Available online at www.sciencedirect.com
ScienceDirect
Sensors and Actuators B 132 (2008) 216–223
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Alumina MEMS platform for impulse semiconductor and IR optic gas sensors

A.A. Vasiliev [a,*], R.G. Pavelko [a], S. Yu. Gogish-Klushin [b], D. Yu. Kharitonov [b], O.S. Gogish-Klushina [b], A.V. Sokolov [b], A.V. Pisliakov [b], N.N. Samotaev [c]

[a] *University Rovira i Virgili, DEEEA, Tarragona, Spain*
[b] *RRC Kurchatov Institute, Moscow, Russia*
[c] *Moscow Institute of Physical Engineering, Moscow, Russia*

Received 26 August 2007; received in revised form 15 January 2008; accepted 16 January 2008
Available online 30 January 2008

Abstract

In this paper, we discuss the use of a novel ceramic MEMS (CeraMEMS) technology based on the application of thin alumina film (TAF). The membrane is fabricated by the electrolyte spark oxidation of aluminum, consists of nano-crystalline γ-aluminum oxide, and has a thickness of 10–30 μm. The MEMS chip is formed by the fixation of the membrane on alumina ceramic substrate with holes. The MEMS platform demonstrates very high stability at working temperatures up to 600 °C (life time >5 years, drift of heater resistance ∼3% per year at 550 °C). It was shown that this membrane chip could be used for the fabrication of gas sensors (semiconductor, thermocatalytic, and NDIR optic) operating in impulse regime. The thermal response time of the heater is of about 80 ms, the chip remains working after 7 millions on–off cycles at 450 °C. Average power consumption of methane sensors based on these platforms is <1 mW. This low power consumption enables the application of CeraMEMS sensors in wireless networks.

Keywords: Thin alumina film (TAF); CeraMEMS; Semiconductor; Optic gas sensor; Wireless network

1. Introduction

Recently, many research groups in the world investigate the possibility of the fabrication of high-temperature gas sensors of different types based on micromachining technology (for example, [1–3]). The application of this technology enables a very important improvement of characteristics of semiconductor [1,2], thermocatalytic [4], and IR optic (NDIR) [5] gas sensors. In particular, it makes possible the fabrication of autonomous, wireless instrument, where it is important to minimize power consumption of the sensor operating at high temperature. For these applications, the sensor must work not only at high temperature, but also has to maintain pulsing temperature operation mode necessary for the minimization of power consumption.

The operation principles of gas sensor devices are well known and consist in the following. The semiconductor gas sensor measures a change in the conductivity of sensing layer resulting from a change in charge carriers (electrons or holes) concentration and their mobility due to the chemisorption of gas to be detected. The thermocatalytic sensor determines the heat of the reaction of the oxidation of combustible gases on the surface of catalyst heated up to temperature of 300–500 °C. The concrete value of working temperature depends on the type of gas, which should be measured by the sensor. The heat released in the oxidation reaction leads to an increase in heater temperature, measured by electronic circuit as an increase in its resistance. In the IR optic (NDIR) sensor, the measured value is the reduction of the intensity of IR radiation due to its absorption by a target gas [6]. The absorption bands of the main part of gases important for practical applications lie in a range from 2.5 to 6 μm (for example, HF – about 2.5 μm, hydrocarbons including methane – 3.4 μm, hydrogen sulfate – 3.6 μm, carbon dioxide – 4.2 μm, carbon monoxide – 4.6 μm, nitrogen oxide – 5.6 μm). The main problem, which limits now the application of these very precise and reproducible sensors, is the fabrication of reliable, low cost, and low power consuming radiation

* Corresponding author. Tel.: +34 977 55 86 53; fax: +34 977 55 96 05.
E-mail address: A-A-Vasiliev@yandex.ru (A.A. Vasiliev).

0925-4005/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2008.01.043

sources for this wavelength range. The most promising are light emitting diodes (LED). These diodes based on various semiconductor materials, for example, Pb–Se–Te [7–9] can operate with thermoelectric cooling down to a temperature of about −30 or −60 °C (one or two cooling cascades, respectively) and are characterized by emission band width of ∼0.6 μm. This relatively broad emission band requires the application of interference filters corresponding to exact spectral position of absorption band of a particular gas. The main disadvantage of such sources of IR radiation is their high cost. Therefore, cheaper and simpler thermal sources of IR radiation and, first of all, sources fabricated using micromachining technology are of interest. A very promising radiation source was developed by Patinor Coating Ltd. [5]. In this source, the diamond like carbon film (DLC) was deposited on SiO_2/Si_3N_4 membrane. The film can be used as a source of radiation for at least one year; however, possible oxidation or hydrolysis of DLC material pushed us to look for other solutions described in this paper. Therefore, the target of this research was the development of new CeraMEMS platforms, which could be used for the fabrication of semiconductor and thermocatalytic gas sensors and as IR radiation sources of NDIR gas sensors.

In spite of strong efforts paid to the optimization of MEMS technology, usual membranes based on silicon wafers and consisting of several layers of silicon oxide/silicon nitride meet some technical and economical problems. The most important among them is insufficient adhesion of platinum used as a heater material to the top layer of the membrane (silicon oxide or silicon nitride). Adhesion can be improved by the application of adhesive layers, for example, titanium [10,11], tantalum or chromium [12]; however, this improvement is significant only at room and moderate temperature. The platinum layer fabricated with the application of these adhesive layers is wire bondable, if it is not heated up to temperature exceeding ∼400 °C. However, the operation temperature of methane sensors is 450–500 °C. At such high temperature, the adhesive layer is oxidized, and platinum adhesion is lost. Moreover, usual process of the formation of metal oxide sensing layers of semiconductor and thermocatalytic gas sensors requires annealing at temperature in a range of 700–800 °C. Therefore, the whole wafer with deposited sensing layers should be annealed at such high temperature before dicing and wire bonding to meet the requirements of mass-fabrication. Unfortunately, until now the deposition of platinum layers, which could be used for these heaters, remains to be a problem. Another problem is the stability and fatigue of the membrane and chemical stability of silicon nitride in the reaction of pyrohydrolysis at high temperature. Both these problems arise especially in pulsing temperature mode of sensor operation. The third, economical problem is the application of clean rooms and other expensive equipment for the fabrication of silicon oxide/silicon nitride based micromachined heaters. High cost of maintenance of this equipment makes expensive the production of such devices, if they are produced in a scale typical of gas sensors that is maximum several millions units per year. This limitation is especially important, when a new gas sensor production line starts up.

