Sensors and Actuators A 194 (2013) 176–180

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

Energy efficient planar catalytic sensor for methane measurement

Evgeny E. Karpov[a], Evgeny F. Karpov[a], Alexey Suchkov[a], Sergey Mironov[a], Alexander Baranov[b,*], Vladimir Sleptsov[b], Lucia Calliari[c]

[a] Scientific and Technical Center of Measuring Gas Sensors, Electrifikatsii st. 26A, 140004 Lubertsy, Moscow region, Russia
[b] "MATI" – Russian State Technological University, Orshanskaya 3, 121552 Moscow, Russia
[c] FBK – Centro Materiali e Microsistemi, Via Sommarive 18, 38123 Trento (TN), Italy

ARTICLE INFO

Article history:
Received 21 September 2012
Received in revised form 24 January 2013
Accepted 24 January 2013
Available online 9 February 2013

Keywords:
Catalytic gas sensor
Sensor operation
Alumina membrane
Methane measurement
Energy consumption

ABSTRACT

We present results on research and development of catalytic sensors fabricated by planar technology on anodic alumina membranes. A method to detect methane was developed which prevents humidity from affecting the sensor performance and, at the same time, reduces energy consumption. The method, based on step heating the sensor during measurements, enables the power consumption of the sensor to decrease from 35 mW typical of the conventional measurement method to 1.2 mW. As a result, a wireless sensor node equipped with a planar sensor and powered by three AA batteries could operate for about one year.

1. Introduction

Europe is full of industrial sites which use volatile, combustible, explosive and toxic agents. Potential risks connected with the presence of these chemical substances are made even worse by the concentration of a lot of people in metropolitan areas that include such sites. The use of methane for cooking and heating is an additional source of risk in metropolitan areas. All of this would require to permanently monitor the atmosphere around industrial enterprises and inside houses and, in case of danger, to timely alarm citizens and, above all, proper services.

To provide quick information about the environment in different places (industrial sites, buildings and houses), gas sensors should be organized in wireless sensor networks that are currently a very active area of research [1–3]. However, most of wireless gas sensor nodes produced nowadays are either powered by grid connection or they could work autonomously only for a short time because of high energy consumption. This limits use of the wireless technology, particularly concerning the development of monitoring systems designed to operate in the absence of power supply from the grid.

In a wireless gas sensor node, energy is mainly used either in the analog circuit for gas measurement or in the digital circuit including a wireless modem and a microcontroller. While rapid development in digital electronics has led to decreased power consumption, progress in gas sensor technology was not that fast. As a result, gas sensors (more exactly, the analog circuit as a whole) are mainly responsible for power consumption in sensor nodes. Power requirements by a selection of commercially available sensors and electronic components involved in the associated circuitry are given in Table 1.

Catalytic, semiconductor and optical sensors are typically used to detect combustible gases. However, in the concentration range of Lower Explosive Limit (LEL), catalytic sensors are most widely used, due to high sensitivity and selectivity, linear response and low cost. Semiconductor sensors are in fact poorly selective and they are highly sensitive in the ppm range, a range not relevant for combustible gas detection. Optical sensors on the other hand, are more expensive (by a factor of 10 and more) than catalytic sensors, though a big progress has been made concerning energy consumption [4] for these sensors. Finally, we should mention that research is underway on colorimetric chemical sensors for gas detection. Up to now however, colorimetric sensors do not provide the required accuracy and sensitivity. Moreover, they have a response time of several minutes [5,6], too long to comply with the safety standards for combustible gases [7].

To overcome the energy efficiency problem, silicon-based [8–11] and MEMs ceramic micromachining technologies [12], enabling lowering energy consumption, have been developed for calorimetric (included catalytic) [11,13] and semiconductor gas sensors [8,9].

---

[*] Corresponding author. Tel.: +7 495 9155719; fax: +7 495 9155719.
E-mail address: baranov@mccinet.ru (A. Baranov).

0924-4247/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.sna.2013.01.057

Table 1
Power consumption for some sensors and electronic components available on the market.

