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Microsystem in LTCC technology for measurements of gas concentration in a sub-ppm range

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Abstract

Commonly used substrates for resistance-type oxide sensors are mainly alumina plates. Other types of ceramics, e.g. based on Low Temperature Cofired Ceramics (LTCC) technology could also be used for this purpose. This technology is well established and enables a creation of 3D structures with channels and cavities that can be formed inside a LTCC micromodule.
The work describes manufacturing of the microsystem containing a gas preconcentration chamber and sensor substrates with improved thermal properties, all fabricated in LTCC technology.

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Keywords: gas sensors; gas preconcentration; adsorbents; LTCC microsystems

1. Introduction

Commonly used in the industry semiconductor gas sensors are good alternative to other detectors due to their low cost, small dimensions and acceptable sensitivity for inspected gases. There is a growing area of applications where very low gas concentrations of a few part per billion (ppb) are needed. Unfortunately, commercially available gas sensors are usually sensitive at levels of several tens of part per million (ppm). Many of gases present in human exhaled air, interesting from the medical point of view, e.g. nitride oxides, acetone, benzene and some VOCs, are in the ppb range [1]. Analysis of exhaled human breath is a non-invasive method for diagnosis of patients' diseases. For example patients with (uncontrolled) *diabetes mellitus* exhale acetone with higher concentration [2]. Sensors able to detect gases at extremely low levels are also needed in other areas, e.g. for detection of explosives or drugs. The European Union directive [3] states that beginning from 2010, the exposure level for benzene in air is as low as

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1.6 ppb, while the limits for toluene and xylene are 70 and 200 ppb, respectively. Sensitivities of oxide based chemoresistive sensors are above this level.

One of the solutions to utilize these sensors is preconcentration of the analyzed gas [4]. In this process a special kind of material (adsorbent) collects gas molecules on its surface and then releases them in a thermal desorption process. Three different types of adsorbents are commercially available: materials based on carbon particles, powders of inorganic oxides and polymeric materials. There is no universal adsorbent working well for all gases, so it is very important to choose the best adsorbent for the application, taking into account the particle size, pore size, surface area and the density of each tested material.

The preconcentration method enables to increase the sensitivity for a specific gas, achieving the concentration factor even more than 1000 [5]. Conventional preconcentrators are typically made of stainless steel tube filled with different adsorbents and a heater wire coiled around the tube [6-8]. The dimensions of such preconcentrators are usually of order of 10 cm or more and the power consumed during the desorption process is even 20 W, so this kind of device is not best suited for using in a portable equipment but rather in the laboratory. The need for smaller and less power consuming preconcentrators led researchers to develop such a device in well-known silicon technology. The micro-preconcentrator could analyze almost 50 gases in 10 min, while power consumption was only 1.5 W [9].

2. Microsystem structure

The authors propose manufacturing of the microsystem containing both a gas preconcentration chamber and sensor substrates developed in LTCC technology. The schematic view of the microsystem is shown in Fig.1.
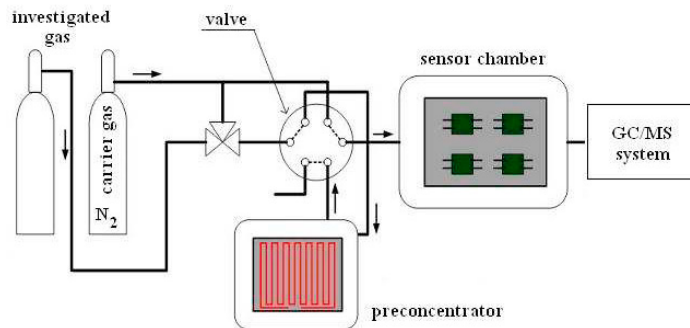

Fig. 1: Schematic view of the measurement microsystem consisted of a preconcentrator and a reaction chamber with sensors array.

