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A Highly Sensitive Catalytic Gas Sensor for Hydrogen Detection Based on Sputtered Nanoporous Platinum

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Abstract

This paper presents a new thermal gas sensor for hydrogen detection based on a catalytic thin film made of sputtered nanoporous platinum. Due to an increased porosity of sputtered catalytic layers, sensitivity could remarkably be raised from commonly 6 µV/ppm [1] up to 18 µV/ppm. As sensing element a thermopile made of p-doped polysilicon and an alloy of tungsten titanium is used. A second thermopile is placed for reference measurement and reduced cross sensitivity on same membrane.

Keywords: catalytic; gas sensor; hydrogen; nanoporous; platinum;

1. Introduction

Catalytic gas sensors are thermal devices for measuring of combustible gases in air. In principle, a catalytic layer is heated by an external heating source and the power of the heating source or temperature of the catalytic layer is measured. When certain amounts of combustible gases, e.g. hydrogen, ethanol or isopropanol, are added to the environmental air, the gases will react with oxygen. The heat of reaction leads to a temperature change in the catalytic layer which can be measured directly or indirectly by a change of the heating power.

For many applications platinum wire coils surrounded with porous alumina ceramics are used. Approaches using thin film technology have been made by Aigner et.al. [2] and Houlet et. al. [1] having high sensitivities and comparably low power consumption. In Aigner et. al. a heated membrane of silicon nitride and a catalyst of porous platinum has been used. The gas concentration is determineded by measuring the change of the heater power. Here, a sensitivity of 2 µW/ppm for hydrogen and 1 µW/ppm for methanol has been determined. Houlet et. al. uses an another approach. Here, a heated membrane of PECVD-SiO_2 and a platinum-alumina ceramic catalyst is used. The

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gas concentration is determined by measuring the temperature of the catalytic layer by means of thermopiles. A sensitivity of 6 µV/ppm could be realized.

For the gas sensor presented here, the temperature of the catalytic layer is also measured by means of thermopiles. Here, a thermal flow sensor [3, 4] has been adapted by deposition of a catalytic layer. A heater is placed in the middle of a membrane with thermopiles as sensing elements on both sides (see Fig. 2). The hot end of one thermopile is covered with catalytic nanoporous platinum. In active mode, the heater is running on a constant temperature of up to 140°C. As mentioned for the approaches of Aigner et. al. and Houlet et. al., an increasing temperature and large surface area of nanoporous platinum accelerates the chemical reaction of available hydrogen and oxygen to water respectively. Due to heat of reaction, the hot junctions of the thermopile with catalytic layer have - depending on the hydrogen ratio – a higher temperature than the hot junctions on the reference thermopile. So, temperature difference between both thermopiles can be interpreted as hydrogen gas concentration.

2. Technological Approach

All functional elements are embedded in a 600 nm low stress silicon rich silicon nitride membrane made by LPCVD (low pressure chemical vapor deposition). A schematic view of the catalytic gas sensor is illustrated in Fig. 1. The processing starts with a first 300 nm layer of LPCVD silicon nitride followed by deposition and structuring of *in-situ* p-doped polysilicon as one thermopile material. As second thermopile material tungsten titanium is used.

Due to the later following high thermal load, a thin layer of titanium nitride is used as a diffusion barrier between polysilicon and tungsten titanium. The already mentioned high thermal load of up to 800°C is applied when depositing the second 300 nm layer of LPCVD silicon nitride for passivation of heater and thermopiles. So, a pin-hole free membrane with high thermal, mechanical and chemical stability could be realized.

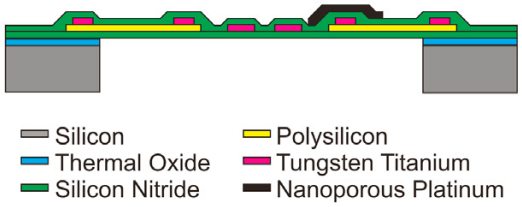

Fig. 1: Schematic view (cross section) of the catalytic gas sensor.