Sensor	Manufacturer	Detected gas	Power consumption (mW)
MIPEX (IR- sensor)	Optosense (Russia)	Methane	5
DTK-2 (catalytic)	STC-MGS (Russia)	Methane	120
TGS2610 (semiconductor)	FIGARO	LP gas	280
NAP-66A (catalytic)	Nemoto	Flammable gases	360
CAT16 (catalytic)	SIXTH SENSE	Combustible gases	<580
CH-A3 (catalytic)	Alphasense	Combustible gases	190
SB-12A (semiconductor)	FIS	Methane	120
MSH-P-HC (IR- sensor)	Dynanment	Methane	220–420

Electronic component	Manufacturer	Role	Power consumption (mW)
CC2500	Texas instruments	Transceiver	Tx: 21.2 mA (0 dBm) Rx: 13.3 mA
ETRX35x	Telegesis	Transceiver	Tx: 31 mA (+3 dBm), Rx: 25 mA (12 MHz clock speed)
MSP430F247	Texas instruments	Microcontroller	Active mode: 321 μA (3 V/1 MHz) Low power mode: 1 μA (3 V/32 kHz)
ATxmega32A4	Atmel	Microcontroller	Active mode: 1.1 mA (3 V/2 MHz) Power-save mode: 0.7 μA (3 V/32 kHz)

The power consumption of silicon-based catalytic and semiconductor sensors is 20–40 mW if operated in the continuous mode. The main element of silicon-based sensors is a membrane of silicon oxide/nitride which supports a platinum heater (in some cases a polysilicon [13,14] or Nickel heater [8]), platinum electrodes and either the catalyst layer, based on Pt/Pd, (for catalytic sensors) or a semiconductor layer of SnO2, ZnO, etc. (for semiconductor sensors). Such a silicon-based membrane faces however problems: insufficient stability and low fatigue resistance for multilayer silicon oxide/silicon nitride membranes, instability of silicon nitride toward hydrolysis at high temperature, poor adhesion of Pt electrodes and of sensing layers to the membrane material.

To solve these problems, a $\gamma\text{-Al}_2\text{O}_3$ MEMs membrane, obtained by anodic oxidation of Al in electrolyte and subsequent annealing, has been proposed [14]. The power consumption of these micro hotplates is around 70 mW in the continuous operation mode. The $\gamma\text{-Al}_2\text{O}_3$ membrane is stretched on a rigid ceramic substrate with previously drilled holes, a layout which often leads however to membrane failure because of bending caused by thermal expansion during heating. The problem can be solved using a free wedge-shaped membrane or a membrane only partially linked to a rigid ceramic frame.

The present work considers the development of catalytic sensors for methane detection. The goal is to minimize energy consumption through consideration of issues related to both sensor fabrication and sensor operation. Crucial points in this regard are

- the transition from traditional catalytic bead sensors to a planar design;
- the use of free edge alumina membranes;
- the use of analog circuits with a single sensor instead of the traditional Wheatstone bridge which involves two sensors;
- sensor operation in a pulsed, instead of a continuous, regime.

2. Experimental

Sensor supports are 30 μm thick nano-porous gamma alumina membranes fabricated by anodic oxidation of an Al foil (Fig. 1a). Micro-heater patterns are formed by lithography on top of the membrane. Micro-heaters are deposited by magnetron sputtering of a platinum target and covered by thin film layer of Al_2O_3 to prevent its degradation. The heated area is about $200 \times 200\,\mu m^2$. To avoid bending of the membrane during periodic heating (eventually leading to membrane failure) and to further decrease energy consumption, we use a free wedge-shaped membrane, without linking it to a rigid alumina frame (Fig. 1b).

The porous gamma alumina membrane is impregnated with catalytic metals (Pd and Pt) using salts of palladium chloride ($PdCl_2$) and platinum acid (H_2PtCl_6) which are separately dissolved in water solution of HCl at room temperature. The obtained solutions are alternately dropped onto the membrane. After annealing at 500 °C, noble metal clusters are formed on the catalyst support (Fig. 1c).

The measurement circuit is based on the microcontroller ATxmega32A4 with wireless interface between the sensor node and the computer. Wireless data communication between sensor node and computer is provided by Telegesis ETRX357 and Telegesis USB transceivers, located at the sensor node and at the computer, respectively. MathWorks MATLAB with specific software is used to control the sensor node, for data acquisition and processing, as well as for real time data display. A detailed description of the electrical circuit is given in [15,16].

