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Micro-pellistor with integrated porous alumina catalyst support

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Abstract

Micro-pellistors capable to detect hydrocarbons below 50 mW power consumption at 550 °C operation temperature were developed by a novel processing technique. On the top of the full membrane type micro-heaters 1.4 µm thick porous alumina was formed by laterally selective electrochemical etching of the deposited aluminum layer. The porous alumina of the active element is selectively covered by finely dispersed Pt catalyst using alternative methods; such as dropping of $H_2[PtCl_6]$ and sputtering technique, all aiming at deposition of controlled volume and structure of the catalyst. Constant current method in a Wheatstone-bridge configuration was applied in functional tests.

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Keywords: pellistor, porous alumina, micro-hotplate

1. Introduction

Micro-catalytic gas sensors are essential devices for detection of combustive gases up to lower explosion limit (LEL). As the power dissipation of Pt coil based sensors are 300-500 mW intensive research is devoted to reduce it to the 10 mW range while preserving sensitivity and stability. The reported micro-hotplate structures can operate up to 600 °C at a cost of 20-100 mW power consumption [1,2]. Nowadays the research activity is focused on development and processing of stable, nano-structured catalyst layer in MEMS compatible thin film form in terms

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of thermal characteristics and processing issues. In the majority of proposed processes two alternatives are considered; adaptation of dispensing technique used in conventional Pt coil based sensors by deposition of porous oxide suspension mixed with catalyst or deposition of catalyst on the flat surface of the hotplate Being non-compatible with thin-film membranes, the first option raises massive reproducibility and stability issues, e.g. deposition uniform thickness of the sensing matrix as well as adhesion problems [3].

Present works describes a modified processing sequence of a full membrane micro-hotplate to form porous alumina layer on the top for catalyst support, followed by deposition of Pt catalyst. Devices are tested for detection of LPG components.

2. Results and discussion

2.1. Processing

Full membrane micro-hotplate was fabricated focusing on low thermal dissipation and mechanical stability. On the basis of FEM calculations and experimental verification a multilayer structure was selected for catalyst support with embedded Pt heater [4]. In order to improve device performance, the porous catalyst was formed by novel thin film processes. 1µm thick evaporated aluminum film was selectively etched in 0.15mol/l $(COOH)_2$ based electrochemical process using SiO_2/photoresist masking layer. The diameter of pores can be tuned by current density between 20-50 nm. The alternative H_2SO_4 etching couldn't be considered due to the detectable S traces in the porous alumina even after careful cleaning. Sulphur is known as one of the most critical inhibitor in catalyzed combustion.

Having formed the porous alumina layer on the hotplate, the aluminum contacts needed for the electrochemical process were removed by wet etching through inverse photoresist patterns. The final layer structure was formed by further widening the pores with electroless etching in 7mol/l H_3PO_4 (Fig. 2). Membranes were released by deep RIE from the backside (Fig. 1).

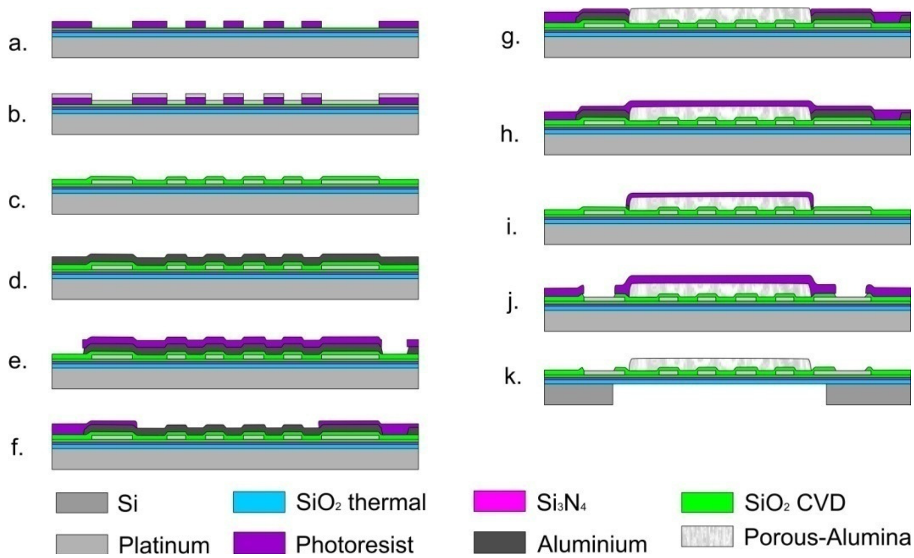

Fig. 1. Process flow of hotplate fabrication. Deposition of multilayer structure with embedded Pt filament (a-c), Laterally selective formation of porous alumina by electrochemical etching (d-k)