We introduced a new MEMS technology based on the application of thin alumina ceramic films (CeraMEMS) [13]. This technology is free of the disadvantages mentioned above. However, the application of these membranes was limited until now by insufficient stability at pulse heating, which is necessary for wireless instruments with very low power consumption and for gas recognition in pulsing heating mode [14,15]. In this work, we report recent progress in the fabrication of MEMS platforms based on thin alumina film membranes (TAF), which enables the fabrication of microhotplates stable at high temperature (working at temperature up to 600 °C) and in sharp heating mode.

2. Experimental

The scheme of the CeraMEMS chip is presented in Fig. 1. It consists of a rigid frame made of commercial Rubalit 710^{TM} alumina ceramics (1); a thin alumina film, TAF (3) is fixed on this frame with glass binder (2) and covers a laser drilled hole (5). On top of this film, the sensing layer (4) equipped with a meander shaped heater (6) and a digit electrode (8) was deposited by screen printing or drop deposition techniques. The contact pads to the sensing layer and heater (7) are located in room temperature area and enable wire bonding to the TO-8 holder. The CeraMEMS process flow consists of the following steps. (1) Initial material for the substrate is Rubalit 710^{TM} ceramics. The size of the substrate was of 48 mm × 60 mm. (2) Eighty holes were drilled in the ceramic substrate by laser beam. The substrate was laser pre-cut into 80 chips (6 mm × 6 mm). (3) In parallel, the thin alumina membrane (TAF) was fabricated by electrolyte spark oxidation of aluminum foil; the membrane was separated from aluminum by wet etching. (4) Thick film ink consisting of glass particles suspended in a solution of ethylcellulose in terpineol was deposited onto the ceramic substrate using a screen-printing machine. (5) The membrane was pressed to the ceramic substrate covered with the ink. (6) The substrate with the ink and the membrane was dried and then fired at 850 °C. The glass after melting and subsequent solidification fixed the membrane on the ceramic substrate. (7) Platinum heaters and digit electrodes were deposited through a shadow mask onto the whole substrate with membrane. (8) A sensing layer of semiconductor or thermocatalytic type was deposited onto the meander

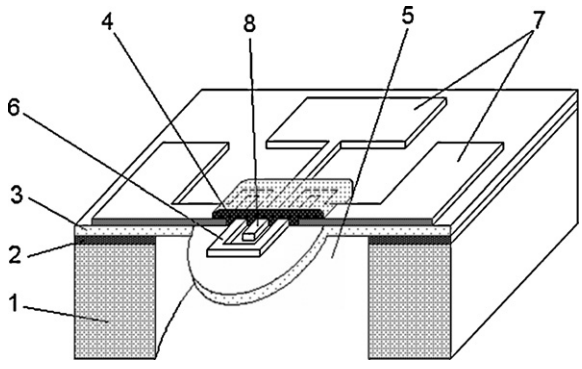

Fig. 1. The scheme of the CeraMEMS chip based on thin alumina film (TAF) designed for gas sensor application. 1–0.6 mm thick ceramic substrate with hole (Rubalit^{TM}; 2 – glass binder layer; 3 – thin alumina film fabricated by electrolyte spark oxidation of aluminum; 4 – gas sensing layer; 5 – laser drilled hole; 6 – meander shaped platinum heater; 7 – contact pads to heater and digit electrode; 8 – digit electrode to the sensing layer.

area of the heaters. (9) The substrate with sensing layers was fired at 720 °C to provide optimal gas sensitivity. (10) The precut substrate was separated into individual chips. (11) The chips were wire bonded onto TO-8 holders; the holders were covered with caps providing explosion proof of the device.

The alumina membrane (with a thickness of about 20 μm) was fabricated by electrolyte spark oxidation of aluminum. In this process, high-voltage break-down runs around the surface of the metal dipped into the electrolyte. At several hundreds volts, the dielectric layer on the electrolyte/metal boundary is broken; this results in micro-sparks. This process leads to the growth of oxide layer. The spark's high temperature forms a uniform, polycrystalline oxide on the surface of metal that adheres efficiently to the metal surface. Electrolyte composition and applied high voltage enable a desired oxide layer to form with certain thickness (in a range from 5 to 100 μm) and with specific distribution of oxide nanoparticles. The optimal thickness of the membrane, which enables the minimization of heat loss due to thermal conductivity of the membrane material and acceptable mechanical properties of the membrane, is equal to about 20 μm. This membrane thickness was used in our experiments. The process of electrolyte spark oxidation used for the fabrication of thin alumina films was described in detail in ref. [16]. The membrane was separated from metal by wet etching in acidic solution and fixed on ceramic wafer with holes (3 mm in diameter) drilled preliminarily using laser beam. For this, the ink containing glass particles suspended in a solution of ethylcellulose in terpineol was spread over the surface of ceramic substrate, the membrane was pressed to the substrate, and the ink was dried and fired at about 850 °C.