The methane concentration is measured using a circuit with a resistivity divider which is included working sensor and calibrated sensor (the measured method is described below). The sensor temperature is monitored by measuring changes in the heater resistance. As a further means to reduce energy consumption, the sensor is operated in a periodic, rather than continuous, regime.

3. Sensor operation

A *Wheatstone bridge* analog circuit, involving working and reference sensor, is typically used in most gas detection systems to prevent environmental parameters (in particular, humidity and temperature) from affecting measurement results. To reduce energy consumption, we developed a measurement method based on an analog circuit with a single working sensor. The idea is to have this single sensor operating as working and reference sensor.

To this end, measurements are performed at different temperatures, above and below the methane oxidation temperature on the catalyst. As the influence of environmental parameters on the sensor is the same at different temperatures, this is a way to compensate the influence of humidity, ambient temperature and other uncontrolled factors on the sensor response. Temperatures to be used in the measurements were defined on the base of physical process during methane burning and are taken before the beginning of the kinetic region (~200 °C) and after the beginning of the external diffusion region (above ~400 °C) for methane. We have chosen 200 °C and 450 °C, respectively.

At a temperature of 200 °C, combustion of methane does not occur, but the sensor response is affected by environmental parameters (ambient temperature, humidity, pressure and other non-controllable factors). At a temperature of 450 °C, the

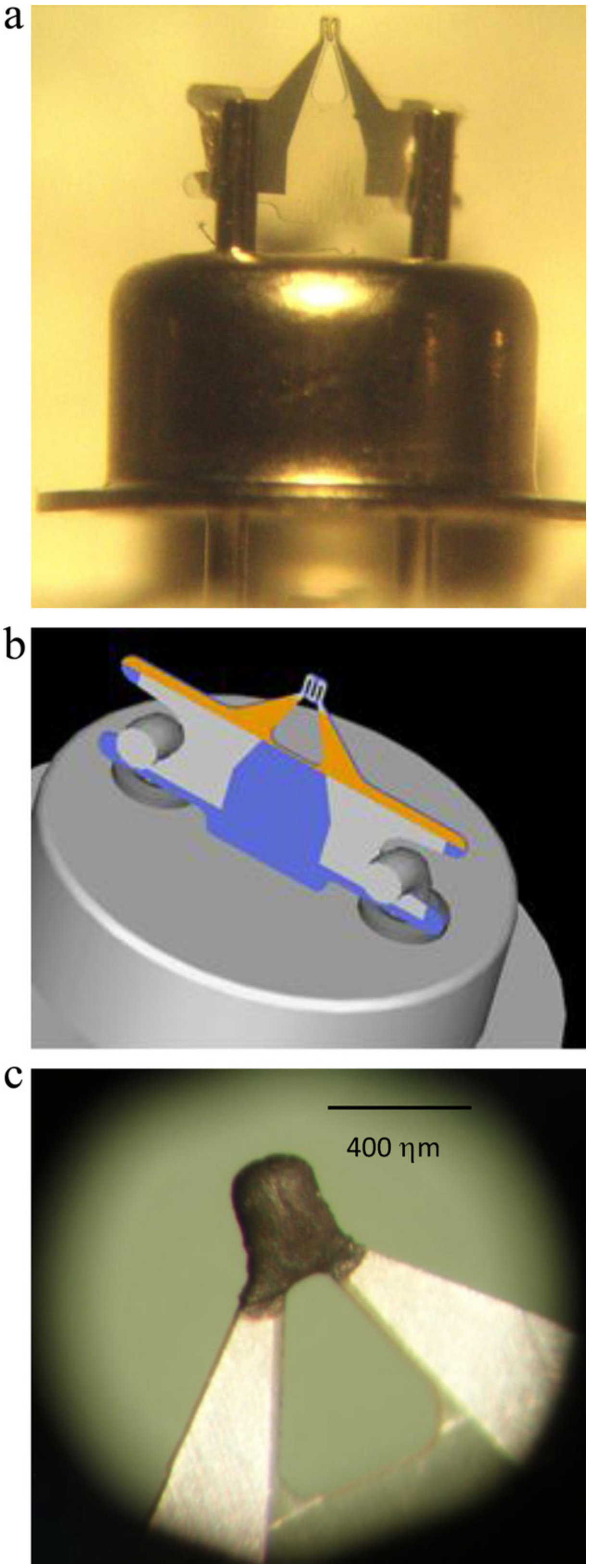

Fig. 1. (a) Optical image of the sensor fixed in the casing TO-8, (b) Sketch of the sensor membrane with microheater (blue – alumina membrane, gray – platinum and yellow – thin film passivation layer of Al_2O_3), (c) Scanning electron micrograph of the microheater covered by the catalyst. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