2.2. Thermal properties

The sensor chip contains a hotplate pair of identical thermal properties (Fig. 2.a). One is sensitized by catalyst, the other serves as passive reference element for the signal read-out of a Wheatstone bridge configuration. Our goal is to detect LPG or methane; thereby the sensor must be operated at temperature over 450 ^{o}C. The temperature-power characteristics of the hotplate-pair reveal that power of 50 mW is required to exceed 600 °C. The power-temperature characteristics of the hotplates were calculated by FEM and experimentally confirmed by MMP (micro melting point) technique [4] as shown in Fig. 2.b. Finely dispersed materials in glycerol with melting points in temperature range between 200-900°C were transferred to the surface of the hotplate and dried. The melting-solidification points were determined under stereo microscope to determine the average temperature of the hotplate.

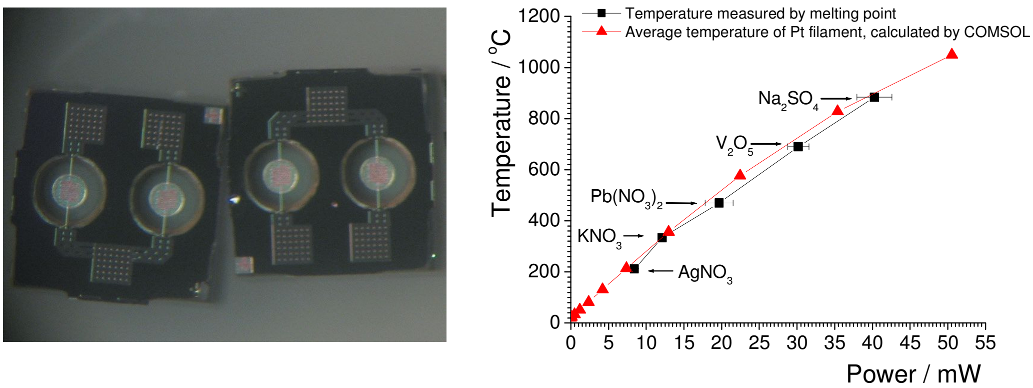

Fig. 2. Optical view of the 1x1mm² pellistor chips. The heaters in the centre of the membranes are coated by 120 µm diameter circular porous alumina layers (left). Calculated and measured power-temperature characteristic of the hotplates (right).

2.3. Catalyst deposition

Two methods were investigated for deposition of Pt: sputtering via mask and drop coating of preprocessed $H_2[PtCl_6]$ diluted in water [5]. A single drop hanging on a capillary is gently attached to the porous surface. Due to surface tension the deposition is laterally limited by the porous surface. The transferred drop was dried and $H_2[PtCl_6]$ was decomposed by programmed self heating of the hotplate. The amount of transferred Pt was controlled by the concentration of solution (Fig. 3.)

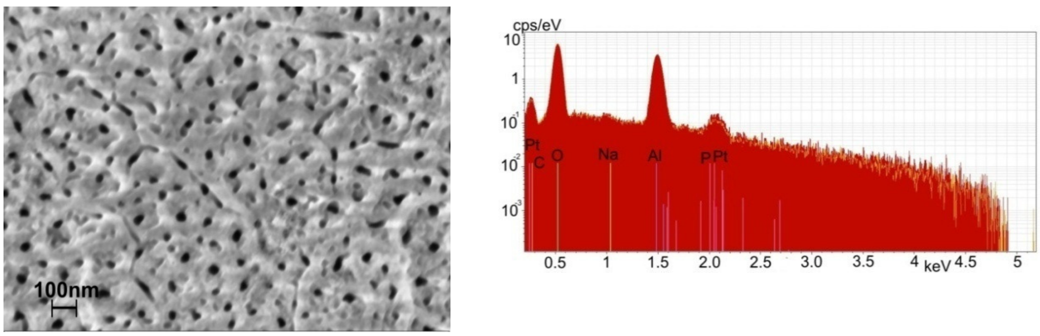

Fig. 3. SEM view (left) and EDS spectrum (right) of porous alumina after accomplishment of drop coating. The diameter of the 1.4µm deep perpendicular pores is in the range of 30-40nm.