Then, the meander shaped heaters were produced by platinum deposition through a shadow mask. Platinum was magnetron sputtered in Ar atmosphere at 1.8×10^{-3} Torr, the temperature of the substrate was of 330–350 K, and the discharge current and voltage were of 250 mA and 0.57 kV, respectively. The deposition rate was of 57 nm/min. This shadow mask process has an advantage compared to photolithography, because porous alumina absorbs photoresist. The choice of platinum as a heater material was caused by the following reason. It is known that among all materials with positive temperature coefficient of resistance (TCR), which could be used in principle for the fabrication of high-temperature sensor heaters (polysilicon, silicides of different metals, diamond like films, pure metals as tungsten or molybdenum, platinum group metals, etc.) only two materials, platinum and ruthenium dioxide, do not change the composition at high temperature in oxygen containing atmosphere. Coating of the polysilicon or silicides with ~1 μm thick silicon oxide or silicon nitride do not help very much, and the resistance of thin films of these materials drifts at 400–500 °C by 30–50% per year due to oxygen diffusion and slow oxidation [17]. RuO_2 is used in the form of thick film composite material in the sensors produced by Figaro Engineering Inc. [18]; however, this material cannot be deposited by sputtering in argon-containing atmosphere (only in $Ne–O_2$ with a very low sputtering rate), because of insufficient stability of gaseous RuO_2 molecules in collisions with heavy Ar ions. In addition, RuO_2 is reduced at 400–500 °C by high concentration of hydrogen. Therefore, in fact, only platinum can be used as a thin film for the fabrication of sensor heaters operating at high temperature, because platinum oxides are not stable at such temperature.

After deposition, the wafer with platinum heaters was annealed at 800 °C for the stabilization of heater parameters (resistance and thermal coefficient of resistance). Excellent adhesion of platinum to our thin alumina film enables the avoidance of the application of any adhesive layer. Perfect adhesion obtained after annealing enables gold wire bonding of the chips, and further annealing of sensing layers deposited on the whole substrate with sensor chips.

The principles of the design of heaters that is the layout, shape and width of platinum lines were described in detail in refs. [2,17]. The main idea is the application of the heater with hot area dimension of about 300 μm determined by the resolution of screen printing or drop dispenser used for sensing layer deposition, the use of the membrane, which is 8–10 times larger than the heater, and the application of heater with resistance exceeding that of lead platinum lines at least by a factor of 5 at room temperature. The shadow mask deposition of platinum used as a heater of microhotplates permits us to obtain approximately 40 μm wide platinum lines. The minimum distance between lines equals also 40 μm. The thickness of platinum coating and the width of lines were optimized taking into account long-term stability of the platinum heater working under harsh conditions and at a temperature up to 600 °C. For these applications, the thickness of platinum should be of about 1 μm. Resulting resistance of the heater was in a range of 10–30 Ω depending on the uniformity of platinum thickness along the substrate.

In the electrolyte spark oxidation of aluminum, thin alumina film with area of 48 mm × 60 mm was produced. This size of the film is due to the dimension of the ceramic substrate used in our work. Therefore, each substrate contained 80 chips. The technology of alumina film fabrication enables the manufacturing of substrate with membranes with area up to 100 mm × 100 mm and containing up to 400 individual chips. The photo of a part of a substrate with sensor chips and the microphoto of the heater area are presented in Fig. 2.

The gas sensing material used in this research was described in detail in ref. [19]. It was obtained from tin (II) sulfate by hydrolysis and H_2O_2 oxidation under controlled pH and temperature conditions. The nano-particle tin dioxide material had a specific area of about 55 m^2/g. After precipitation, the powder was dried and annealed at 600 °C and then suspended again in water. Palladium (3 wt.%) was deposited on the surface of nano-particles from aqueous solution of palladium chloride by reducing with sodium formate. After preparation, the powder was dried and annealed again at 600 °C. The powder was mixed with a solution of ethyl cellulose in terpineol to form printable ink. The ink was deposited on the microheater, dried for 15 min at 150 °C and annealed at 720 °C for 15 min.

The thermal response time of the TAF MEMS was measured using DC source B5-43A, and the heating voltage impulses were formed by a Promax GF-232 function generator powering Omron G6H electromagnetic relay. The maximum frequency of this relay is of 200 Hz. The heater current was determined by the measurement of voltage drop on a load resistor. The last was

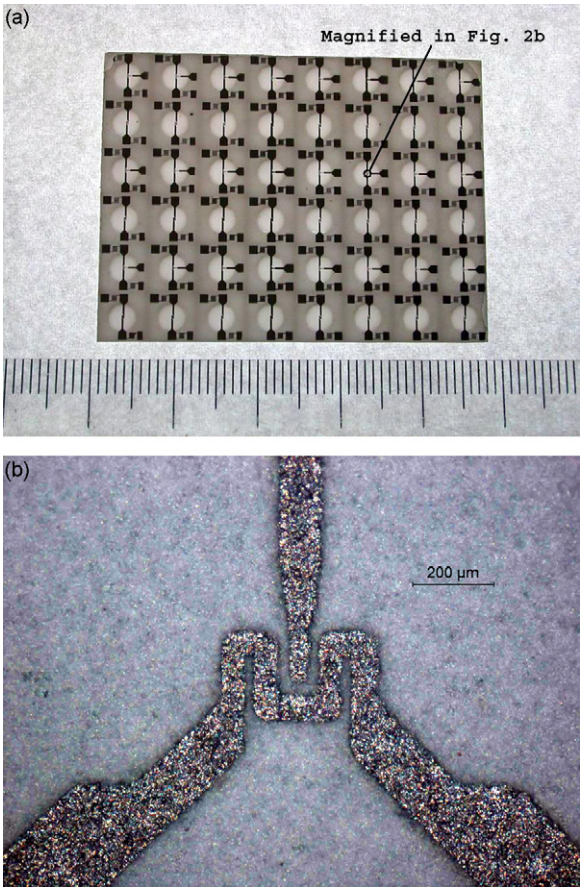

Fig. 2. (a) Photo of a part of an alumina substrate with CeraMEMS sensor chips. The substrate contains microhotplates for semiconductor and thermocatalytic gas sensors. The size of individual chip is of 6 mm × 6 mm, and the heater size is of 250 μm × 400 μm. (b) Microphotography of the central part of the heater and digit electrode of the CeraMEMS chip used for semiconductor sensor fabrication.

recorded by a Tektronix TDS-3012B oscilloscope. The resistance of the heater depending on its temperature was calculated using the value of this current and was saved in a computer for further processing. For the measurement of sensing layer resistance, we used three-electrode scheme of the sensor connection (Fig. 1) that is the sensing layer was deposited between the heater and digit electrode. The current and therefore the resistance of the sensing layer were determined after the measurement of voltage drop on the load resistance connected in series with digit electrode of the sensing layer. The scheme was analogous to that recommended by FIS Inc. for the SB-12A^{TM} gas sensors. This voltage and therefore sensing layer current values as a function of time were also measured by the Tektronix TDS-3012B oscilloscope and were saved in the computer.