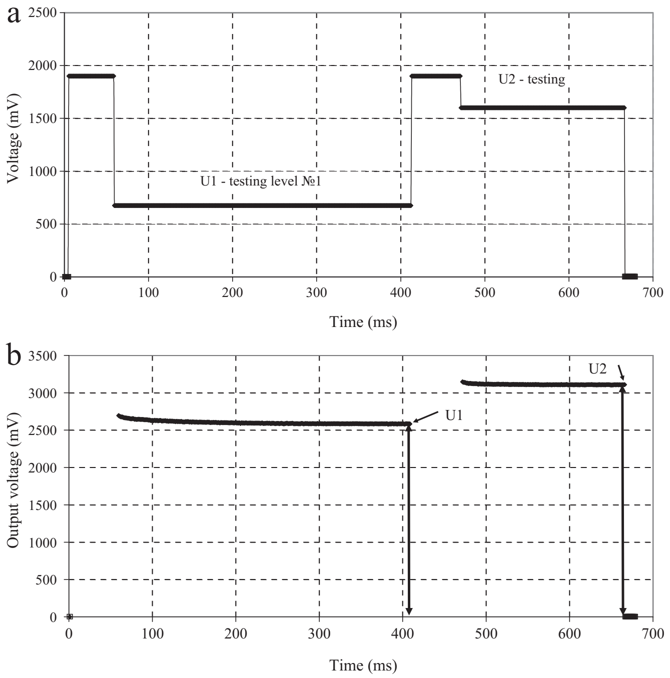

Fig. 2. (a) Voltage pulses applied to the sensor heater, (b) Output voltage of the sensor at the end of the second and fourth voltage pulse. Output signal $\Delta U = U1 - U2$.

sensor response depends both on environmental parameters and on methane combustion. Since environmental parameters remain constant during a single measurement, their effect can be eliminated by taking the difference in the sensor response at the two temperatures, without the need to rely upon a Wheatstone bridge circuit. This operation method will be referred to as “differential method of measurement”.

Several measuring conditions were explored to implement the differential method of measurement, trying to minimize energy consumption on the one hand and the effect of humidity on the other hand. It turned out that the best way to implement the method consists in the application of four voltage pulses in the regime of voltage stabilization. Of these voltage pulses, two are needed to quickly achieve the required temperature (i.e. 200 °C and 450 °C), while the other two are used to take measurements (Fig. 2a).

The first pulse (nearly 1990 mV for 55 ms) provides the sensor with a fast temperature ramp to heat the sensor to the desired temperature (200 °C). Care has however to be exercised to avoid damaging the heater which means, as we could establish, that the heater temperature cannot exceed 500 °C.

The second pulse (around 675 mV for 350 ms) keeps the sensor temperature around 200 °C which corresponds to the beginning of the kinetic region of catalysis and it is sufficient to evaporate water from the sensor surface.

The third voltage pulse (nearly 1900 mV for 55 ms) provides the sensor with a second fast temperature ramp to heat the sensor.

Finally, the fourth voltage pulse (nearly 1600 mV for 200 ms) stabilizes the sensor temperature around 450 °C, where diffusion-limited combustion of methane begins on the catalyst surface. At this fourth stage, the methane concentration is measured. The fourth voltage pulse is followed by a 30 s pause (no voltage pulses are applied) after which a new measurement cycle begins.

Output voltage of the sensor is the voltage difference $\Delta U = U_2 - U_1$ (see Fig. 2b) measured at the end of stage 4 and 2 respectively.

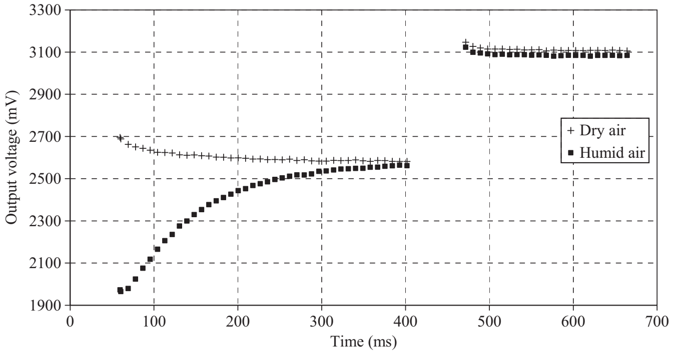

Fig. 3. Sensor response during the second and the fourth voltage pulse in dry and humid (100%) air.

