Micro-catalytic gas sensor operating modes for extended life service, increasing sensitivity to target gases and power consumption reduction

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Micro-catalytic gas sensor operating modes for extended life service, increasing sensitivity to target gases and power consumption reduction

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Abstract. Catalytic gas sensors are among of the most old and widespread gas sensors for combustible gas concentration measurements. However, power consumption these sensors provide is relatively high for modern electronic applications. In this paper research results of combination a silicon MEMS fabrication with operating modes for extended life service, increasing sensitivity to target gases and power consumption reduction are presented. The described solutions allow achieving long-term stability of the sensor in difficult operating conditions - the main requirement for industrial applications, where the continuity of the process is of high value expressed in tangible assets and human lives.

1. Introduction

Nowadays, the industrial safety standards are tougher with respect to monitoring of working environmental conditions. Technological processes became more high value expressed in tangible assets and human lives. Throughout the industry, transportation, and even domestic applications, the concept of IoT is being introduced. For successful implementation of IoT concept requires long-term stable sensors and actuators for different physical values. When IoT control becomes total, instability or drift of the sensor signal results in either a false alarm or incorrect control signals. As an example, one can cite here, an attempt to unite a wireless network of all combustible gas sensors into one network and an attempt to build on their basis a joint map of mine combustible gases emission. Even attempts to create a single picture of gas pollution in local place, for example mine tunnel, based on one type of sensor stumble upon the problem of long-term stability in various application conditions. The same type of catalytic sensors can be found in portable devices on the body of miners which experiencing constant vibration and gas flow changes and stationary devices in the ventilation system, where the vibrations are minimal and the gas flow is stable [1]. It can be seen from these proposals that factors affect a sensor signal localized in one single environment may affect dramatically on sensitivity to target gases. It can be seen from these proposals that factors affect a sensor signal localized in one single environment may affect dramatically on sensitivity to target gases. The separation can be achieved by application of machine learning techniques to data analysis. In terms of machine learning this is the classification task. The result of the classification can be used as equivalent of gas detector thresholds to fire alarms. But for successful implementations of IoT...
conception and machine learning need use gas sensors with operating modes for extended life service, increasing sensitivity to target gases and power consumption reduction [2].

Development of wireless sensors significantly improves safety capability and adds new functionality. Since wireless sensors use batteries as the sole energy source, the energy efficiency becomes critical in such applications. The dominating technique used by the industry in explosive gas measurement exploits the catalytic-calorimetric transduction principle. Due to their primary function the alarming systems may measure the risk concentration of flammable gases without distinguishing the gas types [3]. Although these sensors are still produced in a similar form like in the early fifties [4], in view of the required low energy consumption essential in the expanding field of IoT soon will be exhausted. Currently, the lowest energy consumption of the available beads type wire heaters catalytic sensors (pellistor) is c.a. 120 mW for a 10µ Pt wire covered with SiO2 glass [5], but the typically applied 20µ Pt wires for automatic made catalytic beads [6] dissipate 190-230mW at 450°C constant working temperature for a pair of heating elements.

The modern design of catalytic sensors aims at the reduction of power consumption. The hardware approach involves the development of microhotplate platforms and novel catalyst material [7, 8] - typically using ceramic and silicon MEMS technology, whereas the software solution is the pulsed operation mode instead of the classical stationary mode [9]. In our research we focused on first way using advance which given silicon based MEMS technology for micro-catalytic gas sensor fabrication but changing bulk to planar construction of the sensor need take in account physical principles which can have influence on operating modes for extended life service, increasing sensitivity to target gases and power consumption reduction.

The transfer from the 3D bead type to microplanar design raises many challenges. The highest is the need for novel catalyst what exhibits c.a. one order of magnitude higher chemical activity. It can be the modification of the catalyst mixture of platinum group metals dispersed on nanostructured Al2O3 or ZrO2 ceramics. The stability and behaviour of those materials at high working temperatures has already been tested over tens of years in real working conditions (mines, gas line pipes, leakage alarm systems and etc.). The Pt filament however loses its stability at high temperature (over 550°C) and limits the life time of the device. The straightforward solution is to further develop the catalyst what is effective at lower temperature. Nevertheless, considering the quasi linear heating power-temperature relationship of the hotplate and the corresponding exponential characteristics of the catalytic reactions, an increase in the operating temperature can also correct the device performance, but at a cost of the severely limited long-term stability of the sensors.