Gas concentration of methane in a range from 0.125 to 2.5 vol.% was formed using computer controlled Environics 4000 instrument equipped with mass flow controllers. For this a commercial methane/air mixture from a cylinder (2.5%, Carburos Metalicos) was diluted with synthetic air. The experiments with simultaneous application of three gases, namely CH_4, CO and H_2, were performed also with the application of this instrument, which enabled the formation of up to four component gas mixtures (carrier gas and three admixture gases).

3. Results and discussion

As mentioned above, the application of pulsing mode in TAF CeraMEMS was motivated by three factors: fast thermal excitation of semiconductor sensing material enables the recognition of multiple gases [14,15]; this operation mode makes possible the fabrication of very low power consuming gas sensors (<1 mW in average); it enables the fabrication of simple and cheap source of IR radiation for IR absorption gas sensors. Therefore, in this research we investigated the applicability of the alumina film based platform for these three main applications. For this, we determined thermal response time of the microheater and, therefore, the maximum working frequency of the microhotplate; measured the modulation of temperature at frequencies typical of optical gas detectors (∼10 Hz); and determined methane response of the TAF sensor operating in pulse heating mode.

The material of the TAF membrane was analyzed using SEM (JEOL JSM-6400), element analysis (laser spark spectroscopy of masses), and X-ray diffraction (Siemens D5000). The surface of the TAF membrane (Fig. 3) obtained by electrolyte spark oxidation of aluminum is relatively rough compared to the surface of silicon oxide/silicon nitride one. The relief was found to be of about 1 μm, which means that the platinum film thickness necessary to be deposited as a heater should be at least of about 1 μm as well.

Main impurities (Fig. 4), which were found in the alumina material at relatively high concentration, >0.1 at.%, were B, Mg, Si, Ca and Fe elements, which were common impurities in the initial aluminum alloy used for the oxidation. These impurities cannot migrate into the sensing layer. Sodium and chlorine ions impurities can be removed by careful washing of the membrane in deionized water. A further decrease in impurity level is possible with the application of more pure aluminum as an initial material for the electrolyte-spark oxidation. XRD

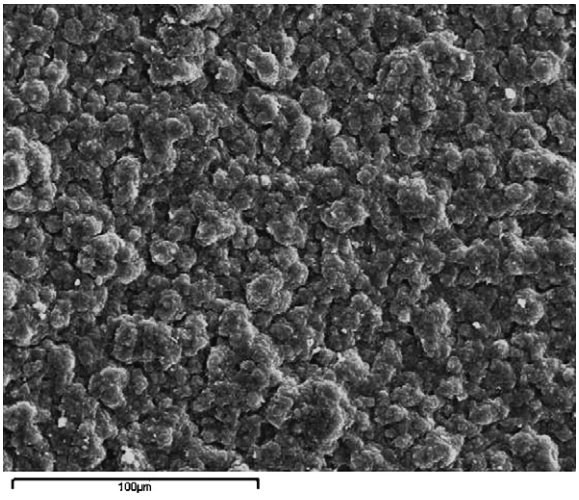

Fig. 3. SEM photograph of the surface of alumina membrane obtained by electrolyte-spark oxidation of Al. The roughness of the surface is of about 1 μm.

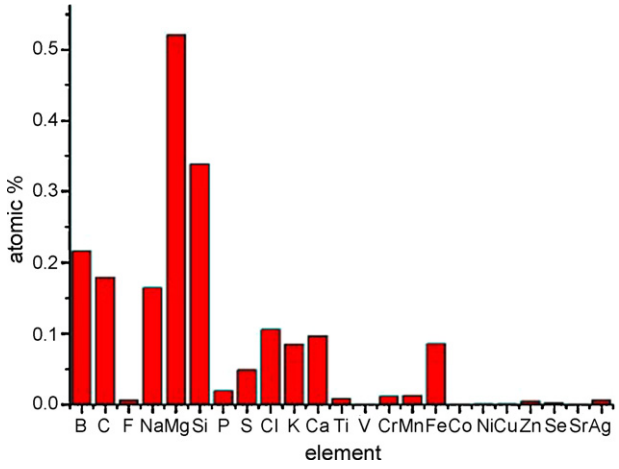

Fig. 4. Results of element analysis of impurities of the TAF membrane used for sensor fabrication. The main material of the membrane is alumina. The membrane was analyzed as-prepared before high-temperature treatment.

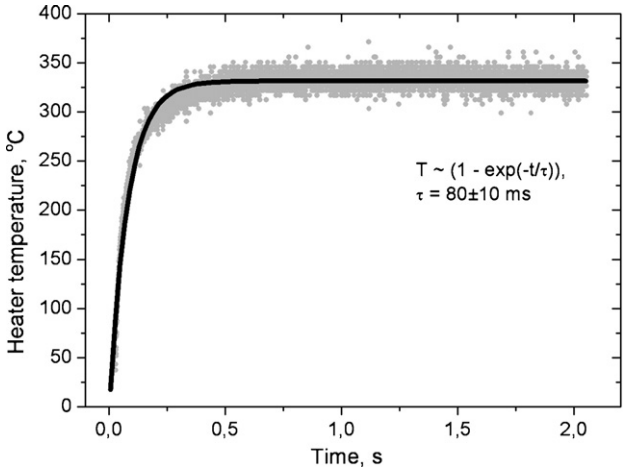

Fig. 6. Thermal response time of the platinum microheater presented in Fig. 1.

analysis (Fig. 5) showed that the TAF material consisted of pure γ-modification of alumina, the crystallite size being of about 20 nm. This crystalline phase is stable up to a temperature of about 1000 °C; above this temperature it transforms into α (corundum) modification. Stability of γ-crystalline phase of our films at working and even annealing temperature assures long-term stability of the sensor microhotplates.