4. Results and discussion

Figs. 3–5 present the sensor response under different working conditions.

Fig. 3 shows the effect of humidity on the sensor response. The sensor is operated in dry and humid air at zero concentration of methane. In dry air, the sensor response is practically constant during the second and fourth voltage pulses. In humid air on the other hand, the sensor response varies greatly during the second voltage pulse. The variation is due to evaporation of moisture, not fully removed during the previous (first) voltage pulse. The duration of the second voltage pulse is indeed chosen according to the time needed to get rid of moisture. At the fourth voltage pulse, the sensor response is the same in dry and moist air. We thus see that measurements results are not affected by moisture if the voltage difference $\Delta U = U_2 - U_1$ is taken as the sensor response.

Fig. 4 shows the sensor response at different concentrations of methane in dry and humid air. In all cases, we see that a pulse duration of 350 ms for the second voltage pulse is enough to completely evaporate the water adsorbed at the sensor surface. Moreover, the sensor response at this second stage does not depend on methane concentration, as the sensor temperature is not high enough for methane combustion on the catalyst surface. On the other hand, the sensor response does not depend on humidity at the fourth stage and it is only affected by methane concentration. During this fourth voltage pulse, the detected methane concentration initially increases with time and then reaches a saturation level (see Fig. 4). As a consequence, the duration of this voltage pulse is chosen in such a way as to ensure reaching the saturation level.

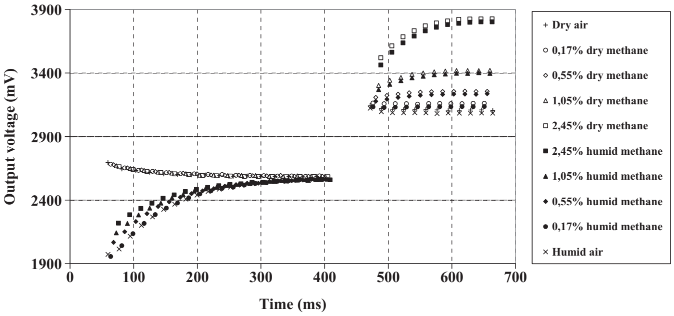

Fig. 4. Sensor response at different concentrations of methane in dry and humid air.

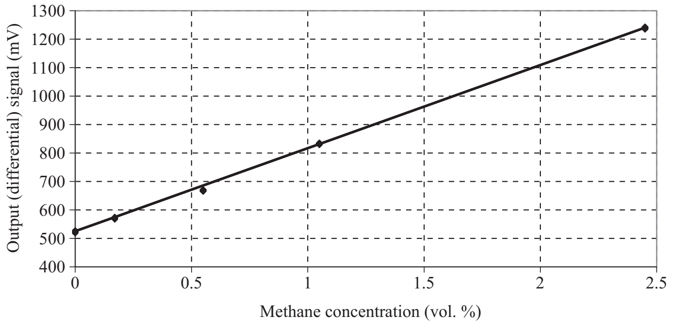

Fig. 5. Output voltage of the sensor as a function of methane concentration.

The sensor output voltage is plotted as a function of methane concentration in Fig. 5. The dependence is linear over the investigated concentration range. The sensitivity of the sensor is 290 mV/% CH_4 for a gain of 20 in the amplifier circuit needed between the sensor and the microcontroller.

The accuracy of the proposed measurement method with respect to changes in humidity and temperature was obtained by analyzing 50 measurements in each point. The error is less than 5% of the measurement scale (the absolute error at measuring the methane concentration is less than 0.1% volume).

For continuous measurements, the total power consumption (average value out of 50 measurements) is $P = 35.53$ mW, while the power consumption associated with each of the four voltage pulses is $P_1 = 3.18$ mW, $P_2 = 8.23$ mW, $P_3 = 7.56$ mW, and $P_4 = 16.56$ mW, respectively.