### 2. Materials and method

The micro-pellistor is contains two identical hotplates heated by embedded Pt filaments. One of the hotplates is covered with catalyst, whereas the other with passive materials to serve as active and reference compensator elements, respectively. There is no additional thermometer embedded, the resistance of the filament is used for temperature read-out. The typical operation range is 450-500°C. If flammable gas is present in the open-air environment, the exothermic combustion on the active element will lead to its temperature increase, whereas the temperature of the reference remains unchanged. This configuration enables to eliminate the effect of humidity, the temperature and the thermal conductivity changes of the ambient as all these parameters lead to similar responses of the two components. Heat transfer related to gas flow is eliminated by a proper encapsulation; a porous cap limits the mass transfer to the diffusion. Nevertheless, due to the different colours of the dark catalytic and the white/grey reference the emissivity is different but this phenomenon becomes dominating only at higher temperatures.

Before developing catalysts and MEMS microhotplates a comprehensive analysis of failures and malfunctions of the sensor based, a list of typical failures arising from the operation of the sensor were compiled. The source of the analysis was both our own work [10-11] and the experience of other authors [12-16]. The list of failures was classified in three areas - technological, functional and electrical, and two parameters related to the parts of the sensor - the catalyst and the microheater. Faults in electrical directions are classified only by the operating mode, since they are associated only with the specifics used to maintain the sensor temperature by the type of electronic circuit. The
classification of failures in the operation of the catalytic beads type wire heaters sensors is presented in Table 1.

| Technological                  | Functional                          | Electric              |
|--------------------------------|-------------------------------------|-----------------------|
| Catalyst                       | Microhotplate                       | Catalyst              |
| Weak catalytic activity        | Contact area decomposition           | Measurement           |
| (a factor in the catalyst      | (a factor of assembly technology -  | at a constant         |
| synthesis methodology)         | as a result of low vibration        | temperature            |
| degradation)                   | resistance of the sensor)           | (the most rational    |
|                                |                                     | mode of operation,    |
|                                |                                     | but reduces the       |
|                                |                                     | sensor signal         |
|                                |                                     | due to the lack of    |
|                                |                                     | autocatalysis)        |
| The imbalance                  | Non uniform temperature profile     | Poisoning with        |
| between the passive and active | (topology design factor -         | organosilicon and     |
| elements of the sensor         | consequence of low selectivity to   | sulfur-containing     |
| (the factor of uneven dosage   | combustible gases)                  | compounds (factor of  |
| of materials on the microheater)|                                     | incorrect arrangement  |
|                                |                                     | of the sensor package -it |
|                                |                                     | is necessary to use    |
|                                |                                     | a filter)              |
| Degradation during operation   | Increased power consumption         | Changing the resistance|
| in air (a factor of the catalyst| (the factor of the presence of the | of the heating element |
| synthesis methodology)         | heat sink - incorrect layout of the | (factor of thermo and |
|                                | sensor package)                     | electromigration of   |
|                                |                                     | heater materials - it  |
|                                |                                     | is necessary to lower  |
|                                |                                     | the temperature)       |
|                                |                                     |                       |
|                                |                                     | Measurement            |
|                                |                                     | at a constant          |
|                                |                                     | voltage (the highest   |
|                                |                                     | signal of work, but    |
|                                |                                     | increases the working  |
|                                |                                     | temperature by         |
|                                |                                     | autocatalysis)         |
| Degradation during operation   | Signal reduction due to high        | Concentration          |
| in air (a factor of the catalyst| humidity (operating factor         | overload               |
| synthesis methodology)         | without a comparative element - a  |                       |
|                                | comparative element - a             |                       |
|                                | comparative element is required)    |                       |
|                                |                                     |                       |
| Degradation during operation   | Measurement without a               |                       |
| in air (a factor of the catalyst| comparative element                 |                       |
| synthesis methodology)         | (reduces power, but memory is      |                       |
|                                | needed for measurements)            |                       |

3. Experimental
Full membrane type microhotplate with identical, embedded double spiral Pt-wire heaters were manufactured and tested. The SEM photo of chip consists of two MEMS microhotplate platforms presented in Figure 1. The diameter of heated area on the membrane is 150 μm. The Pt filaments are sandwiched in TiO$_2$/SiO$_2$ to avoid any contact the ambient during operation. The 25 nm thick TiO$_2$ layers around the 300 nm thick Pt filament is to enhance adhesion to the SiO$_2$. TiO$_2$ is known to prevent the formation of the Pt$_3$Ti inter metallic phase, and thereby offering an improved structural
stability and better TCR of the filament. For the membrane release KOH back side etching was applied. The targeted 550°C operation temperature can be achieved by 27 mW power consumption per one microhotplate element. The long-time stability tests at 600°C after 6 months continuous operation shows 1.1-1.2% resistance change of a single filament. Therefore may conclude that in a Wheatstone-bridge configuration the resistance drift will be much less than the typical for beads type wire heaters required 1% per year [5].

![Figure 1](image1.png)

**Figure 1.** Silicon membrane type microhotplate (a)SEM photo of silicon chip size is 2 x 1.2mm² with two MEMS microhotplate platforms. (b) SEM photo of Pt topology MEMS microhotplate.