The thermal coefficient of expansion (TCE) of γ-Al_2O_3 ($8.4 \times 10^{-6}\,K^{-1}$ at 20–1000 °C) is close to the value of TCE typical of ceramics used as a substrate in our research (Rubalit 710™). The TCE of Rubalit 710 is equal to 8.5×10^{-6} at 20–1000 °C. The close values of TCE enable high stability of the membrane fixed on ceramic substrate in a wide temperature range.

At a constant temperature of 450 °C, the microhotplate (250 μm × 400 μm heater on a ϕ 3 mm membrane) consumes about 90 mW. The value of temperature was determined using the TCR value of 2800 ppm/K measured in our previous experiments [13]. The heating power consumption corresponds to the values found earlier. The maximum working temperature was found to be of 600 °C. At higher temperature platinum begins to evaporate from the necks between platinum grains and, therefore, must be protected by a certain protective layer. This maximum temperature corresponds to the heating with the aid of the platinum heater of the microhotplate. The temperature of technological heating, which can be used for the formation of sensing layers, is limited, in fact, only by the stability of γ-alumina, which is the material of our TAF membrane. Heater resistance drift at temperatures below 550 °C is less than 3% per year. This result was obtained after the analysis of the drifts of 50 microhotplates. The maximum working time for the microhotplates reaches now 5 years. This operation time was found experimentally.

Temperature response time of the microheater was determined as the time necessary for the stabilization of heater resistance (heater temperature) after supplying a step of voltage. For the calculation of the response time, the response curve was approximated by exponential function $R = R_{max}(1 - e^{-t/\tau})$. The characteristic time determined in this way ($\tau_{0.63}$) is equal to 80 ± 10 ms. (Fig. 6). This relatively short response time enables sensor operation at frequencies up to about 10 Hz.

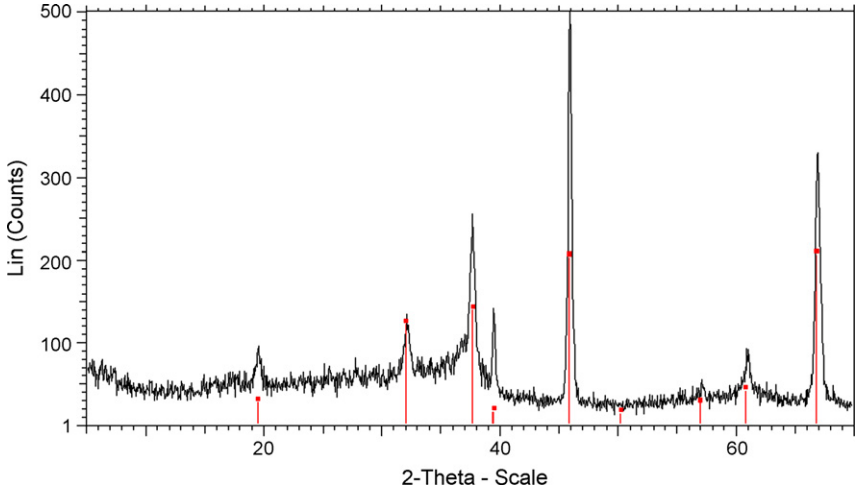

Fig. 5. XRD analysis of the material of TAF membrane. Lines correspond to the γ-alumina.

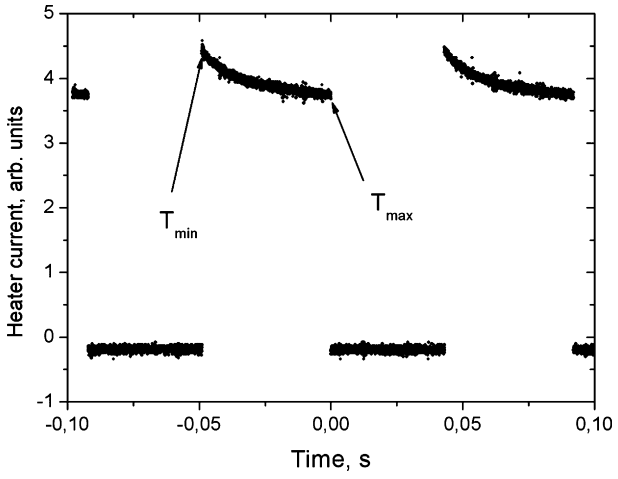

Fig. 7. Heating of the TAF microheater with voltage pulses at frequency of 11 Hz.

The thermal response to a series of impulses was measured at a frequency of 11 Hz (Fig. 7). This frequency corresponds to the requirement of IR gas analytical instrument, because it does not interfere with a 50 or 60 Hz electric network. The estimated difference between maximum and minimum temperatures of the microheater (marked as T_{max} and T_{min} in Fig. 7, respectively) is of about 130 °C (TCR of the platinum layer was taken equal to 2700 ppm/K) at the maximum temperature of 450 °C, that is the modulation of absolute temperature of the heater is ∼18%. This means that according to Stefan-Boltzmann's law, the modulation of the intensity of IR radiation exceeds 50%. This value is sufficient for the application of TAF membrane as a source in IR gas analytical instruments. Vice versa, we proved the possibility to apply indirect heating of the microheater using diode laser radiation. Using 50 mW diode laser beam it is possible to heat the sensing area up to about 450 °C. This means that the chip can be used either for the measurement of radiation intensity (bolometer) or for indirect heating of the sensing layer of gas sensors. Indirect heating improves the stability of the heater compared to heating with electric current and enables high temperature operation of the sensor (>600 °C).