In the continuous mode, the power consumption of the sensor developed is about 35 mW that is comparable with the sensors produced be silicon-based technology. An additional contribution to energy saving comes from taking measurements at well-defined times, instead of continuously operating the sensor.

Assuming the measurement is taken once within a time T, we can define an average power consumption for this measuring frequency, P_{av}, as

$$P_{\text{av}} = \frac{1}{T}\int_0^T u(t) \cdot i(t)\,\mathrm{d}t$$

where $u(t)$ is the sensor output voltage and $i(t)$ is the current through the sensor.

As an instance, if the methane concentration is measured twice per minute (according to requirements of the European standard for combustible gas detection [7]), the average power consumption is 1.18 mW. This means that the catalytic sensor could operate for more than 12 months when powered by three AA batteries (which store energy of about 13 W h).

We should mention here that circuits using a single sensor have a lower voltage output as compared to circuits implementing the Wheatstone bridge (via sensors of the same type). This is result that the output voltage depends not only on the sensor sensitivity but also on the analog circuit (resistivity divider or Wheatstone bridge) used for the measurement. Such a lower voltage output (requiring in some cases an additional amplifier circuit) is however more than compensated by the energy saved (practically a factor of 2).

5. Conclusions

A planar catalytic sensor for combustible gas detection and characterized by low energy consumption was developed and characterized. The sensor consists of a free wedge-shaped alumina membrane supporting a micro heater covered in turn by a catalytic layer.

Moreover, a novel method is developed to measure methane concentration. The method is based on analysis of transient processes taking place while a sequence of voltage pulses is applied to the catalytic sensor. The major advantage of the method is that a single catalytic sensor is used (instead of two as in the Wheatstone bridge circuit), thus leading to reduced power consumption, while, at the same time, measurements are not affected by environmental factors (ambient temperature, relative humidity and atmospheric pressure). The primary reason for using Wheatstone bridge circuits is in fact to make measurements independent from environmental factors.

When sensor is operated in the continuous mode, the power consumption is comparable with the sensors produced be silicon-based technology. On the other hand, if measurements are taken twice per minute, in agreement with the requirements of European standards concerning the detection of combustible gases, the power consumption is reduced to 1.2 mW.

The proposed method of sensor operation presents good perspectives for further research. Temperature is in fact an additional parameter which can be used to extract additional information, for example, to improve selectivity when a gas mixture is measured. In the future, we plan to optimize this 4 voltage pulse with respect to energy consumption and methane sensitivity.

Acknowledgments

This work was sponsored by Russian Federal Program, Grant No. 16.426.11.0022 and by NATO Collaborative Linkage Grants CBP.CLG.984158.

References

[1] C. Becherb, P. Kaulb, J. Mitrovicsa, J. Warmer, The detection of evaporating hazardous material released from moving sources, using a gas sensor network, Sensors and Actuators B 146 (2010) 513–520.

[2] J. Bonvoisin, A. Lelaha, F. Mathieuxa, D. Brissauda, An environmental assessment method for wireless sensor networks, Journal of Cleaner Production 33 (2012) 145–154.

[3] A. Somov, R. Passerone, D. Spirjakin, M. Ivanov, I. Khromushin, A. Baranov, A. Savkin, Combustible gases and early fire detection: an autonomous system for wireless sensor networks, in: Proceedings of the e-Energy 2010—1st International Conference on Energy-Efficient Computing and Networking, Passau, 2010, pp. 85–93.

[4] http://www.mipex-tech.com/en/technology.html

[5] A. Sen, J.D. Albarella, J.R. Carey, P. Kim, W.B. McNamara III, Low-cost colorimetric sensor for the quantitative detection of gaseous hydrogen sulfide, Sensors and Actuators B 134 (2008) 234–237.

[6] J. Hayes, S. Beirne, K.-T. Lau, D. Diamond, Evaluation of a low cost wireless chemical sensor network for environmental monitoring, in: 7th Conference on Sensors, Lecce, Italy, 2008, pp. 530–533.

[7] Standard EN 50194:2000, Electrical apparatus for the detection of combustible gases in domestic premises, Test methods and performance requirements (2000).

[8] P. Bhattacharyya, P.K. Basu, B. Mondal, H. Saha, A low power MEMS gas sensor based on nanocrystalline ZnO thin films for sensing methane, Microelectronics Reliability 48 (2008) 1772–1779.