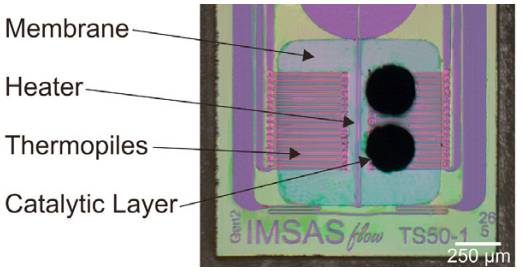

Fig. 2: Membrane of thermal flow sensor with catalytic layer on top to be used for gas sensing. A second thermopile without catalytic layer is used for reference measurement.

The catalytic layer made of nanoporous platinum is deposited by means of a sputtering process. For this purpose a magnetron radio frequency sputtering (RF sputtering) plant for porous materials has been adapted. The modified magnetron uses a strong magnetic field, which makes it possible to sputter at higher pressures of up to 150 Pa. This leads to high porous coatings with structure sizes down to 10 nm and up to 95% porosity. A thickness of 13 µm has been chosen for the catalytic layer.

A structuring of the catalytic platinum layer has been made by means of 70 µm polyimide shadow mask. SEM-pictures of nanoporous platinum layers are shown in Fig. 3 and Fig. 4.

A picture of a membrane consisting of heater and thermopiles with a catalytic layer on top is shown in Fig. 2. As can be seen, only one thermopile is coated with the catalytic layer. The other thermopile is used as reference for reduction of cross sensitivity (e.g. temperature compensation).

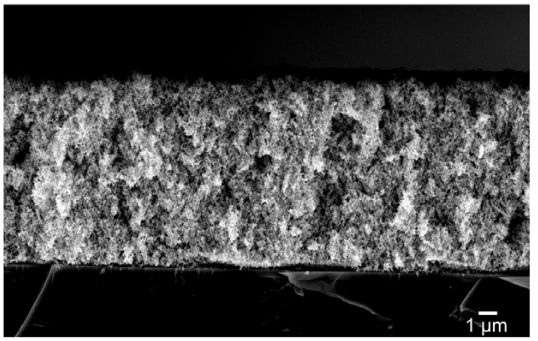

Fig. 3: SEM-picture (cross section) of 13 µm thick nanoporous platinum layer deposited by magnetron RF sputtering. This layer has been used as catalytic layer for the thermal gas sensor.

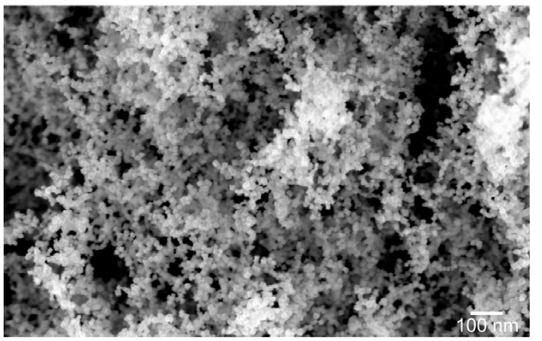

Fig. 4: SEM-picture (enhanced view) of nanoporous platinum layer deposited by magnetron RF sputtering.

3. Measurements

Measurements with the sensor have been made by using a variety of gases and different gas concentrations. A measurement setup for the developed catalytic gas sensor can be seen in Fig. 5. The results of the output voltage – which is the voltage difference between both thermopiles - for different gas concentrations between 100 ppm and 10000 ppm are presented in Fig. 6. The graph shows a linear behavior with a sensitivity of 15 µV/ppm for hydrogen at a heater temperature of 140°C and a relative humidity of 5%. Lower heater temperatures lead to a reduced sensitivity, but it could be observed, that temperatures <100°C contaminate the catalytic film due to water inclusion. Higher heater temperatures will clean the sensor again but temperatures above 140°C should be avoided. Here sintering effects of the nanoporous platinum lead to agglomeration of porous structures reducing the surface-to-volume ratio and therefore the catalytic properties. Furthermore at higher temperatures a delamination of the whole catalytic layer has been observed. The reasons are not determined yet but can originate from reduction of adhesion and different coefficients of thermal expansion between catalytic layer and silicon nitride membrane.