3. LTCC preconcentrator

The preconcentrator consists of 8 layers of LTCC green tape foils (DuPont 951, 210 μm thick each), Fig. 2a, and has lateral dimensions 2 by 2 cm. It has thickness of 1.68 mm. There is a spiral-shaped channel filled with adsorbing powder inside the preconcentrator, Fig, 2b. Two heaters covered by the ceramic foils are embedded over and below the channel. The heaters are used to control the temperature needed in thermal desorption cycle. An overall view of the final structure is shown in Fig. 2d. After fabrication of the preconcentrator substrate one has to fill up the internal channel, so it has to be deep and long enough (in our case 500 μm and 12 cm, respectively) to fit the adsorbent particle size and quantity. After filling the channel with the adsorbent (the authors used Carboxen-1018) and gluing the needles (Luer lock connection) the preconcentrator is ready for the tests.
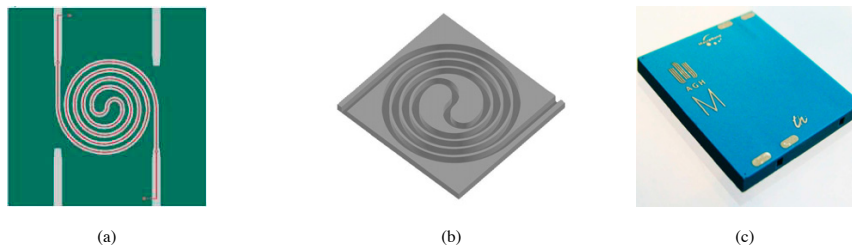
Fig. 2: The LTCC preconcentrator: the spiral heater (a), the laser cut channel (b), and its overall view (c).

4. LTCC sensor

The authors manufactured the detector part of the microsystem using an array of sensors previously fabricated. For many years the authors are using sensors based on metal oxides deposited onto LTCC structures [10]. These ceramic substrates exhibit very good temperature stability and moderate power consumption (570 mW in air at 350^0C). With the goal to reduce the power consumed, what is very important condition for a portable measuring system, the new substrate with a buried heater was designed and experimentally tested. The diameter of the disc was lowered to 3 mm, and by laser cutting a special shape was formed to reduce the thermal mass, Fig.3a. As can be seen from Fig.3b, the temperature distribution in the area of sensor electrodes is very uniform. The power consumption is however still too high and optimizing work is in progress.

Fig. 3: The design (a) and infra-red picture of improved LTCC sensor substrate (b).

5. Experiments

A very important issue is the preconcentrator working environment is that the device is very hot during the purification (300^OC) and desorption (250^OC) processes so a kind of safe chamber was needed. The device temperature should be known and controlled, so a kind of isolation was used. The smallest power losses were obtained for preconcentration chamber made of PTFE and filled with Minus Cryogel Z material (Aerogels Poland Nanotechnology) with very low thermal conductivity coefficient of 0.0014 W/mK. At first the authors tested the time needed to obtain temperature of 300^OC, Fig. 4a, for different amounts of power supplied. Then the optimal parameters for the investigated structure in the chamber were chosen. The adsorbent was preconditioned using the following temperature program: 0.5h at 100ºC, 1h at 200ºC, 1h at 300ºC and 0.5h at 350ºC under the dry nitrogen flow of 50 sccm. As a reference the authors used gas chromatograph SRI 310C. Preconcentration process consisted of 4 phases: adsorption of gas (30 min, at room temperature), system cleaning with N_2, desorption (temperature rise

to 220 ºC) and again cleaning with N_2 at room temperature. As a result the obtained concentration factor (CF) for CH_4 was of order of 100, Fig.4b.
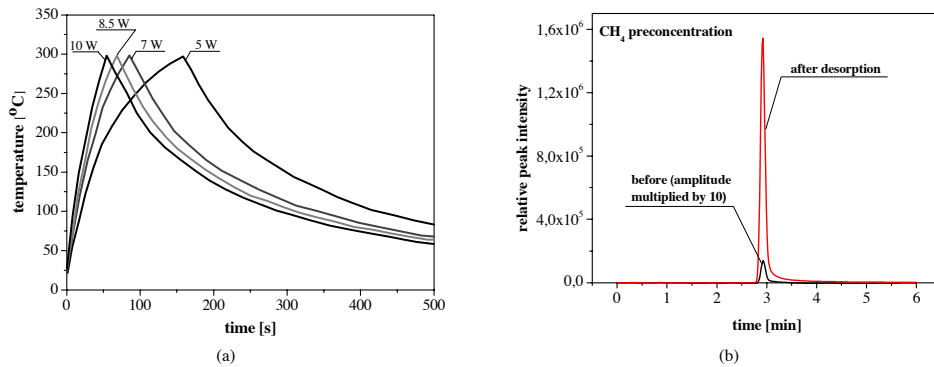

Fig. 4. The tests of a preconcentrator: temperature vs. time for a changing power (a), chromatograms for CH_4 before and after the preconcentration (b).

6. Conclusions

The structure of the preconcentrator manufactured in LTCC technology was presented. The preliminary results of gas concentration showed the CF of about 100. The CF can be higher, depending on the amount and type of the adsorbent selected, adsorption temperature and time, gas flow rate etc. The process parameters and also the channel filling technology should be optimized. The next step is to connect the developed preconcentrator with the gas sensor array. The works are in progress.

Acknowledgements

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