form a 3 µm thick film from the Pt electrode paste to ensure that the temperature limit of the electrode was higher than the combustion temperature of the sensor in 4% CH4, a maximum heating temperature of 900 °C was applied.

Figure 2. Sensitive chip manufacturing process, (a) anodized aluminum foil, (b) preliminary stage of aluminum foil anodization, (c) the secondary anodization of aluminum foil forms porous array template, (d) chemical injection into oxide carrier, (e) coating catalyst to carrier, (f) Formation of a heat-sensitive electrode chip.
EXPERIMENTAL RESULTS AND DISCUSSION

Structural and Morphological Characteristics

The morphology and microstructure were investigated by scanning electron microscopy (SEM, Hitachi S-4800) which was operated at an accelerating voltage of 20 kV. Figure 3 shows the schematic diagram of the in situ growth of porous Al2O3 ceramic membranes and Figure 4 shows the electron microscopy analysis of elemental composition of the Al2O3/ZrO2/ThO2 nanotube composite carrier.

Figure 3. Schematic diagram of the in situ growth of porous Al2O3 ceramic membranes, (a) SEM image of Al2O3 template surface, (b) SEM image of Al2O3 nanotube carrier.

Figure 4. Electron microscopy analysis of elemental composition of the Al2O3/ZrO2/ThO2 nanotube composite carrier.
Assembly and Packaging of the Sensor

We combined the chip and the lead with silver welds and used percussion spot welding to weld the lead and chip to the column shell. The metal sealing cap was connected to an air vent, the sensing element and the compensating element were identical, and the glue seal was encapsulated in a powder metallurgy enclosure to achieve explosion-proof packaging of the sensor. The assembly and encapsulation of the sensor is shown in Figure 5 (a). Figure 5 (b) depicts chip assembly of the sensor, and Figure 5 (c) depicts the explosion-proof encapsulation of the sensor.

Gas Sensing Mechanism

ESTABLISH OF A DYNAMIC TEST SYSTEM

The dynamic testing device for evaluating the sensor performance included the following components: standard methane gas (0.5%, 1.0%, 1.5%, 2.0%, 2.5%, and 3%), a standard gas chamber, sensors (placed in the standard gas chamber), a DC power supply (to provide a working voltage to the sensor), an infrared gas analyser (to monitor the concentration of methane in the standard gas tank), and a computer test system (to monitor the function of the signal sampling and process the testing curve). A diagram of the device is shown in Figure 6.
A Wheatstone bridge was adopted to test the performance of the sensor, where the proportional resistor utilises a 2 KΩ fine metallic film resistor, the adjustable resistor is 1 KΩ in constant voltage operation mode, the range of the heating voltage is 2 to 3 DVC, and the voltage signal output of the sensor is on the order of mV.

WORKING VOLTAGE RESPONSE OF THE SENSOR

Use the standard methane gas with a volume concentration of 1%. The working voltage range of the sensor was adjusted from 0.4 V to 3.0 V, and the corresponding data were recorded every 0.2 V. When the working voltage increased, the output voltage of the sensor initially increased and then decreased. When the working voltage reached 2.5 V, the sensor achieved the maximum sensitivity via experiment text. Therefore, 2.5 V is chosen as the working voltage of the sensor.

RELATIONSHIP BETWEEN THE SENSOR OUTPUT AND GAS CONCENTRATION

The dynamic gas test system was used to test the sensor, and the standard methane gas concentration was determined by an infrared gas detector. The operating voltage of the sensor was 2 ± 0.02 V, the ambient temperature was 23 ± 2 °C, and the relative humidity was 35 ± 3%. We used a glass float to control the standard methane gas flow at 150 mL/min. Figure 7 shows the relationship between the sensor output voltage and the methane concentration, in which the output voltage of the sensor bridge circuit is linearly related to the methane concentration.

![Figure 7](image)

Figure 7. Relationship between the sensor output and the methane concentration.
SENSOR RESPONSE AND RECOVERY

We adopted a dynamic gas testing system to test the sensor, which was based on the data recorded by an infrared gas detector. We used the standard gas at different selected concentrations of 1.26%, 2.46%, 3.81%, and 4.8% to test the response and recovery performance of the sensor.