2.4. Functional test

Responses on propane up to LEL were measured for sensors containing different amount of Pt as shown in Fig. 4. The rise time (t_{90}) is below 13 s in all cases, however sensors by drop deposited Pt exhibit better reproducibility.

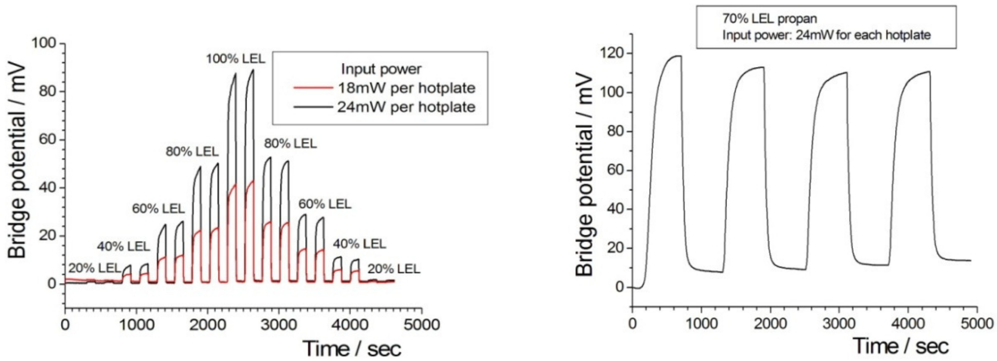

Fig. 4. Pellistor response for propane – dropped $H_2[PtCl_6]$ resulting in ~4w% Pt in porous alumina *(left).* Pellistor response for propane – sputtered Pt. 10w% Pt in porous alumina (right).

The cumulative effect of pore size and Pt content is shown in Fig. 5. The sensitivity increases with Pt content until the alumina layer remains porous. If the amount of deposited Pt is so high that starts to fill the pores, the active surface drastically reduced and may become flat. This is manifested in the remarkable drop in sensitivity (Fig. 5. b.).

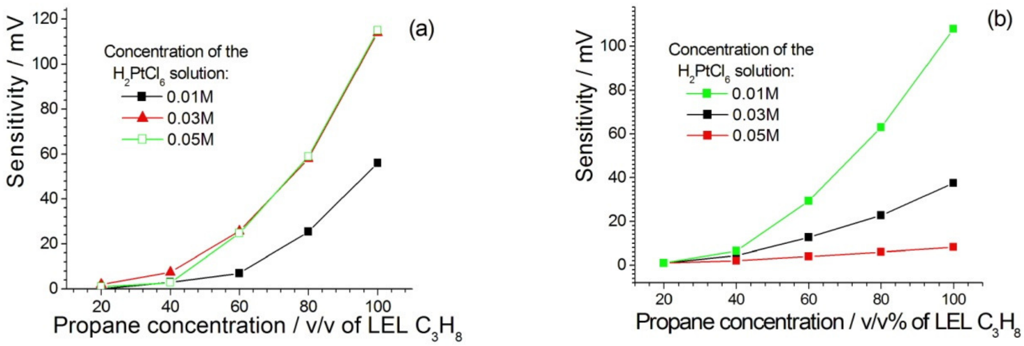

Fig. 5. Pellistor responses for propane . Activation by 1-1 drop $H_2[PtCl_6]$ in all cases. Average pore diameter is 50nm (a) and 20 nm (b)

3. Conclusion

Micro-pellistors were constructed by adaptation of laterally selective electrochemical etching of Aluminum layer. The resulted thin film porous alumina on the top of micro-hotplates in combination with a subsequent catalyst deposition process provides high surface and enables to form uniform micro-pellistors with better sensitivity and controllable characteristics.

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