For deposition of the catalytic layer onto the microhotplate inkjet printing technology was used. The parameters of this technology determine the requirements for the particles of the catalyst carrier. The main parameter for inkjet printing systems is the viscosity – the viscosity used ink must to be low and inks must consist maximum diameter of solid particles no more 100 nm. MEMS microhotplates were covered by ink containing CeO₂/ZrO₂ particles. The ZrO₂ powder with a characteristic particle size of 60 nm was chosen for the carrier of the catalyst and was impregnated with CeO₂ followed by addition of Pt and Pd catalytic clusters. The catalytic activity of the suspension was improved by addition of Pt and Pd clusters in various amounts and size. Apart from the elemental compositions a significant difference is found in the deposition of the two pastes, i.e. the active and the reference material. The catalyst containing ink is better wetted by the organic binder, and therefore, we have a different mass of materials in the two types of inks with similar viscosity. To select and verify the ink viscosity, a minimum volume of 0.5-2 ml is necessary. In view of the amount needed for the complete coverage of a single microhotplate, this volume is colossal and enough for processing hundreds of sensors, but it is necessary to go on such expenses of material if necessary equal dosage of both materials.

4. Results and Discussion

The presented catalyst exhibits better performance compared to our previous work [17] however, we are still far from the ideal composition. Our main goal, i.e. to synthesize catalyst with high enough chemical power in such a small volume what can deposited on the top of a planar microheater still needs significant effort. Unfortunately, further increase of operation temperature is not viable as leads to deterioration of both the catalyst and the Pt filament as well. We think that the right answer to the problem lies in the application of other materials, e.g. ZrO₂ mixed with novel additives of rare earth metals. The six decade long history of the catalyst development indicates the gravity of the problem.

The detected response signal is the consequence of thermal responses of the active and passive elements, what, beside the chemical activity, is also affected by the difference in the quantity of the
deposited CeO$_2$/ZrO$_2$ catalytic carrier suspensions. In order to get reliable responses the chemical reaction induced temperature change must exceed the value resulted by the above mentioned physical phenomena. Given this phenomenon, before the chemical impregnation the batch of CeO$_2$/ZrO$_2$ material were divided into two equal parts – one for synthesis of the active catalytic material and the other for the reference, chemically inert element. This way both elements exhibit similar specific surface. In order to impregnate the catalyst support with the catalytic metal, salts of palladium chloride (PdCl$_2$) and platinum hexachloro-acid (H$_2$PtCl$_6$) were used. During annealing at high temperature, noble metal clusters form in the catalyst carrier. Both powders (carrier with and without catalysts) were mixed with a glycol/water based solvent to make the inks suitable for inkjet deposition on top of the silicon MEMS microhotplate. The SEM photo of CeO$_2$/ZrO$_2$ particles covered by Pt-Pd catalysts and result of test CeO$_2$/ZrO$_2$ catalysts tests on methane sensitivity is present on Figure 2.

![SEM photo of CeO$_2$/ZrO$_2$ particles covered by Pt-Pd catalysts](image1)

**Figure 2.** Result of test CeO$_2$/ZrO$_2$ catalysts (a) SEM photo of CeO$_2$/ZrO$_2$ particles covered by Pt-Pd catalysts; (b) Sensitivity to CH$_4$ for catalysts based on CeO$_2$/ZrO$_2$ material. Constant temperature method in PWM electronic configuration scheme was using for sensors tests. Response signal is heating power of MEMS microhotplates in relative units for each element.

Also, the geometry of the microhotplate is determining both in lifetime and stability. Due to the temperature gradient related phenomena [14] both the temperature and its gradient along the microhotplate must be kept as low as possible, thereof the temperature of the hotplate surface must be uniform. Our microhotplates were analysed by high resolution visible pyrometry method and very good temperature uniformity was found. The heated area exhibits less than ±10°C temperature difference at the average of 550°C.

### 5. Summary

We presented an approach how to improve the stability of micropellistors. The well-known Wheatstone-bridge configuration enables to detect combustive gas concentration up to and even over their LEL values. The achieved results indicates the great potential for the industries dealing with the combustible and hazardous gases detection in harsh environments - coal mines, oil refactoring. For developed silicon based MEMS microhotplate 550°C operation temperature can be achieved by 27 mW power consumption per one microhotplate element. The long-time stability tests at 600°C after 6 months continuous operation shows 1.1-1.2% resistance change of a single filament. Therefore may conclude that in a Wheatstone-bridge configuration the resistance drift will be much less than the typical for beads type wire heaters required 1% per year.

With further development of the catalyst material we expect to improve the sensitivity, and thereby to expand the detection limit much below the 10% LEL. Our future work will also aim at the integration of the sensor with the wireless network as a new perspective for the application of the device [18, 19].
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