The testing system was operated under a working voltage of 2.5 V, ambient temperature of 20 ± 0.5 °C and humidity of 50 ± 2% RH. A glass float flow meter was used to control the standard methane gas at a flow rate of 200 mL/min, and the response curve is shown in Figure 8.

RESPONSE TIME TO METHANE

Standard CH4 gas at a concentration of 2.46% was selected as the test environment to determine the high-concentration response of the sensor, and clean air was used as the reference environment. The response time of the sensor was tested by the two concentration differences, and the testing conditions remained unchanged. Figure 9 shows that the response time of the sensor to 90% CH4 was 6 seconds, and the recovery time of the sensor to 90% CH4 was 5 seconds.
STABILITY TEST OF THE SENSOR

The stability test of the sensor simulated the actual working conditions, i.e., normal atmospheric conditions. The sensor was connected to a power supply and operated in the presence of 1% and 2% CH₄, and every 10 days over the course of 60 days, the average value of two measurements was recorded. The resulting test curve is shown in the following Figure 10.

**Figure 10. Stability curve of the sensor.**

Synergistic Effects of the Double Noble Metal Catalyst

Maintaining high catalytic activity is key to ensuring the stable functioning of a catalytic sensor. Pd and Pt were used to prepare a double noble metal catalyst and maintain a high catalytic efficiency in the catalytic flameless methane combustion reaction.

When the supported Pd/Pt catalyst was substituted for a single Pd catalyst, the catalytic activity and stability were further improved. In terms of the catalytic stability, the Pt (1.5%)/Pd (2.5%)/Al₂O₃ catalytic carrier was more stable than the Pd (2.5%)/Al₂O₃ and Pt (2%)/Al₂O₃ catalytic carriers for methane sensing. The stability of the sensor has been proven to be related to the contents and interactions of Pt and Pd in the catalyst. The Pt in a double noble metal catalyst inhibits the sintering failure of Pd/PdO and ensures the long-term stability of the catalyst. For the γ-Al₂O₃/ZrO₂/ThO₂ material used as the carrier for the Pt and Pd catalysts in the catalytic combustion of methane, Pd was introduced into the ZrO₂/ThO₂ supported catalyst by Pt, which significantly reduced the ignition and complete conversion temperatures for the complete oxidation of methane. The activity of the current catalyst in the complete oxidation of methane is better than that of the Pd/Al₂O₃ catalyst with the same noble metal loading capacity; this higher activity is due to the synergistic effects of Pt and Pd on the Al₂O₃ support,
which enhances the activity of methane oxidation and leads to a lower temperature threshold for the catalytic reaction.

CONCLUSIONS

A porous Al2O3 ceramic template was prepared by an in situ growth method, and an ordered nanotube array of the Al2O3/ZrO2/ThO2 composite carrier was fabricated from the porous ceramic template. The Pd/Pt double noble metal catalyst was prepared by thermal decomposition of a noble metal nitrate solution. The in situ preparation of the porous Al2O3 template was simple and could be precisely replicated by chemical methods to form a controllable catalyst carrier of ordered composite nanotubes for application in a high-performance catalytic gas sensor.

The sensitive performance of the gas sensor relied on doping of the main γ-Al2O3 carrier material, where different dopants could improve the thermal stability of the carrier, and the adsorption effect of the catalyst by inhibiting the catalyst and carrier aggregation caused by migration.

The preparation of nanotube array composite carriers by an in situ growth method, the improvement of their morphology, the optimisation of the surface modification technology of the carrier, and the improvement of the dispersion and stability of the catalyst on the surface of the carrier are points of focus for future studies. The unique physical and chemical properties of Al2O3 nanotube arrays in sensors have been utilised in an increasing number of applications. With these key technologies and the gradual resolution of scientific problems, the performance of Al2O3 nanotube arrays in catalytic gas sensors will gradually improve, allowing them to be applied in the future.

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