Long-term stability of the heater operating in pulsing heating mode was measured at the maximum temperature of 450 °C and a frequency of 5 Hz. The application of the relatively high frequency was necessary to shorten the time of tests. A temperature of 450 °C is typical of semiconductor and thermocatalytic sensors detecting methane and corresponds to the maximum temperature used for operating tin dioxide based sensors. The microheater does not change considerably the resistance even after 7×10^6 on–off cycles. According to the law, for safety applications, a sensor must measure CH_4 concentration at least every 20 s, and therefore this number of cycles corresponds to more than 3 years of normal sensor operation.

We tested the responses of the sensor with SnO_2/Pd sensing layer to CO and CH_4. These two gases are the most important for domestic and industrial safety applications. Gas responses to different concentrations of methane were determined in two different operation modes of the sensor. The sensor response measured at a constant sensor temperature equal to 450 ± 10 °C

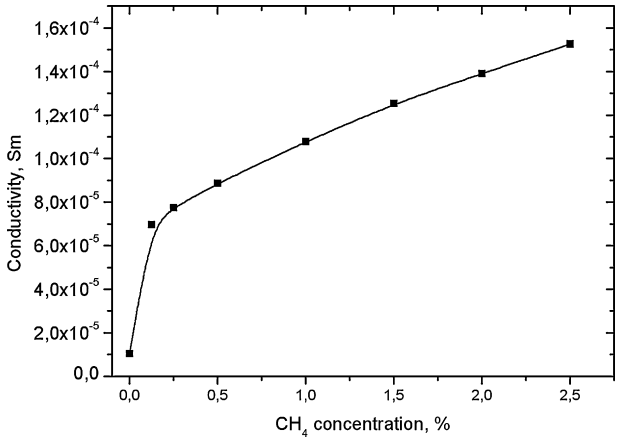

Fig. 8. Response to methane of the CeraMEMS sensor operating at a constant temperature equal to (450 ± 10 °C). Diluting gas is synthetic air.

is presented in Fig. 8. The relative sensor conductivity ($\Delta G/G_0$, where ΔG is a change of conductivity in a certain methane concentration and in pure air, and G_0 is the conductivity in pure air) as a function of methane concentration obeys a law close to the usual square root function typical of the behavior of tin dioxide semiconductors in methane containing atmosphere [20].

The responses of the TAF based sensor operating in pulsing heating mode to different methane concentrations were measured at heating for 250 ms up to 450 °C followed by cooling down to room temperature. The heating time chosen in these experiments is approximately 3 times longer than the thermal response time $\tau_{0.63} = 80$ ms measured earlier. The time $t = 3\tau_{0.63}$ is sufficient for the temperature to reach 95% of the maximum value. An appropriate plot is presented in Fig. 9. It shows that short time of the measurement of sensing layer conductivity could be used for the determination of methane concentration in air. It is clear that, in principle, a time shorter than $3\tau_{0.63}$ can be also applied for the measurement of methane concentration. However, this is not useful, because the sensor temperature in

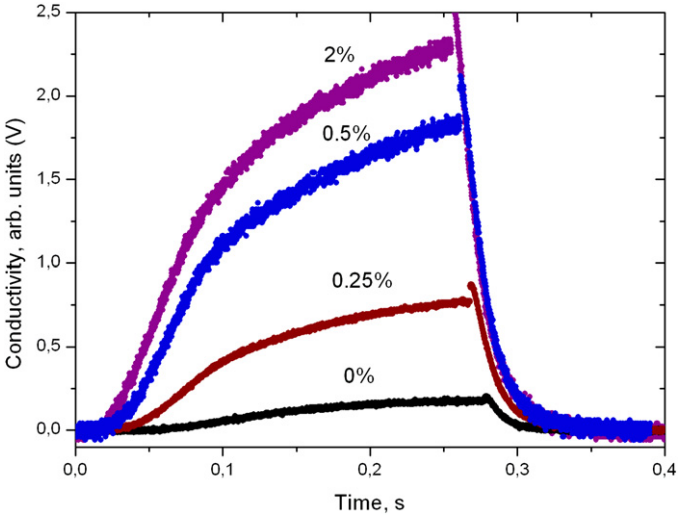

Fig. 9. Responses of the TAF MEMS gas sensor to different concentrations of methane measured in pulsing heating mode. Temperature of the sensor at the end of heating cycle (250 ms) is of 450 °C.

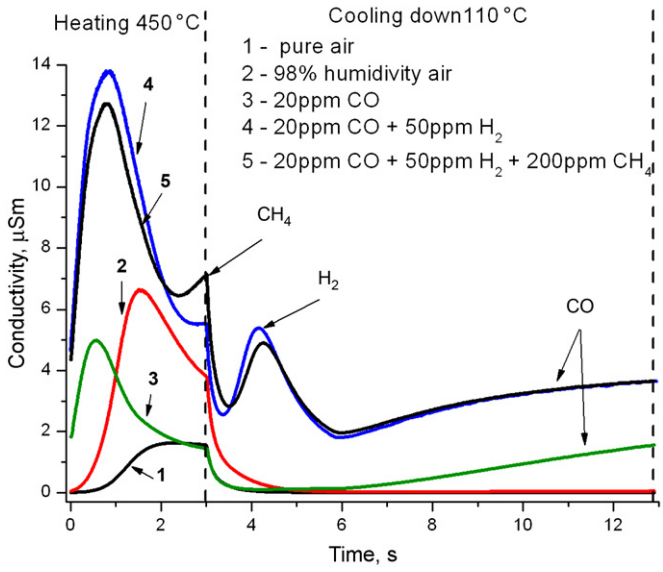

Fig. 10. The response of the sensor operating in cycling pulse heating mode (3 s of heating up to 450 °C followed by 10 s at 110 °C) to methane, carbon monoxide, and hydrogen.

this case would be lower, and therefore the influence of interfering gases, for example H_2, CO, and humidity, would increase. This influence at temperatures lower than 450 °C is illustrated by the plots presented in Fig. 10. In this last case, the sensor was heated up to 450 °C for 3 s, and parasitic maxima corresponding to interfering gases were observed during this heating process.

Therefore, the sensors operating in this mode can be successfully used for low power consumption sensor applications, for example in wireless networks. Indeed, the average power consumption of the sensors, if the interval between measurements is equal to 20 s required by standards, can be below 1 mW.