Tests at relative humidities between 5% and 90% have been done. It could be shown that higher relative humidities lead to lower output signals which can be explained by a reduced removal of the generated water.

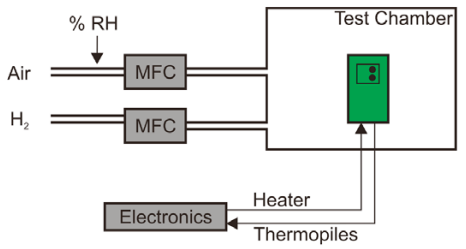

Fig. 5: Measurement setup for characterization of the developed catalytic gas sensor at different concentrations of hydrogen or other gases.

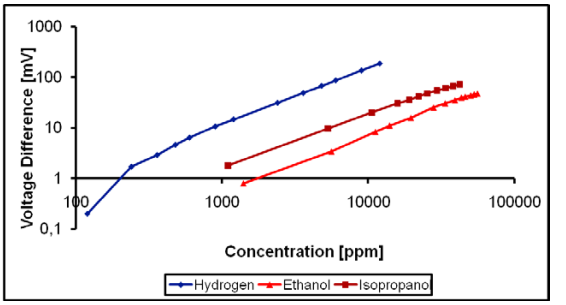

Fig. 6: Measurement results for different volume concentrations of hydrogen, ethanol and isopropanol at a heater temperature of 140°C (T=25°C).

As illustrated in Fig. 6, further measurements have been done with ethanol and isopropanol. Here, lower output signals have been determined caused by the lower heat of reaction compared to hydrogen. First response time measurements have been done with comparably fast performance in the range of seconds [5]. More exact

measurements are planned, but for response time measurements of the aimed time range fast changes in gas concentration are necessary. These fast changes in gas concentration result in high gas flow rates. Because a thermal flow sensor is used as basic element of the catalytic gas sensor, a high cross sensitivity to gas flow rates exists which would then be interpreted as a change in gas concentration. So, the exact time constant could not be determined yet.

Table 1: Measured characteristics of the catalytic gas sensor. Hydrogen has been used for measurement.

Sensitivity at RH=5%	18 µV/ppm
Sensitivity at RH=50%	13 µV/ppm
Sensitivity at RH=90%	9 µV/ppm
Response time (range)	seconds
Heater temperature	140°C
Power consumption (140°C heater temperature)	10-13 mW

Table 1 gives an overview of the measured characteristics having been determined for the catalytic gas sensor. The results are maximum values because different heights and porosities of the catalytic layer lead to different output voltages (e.g. Fig. 6 shows a sensitivity for hydrogen of 15 µV/ppm). All tests have been done with different relative humidities (5% - 90%) and environmental temperatures (25°C – 55°C). It could be shown here that sensitivity for hydrogen without temperature and humidity compensation is still 9 µV/ppm. The power consumption has also been determined. Here, 10-13 mW have been measured which is, due to the micromechanical fabrication process, comparably low.

4. Conclusion and Outlook

A catalytic gas sensor for hydrogen detection based on sputtered nanoporous platinum has been developed. Therefore, a membrane with heater and thermopiles has been coated with highly porous platinum by means of magnetron RF sputtering. Measurements have been done determining a sensitivity of 18 µV/ppm for hydrogen at maximum. Other combustible gases as ethanol and isopropanol have also been tested and result in much lower sensitivities.

Future works are based on improvement of temperature stability to avoid delamination of the catalytic layer at higher heater temperatures and determination of response time.

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