[9] T. Suzuki, K. Kunihara, M. Kobayashi, S. Tabata, K. Higaki, H. Ohnishi, A micromachined gas sensor based on a catalytic thick film/SnO_2 thin film bilayer and thin film heater Part 1: CH4 sensing, Sensors and Actuators B 109 (2005) 185–189.

[10] P. Furjesa, Cs. Ducso, M. Adama, J. Zettnerb, I. Barsonya, Thermal characterisation of micro-hotplates used in sensor structures, Superlattices and Microstructures 35 (2004) 455–464.

[11] E.-B. Lee, I.-S. Hwang, J.-H. Cha, H.-J. Lee, W.-B. Lee, J.J. Pak, J.-H. Lee, B.-K. Ju, Micromachined catalytic combustible hydrogen gas sensor, Sensors and Actuators B 153 (2011) 392–397.

[12] A.A. Vasiliev, R.G. Pavelko, S.Yu. Gogish-Klushin, D.Yu. Kharitonov, O.S. Gogish-Klushina, A.V. Sokolov, A.V. Pisliakov, N.N. Samotaev, Alumina MEMS platform for impulse semiconductor and IR optic gas sensors, Sensors and Actuators B 132 (2008) 216–223.

[13] E. Vereshchagina, R.A.M. Wolters, J.G.E. Gardeniers, Measurement of reaction heats using a polysilicon-based microcalorimetric sensor, Sensors and Actuators A 169 (2011) 308–316.

[14] S. Udina, M. Carmona, A. Pardo, C. Calaza, J. Santander, L. Fonseca, S. Marco, A micromachined thermoelectric sensor for natural gas analysis: multivariate calibration results, Sensors and Actuators B 166–167 (2012) 338–348.

[15] A. Somov, A. Baranov, A. Savkin, D. Spirjakin, A. Spirjakin, R. Passerone, Development of wireless sensor network for combustible gas monitoring, Sensors and Actuators A 171 (2011) 398–405.

[16] A. Somov, A. Baranov, A. Savkin, M. Ivanov, L. Calliari, R. Passerone, E. Karpov, A. Suchkov, Energy-aware gas sensing using wireless sensor networks, Lecture Notes in Computer Science 7158 (2012) 245–260.

Biographies

Evgeny E. Karpov is a principle scientific researcher in Scientific Technical Centre of Gas Measuring Sensors (NTC IGD), Russia. He received PhD in life safety technology in 2007. His current research interests include the development of wireless-based life safety systems and gas measuring equipments.

Evgeny F. Karpov is a scientific consultant in Scientific Technical Centre of Gas Measuring Sensors (NTC IGD), Russia. He was the project leader on several National and International research projects in life safety technology. He is the author of more than 200 scientific publications. In this number is 7 book and more than 70 patents in theme of gas measuring instruments.

Alexey Suchkov is an engineer-in-chief at the Scientific Technical Centre of Gas Measuring Sensors (NTC IGD), Russia. He received a PhD in life safety technology in 2003 from Academy of Science Mining Engineering Institute named after A.A. Skochinsky. His current research interests include the development of 2D catalytic sensors, synthesis of nanocatalysts and dynamic measuring methods.

Sergey Mironov is an engineer at the Scientific Technical Centre of Gas Measuring Sensors (NTC IGD), Russia. His current research interests include the development of 2D catalytic sensors and dynamic measuring methods.

Alexander Baranov is a Professor at "MATI" – Russian State Technological University. He received a PhD in Physics and Mathematics in 1994 and the Doctor of Technical Science degree in 2003. He is the project leader of several research projects. His current research interests include the development of thin film nanocomposite catalysts for gas sensors by plasma deposition methods, catalytic and semiconductor sensor characterization, and wireless sensor networks.

Vladimir Sleptsov is the chief of Department of Radio-Electronics, Telecommunication and Nanotechnology at "MATI" – Russian State Technological University. Prof. Sleptsov is the project leader on several National and International research projects. His current research interests include the development of thin film materials by ion plasma methods, energy storage system, and wireless sensor networks.

Lucia Calliari is a senior researcher at the Centre of Materials and Microsystems of the Bruno Kessler Foundation (Trento, Italy). Her research interest is in the electronic structure investigation of materials by electron spectroscopy, with focus on semiconductors, metals and C-based materials.