The selective responses to CO and hydrogen were determined in the operation mode described and examined in detail in ref. [15] and, earlier, in ref. [14]. This mode consists in sensor heating up to 450 °C during 2 s necessary for sensing layer activation followed by measurement of sensing layer conductivity at 110 °C during 6–12 s. In the high-temperature phase of the process, palladium oxides PdO and PdO_2 are formed, and then, during the low-temperature phase, these oxides are consumed for the oxidation of hydrogen and CO. An appropriate response is presented in Fig. 10. The curve contains the maxima corresponding to methane, carbon monoxide, and hydrogen. The microcontroller analysis of these data enables the selective determination of the concentrations of these gases in a gas mixture. The limit of detection was found to be of about 50 ppb for CO, 1 ppm for H_2, and 100 ppm for CH_4. Further analysis of the response curve makes also possible taking into account air humidity.

4. Conclusions

The following advantages of polycrystalline aluminum oxide-based platform (CeraMEMS, Fig. 1) compared to usual SiO_2/Si_3N_4 MEMS devices were confirmed: (1) TAF membranes enable the work at higher temperatures up to 600 °C and, prospectively, up to 800 °C; (2) the alumina microhotplate is more robust than a silicon chip with a thin membrane, and (3) the middle scale production of these chips (10^4–10^6 chips per year) is cheaper compared to silicon technology because it does not need the application of clean-room technology, which is very expensive at this production scale.

It was shown that the alumina-based TAF CeraMEMS platform can be successfully used for the fabrication of semiconductor and thermocatalytic gas sensors operating in pulsing heating mode and as a source of IR radiation for NDIR optical gas sensors. The maximum frequency of the platform is of about 10 Hz (thermal response time $\tau_{0.63}$ is of 80 ms). Operation temperature of the platform can be up to 600 °C at direct heating with electric current. Indirect heating with laser beam can be used for higher temperatures. The sensor can withstand about 7×10^6 on–off cycles sufficient for at least 3-year operation of methane sensor. In the methane detection, the average power consumption of the sensor can be below 1 mW. Selective detection of CO, H_2, and CH_4 was demonstrated to be possible, if the sensing material was excited by heating for 3 s at 450 °C, followed by measurement for 6–12 s at 100–150 °C.

Acknowledgements

The authors acknowledge ISTC grants #2503 and 3424 and CYCIT project #TEC 2006-03671 for partial financial support of the research.

References

[1] P. Fau, M. Sauvan, S. Trautweiler, C. Nayral, L. Erades, A. Maisonnat, B. Chaudret, Nanosized tin oxide sensitive layer on a silicon platform for domestic gas applications, Sens. Actuators B 78 (2001) 83–88.
[2] D. Vincenzi, M.A. Butturi, M. Stefancich, C. Malagi, V. Guidi, M.C. Carotta, G. Martinelli, V. Guarnieri, S. Brida, B. Margesin, F. Giacomozzi, M. Zen, A.A. Vasiliev, A.V. Pisliakov, Low-power thick-film gas sensor obtained by a combination of screen printing and micromachining techniques, Thin Solid Films 391 (2001) 288–292.
[3] F. Udrea, J.W. Gardner, D. Setiadi, J.A. Covington, T. Dogaru, C.C. Lu, W.I. Milne, Design and simulations of SOI CMOS micro-hotplate gas sensors, Sens. Actuators B 78 (2001) 180–190.
[4] C. Ducsa, M. Adam, P. Furjes, M. Hirschfelder, S. Kulinyi, I. Barsony, Explosion-proof monitoring of hydrocarbons by mechanically stabilised, integrable calorimetric microsensors, Sens. Actuators B 95 (2003) 189–194.
[5] V.K. Dmitriev, V.N. Inkin, G.G. Kirpilenko, B.G. Potapov, E.A. Ilyichev, E.Y. Shelukhin, Thermostable resistors based on diamond-like carbon films deposited by CVD method, Diamond Relat. Mater. 10 (2001) 1007–1010.
[6] J. Chou, Hazardous Gas Monitors, McGraw-Hill, 1999 (Chapter 5).
[7] A.A Vasiliev, V.V. Malyshev, E.A. Koltypin, M.A. Maksyutenko, S.V. Nepomnyashchi, Method of divided measurement of methane and propane concentrations with optical sensors, in: 5th International Meeting on Chemical Sensors, Roma, 1994, pp. 654–655 (abstracts).
[8] E.M. Gamarts, A.I. Derniagin, O.G. Zverev, Instruments of XXI century: small analyzers of hydrocarbons, Petersburg J. Electron. (1) (1999) 3–11.
[9] E.M. Gamarts, V.A. Krylov, Optical gas analyzers for safe technologies, Petersburg J. Electron. (1) (2003) 54–59.
[10] http://www.protron-mikrotechnik.de.
[11] A. Vila, J. Puigcorbe, D. Vogel, B. Michel, N. Sabate, I. Gracia, C. Cane, J.R. Morante, Reliability analysis of Pt-Ti micro-hotplates operated at high temperature, Eurosensors XVII, Abstracts, p. 250.

[12] A.A. Vasiliev, R.G. Pavelko, X. Vilanova, N.N. Samotaev, A.V. Sokolov, V.G. Sevastianov, V. Guarnieri, L. Lorenzelli, Micromachined thermocatalytic gas sensor with improved selectivity based on Pd/Pt doped YSZ material, in: 11th International Meeting on Chemical Sensors, Brescia, Italy, July 11–19, 2006, pp. 127–128 (abstracts).
[13] A.A. Vasiliev, S. Yu. Gogish-Klushin, D. Kharitonov, M. Paranjape, A. Pisliakov, V. Pevgov, A. Senkin, The optimization of high-temperature sensor microhotplates based on thin alumina membranes, Eurosensors XVII, Portugal, 2003, pp. 344–347.
[14] A.A. Vasiliev, A.V. Pisliakov, A.V. Sokolov, Thick film sensor chip for CO detection in pulsing mode: detection mechanism, design, and realization, Transducers'01 & Eurosensors XV, Munich, 2001, Proc. vol. 2, pp. 1750–1753.
[15] N.N. Samotaev, A.A. Vasiliev, B.I. Podlepetski, A.V. Sokolov, A.V. Pislaikov, The mechanism of the formation of selective response of semiconductor gas sensor in mixture of CH_4/H_2/CO with air, Sens. Actuators B 127 (2007) 242–247.
[16] I.V. Suminov, A.V. Epelfeld, V.B. Liudin, B.L. Krit, A.M. Borisov, Micro-arc oxidation: theory, technology, equipment, Moscow, "Ecomet", 2005, 352 pp.
[17] A.A. Vasiliev, A.V. Pisliakov, M. Zen, B. Margesin, V. Guarnieri, F. Giacomozzi, S. Brida, G. Soncini, D. Vincenzi, G. Martinelli, M.C. Carotta, M.A. Butturi, Membrane – type Gas Sensor with Thick Film Sensing Layer: Optimization of Heat Losses. Eurosensors XIV, Copenhagen, Denmark, 2000, pp. 379–380.
[18] T. Nomura, Y. Fujimori, M. Kitora, Y. Matsuura, I. Aso, Battery operated semiconductor CO sensor using pulse heating method, Sens. Actuators B 52 (1998) 90–95.
[19] J.H. Kim, J.S. Sung, Yu.M. Son, A.A. Vasiliev, E.A. Koltypin, A.V. Eryshkin, D.Yu. Godovski, A.V. Pisliakov, Propane/butane semiconductor gas sensor with low power consumption, Sens. Actuators B 44 (1997) 452–457.
[20] D.E. Williams, Semiconducting oxides as gas-sensitive resistors, Sens. Actuators B 57 (1999) 1–16.

Biographies

Alexey A. Vasiliev graduated from Moscow Institute of Physics and Technology in 1980, obtained his PhD in 1986 for the "Study of the kinetics of low-temperature reactions of atomic fluorine by ESR method". Gained his doctor of science degree (habilitation) in solid state microelectronics in 2004 for the investigation of "Physical and chemical principles of design of gas sensors based on metal oxide semiconductors and MIS structures with solid electrolyte layer". Recently is working in Sensor group of the University Rovira i Virgili (Tarragona, Spain) and at Russian Research Center Kurchatov Institute. Research interests are related with the study of the kinetics and mechanisms of heterogeneous processes related with chemical sensing, with design and prototyping of gas sensors and instruments based on these sensors.

Roman Pavelko obtained his PhD in Chemistry in 2007 at the Institute of General and Inorganic Chemistry, of Russian Academy of Science, Moscow. At present he is working as scientific associate in Department of Sensor Material Chemistry at the same institute. Also he is doing PhD thesis in Sensor group of the University Rovira i Virgili, (Tarragona, Spain). His research interests concern synthesis of dispersed materials with advanced long-term stability and preset morphology using sol–gel and (co-) precipitation methods and their application as sensing materials for thermocatalytic and semiconductor gas sensors.

Sergey Gogish-Klushin graduated in 1986 from Moscow Mendeleev Institute of Chemical Technology, specialization – engineer technologist in the field of electrochemistry. Works recently as a leading technologist at the Institute of hydrogen power and plasma technology of the Russian Research Center Kurchatov Institute. Research interests are related with the fabrication of protective and decoration coatings on ventil metals and on dielectric materials, semiconductor and thermocatalytic gas sensors based on CeraMEMS technology, and the development of the systems of hydrogen and gas safety and security.

Dmitry Kharitonov graduated in 1975 from Moscow institute of physical engineering, specialization – engineer-physicist in the field of experimental nuclear physics. He obtained his PhD degree in 1988. Recently works at the Institute of hydrogen power and plasma technology of the Russian Research center Kurchatov Institute as general specialist. Main research interests are related with the study of physical and chemical processes at the formation of oxide coatings on ventil metals and at the fabrication of film measuring elements for the systems of hydrogen safety.

Olga Gogish-Klushina graduated in 2004 from Moscow Mendeleev Institute of Chemical Technology, specialization – engineer technologist in the field of electrochemistry. Works recently as an engineer at the Institute of hydrogen power and plasma technology of the Russian Research Center Kurchatov Institute. Research interests are related with the investigation and development of semiconductor and thermacatalytic gas sensors based on CeraMEMS technology and the development of the systems of hydrogen and gas safety and security.

Andrey V. Sokolov received a diploma of electronic engineer in 1979 from Moscow State University. From 1979 to 1983 he was involved in research surface physics phenomena at the Siberian Branch of Russian Academy of Sciences (city of Irkutsk). From 1983 to 1999 he worked in the Russian Aerospace Agency at the department of the design and testing of gas analysis devises. Since 1999 he is research assistant of Standards and Systems Testing Laboratory at the Institute Molecular Physics of Russian Research Center "Kurchatov Institute". His research interests are physics of adsorption phenomena on the surface of the semiconductor material.

Alexandr V. Pisliakov graduated from Polytechnical Institute of Odessa in 1973. He defended his dissertation "Study and development of resistive composition based on tin dioxide for thick film applications" in 1987. He is specialist in physical chemistry and in technology of thick-film gas sensors. His main papers are published in international journal "*Sensors and Actuators B*" and Proceedings of Conferences on Transducers and Chemical Gas Sensors. He is author for more than 50 scientific publications. Since 1979 he works in Central Institute of Precision Machinery now as head of laboratory.

Nikolay N. Samotaev is a PhD student at the Moscow Engineering Physics Institute (State University), Faculty of Automatics and Electronics, Department of Microelectronics and visiting researcher at the Institute Molecular Physics of Russian Research Center "Kurchatov Institute". He has received diploma in electronic engineering in 2005 from Moscow Engineering Physics Institute (Technical University). His research interests are in the physics and technology of different types (metal oxide, MOS FET, thermocatalytic) gas sensors based on semiconductor-integrated technology.