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Application of semiconductor gas sensors for medical diagnostics

S.V. Ryabtsev *, A.V. Shaposhnick, A.N. Lukin, E.P. Domashevskaya

Department of Physics, Voronezh State University, University Square 1, 394693 Voronezh, Russian Federation

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Abstract

The appearance of a small amount of acetone vapour (0.1–10 ppm) in the human expiration means exacerbation of diabetes. This form of disease requires special forms of medical treatment and thus the detection of acetone proves to be an actual problem. Moreover, for some sick persons this parameter correlates with the content of glucose in the blood. The aim of this work is to show the principal possibility of the application of semiconductor gas sensors in the diagnosis of diabetes and the development of the prototype of gas analytical instrument based on these sensors.

Keywords: Semiconductor gas sensor; Diabetes; Acetone vapour

1. Introduction

Gas analysis of human expiration provides an important information on the state and functioning of different human organs, decompensation of some pathologic states or exacerbation of chronic diseases [1]. For example, a quantitative determination of O_2 and CO_2 in the expiration characterizes gas-interchange functions of the blood and lungs.

An application of IR sensors for CO_2 and magnetic ones for O_2 proves to be appropriate for such analysis in the range of rather high concentrations since they have good metrological parameters and good selectivity (advertisement of 'Datex'). However, the control of low-concentration components of the expiration by these methods is impossible without considerable complication of the equipment and the increase of its cost. The methods of analysis using semiconductor gas sensors which are characteristic of a high sensitivity, small dimensions, low power consumption and small cost prove to be the more suitable for these purposes.

One of the important methods in medical diagnostics of diabetes allowing to perform an adequate therapy is the determination of acetone concentration in the blood of a sick person. This is usually made with the help of paper indicators changing their colour under contact with the urine of the sick man. This method has obvious shortcomings in the application; moreover, the constraint between concentrations of acetone in urine and in blood is of more complex character than the correlation of those parameters in expiration and in blood since the blood directly participates in the gas-exchange. In this work we make an attempt to solve this problem applying semiconductor gas sensor.

2. Experimental

Compositions based on polycrystalline n-type semiconductors such as SnO_2, CdO, Nb_2O_5, Fe_2O_3 with the activation impurities of Pt, Pd, RuO_2 were applied as sensitive layers. Chemical agents of 99.99% purity which had been previously finely ground (mean size of the crystallites was ~ 100 nm) were used to prepare these compositions; the layers themselves of $\sim 10^4$ nm thickness were deposited from the water suspensions of these agents onto Al_2O_3 substrates. The plane substrates with the size of 3 mm $\times$ 3 mm have Pt electrodes on one side in order to measure the conductivity of sensor layers and Pt heater on the other side of the substrate which at the same time is used as a resistive sensor of the temperature. After deposition of suspension the layers were dried and thermally treated at the temperatures up to 400°C sweeping by 50°C/h in a flow of pure dried air. The layers were then

* Corresponding author. Fax: +7-502-200-4691; E-mail: phssd28@main.vsu.ru

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maintained at 400°C for 3 h in order to stabilize their electrophysical parameters. After heating up to 300–350°C the resistance of the sensor layer suddenly drops down which is due to sintering of microcrystals and lowering of the energy barriers between crystallites.

Thin-layer technology was used as well as for the preparation of sensor layers which included magnetron deposition of thin (~20–30 nm) layers (Sn or Fe), their following oxidation in the air at 600°C and surface doping with Pt or Pd atoms up to the concentration of 1×10^{16}–5×10^{16} atoms/cm^2 using thermal evaporation of the corresponding metals. In order to obtain the stable electrophysical parameters of the sensors, we have performed a cycle of ageing.

Calibration of the samples was performed in the installation of dynamic mixing of air flow, acetone vapour and some other components modelling the human expiration and next, the prototype of device was tested in clinics on patients with diabetes. An error of the gas mixture preparation in the unit did not exceed 20%.

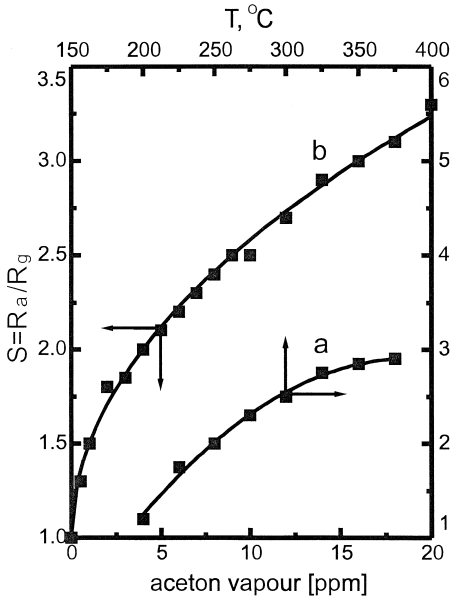

Fig. 1. (a) Dependence of sensor response S with concentration of acetone vapour in air (10 ppm) for various temperatures; (b) dependence of sensor response (300°C) on the concentration of acetone vapour in air.

3. Results and discussion

Preliminary investigations have shown that the range of the measured concentrations of acetone vapour should be of 0.1 to 10 ppm. The problem is complicated by the presence of H_2O, CO_2 impurities hindering acetone detection as well as the decrease of O_2 concentration in the expiration compared with that one in the air. The choice of sensor layer was then determined by these conditions as well as by the requirement of long-term stability of its electrophysical parameters.

Table 1 presents the sensitivity of sensors made from different materials and by different manufacturing technologies. The sensitivity (S) is determined as the ratio of sensor resistivity in the pure air (R_a) to that one in the air containing the controlled gas (R_g). Two-component system of Fe_2O_3 with RuO_2 (5 wt.%) as a promoter has demonstrated the best response at 300°C to acetone vapours and therefore it was further studied in more details. In Fig. 1 the concentration and temperature dependence of resistivity response are presented. One of the drawbacks of this system is rather high electrical resistance of about 300 MΩ. The measurement of such high values which are outside the laboratory conditions proves to be rather difficult. The addition of 7–10 wt.% of CdO resulted in a decrease of the resistance of the sensor layer up to 10 MΩ and meanwhile the sensitivity to acetone was reduced by 15–20%.

The optimum operating temperature of the sensor was ~300°C. Such a choice of temperature was determined by the necessity to combine the long-term stability of sensor parameters with a high sensitivity and a small time response since in the prototype of the device, we applied the forced pumping of the analyzed sampling and the time of its stay in the measuring space was less than 3 s. The temperature above 350°C results in a decrease of sensitivity with time, probably, due to coalescence of microparticles in the semiconductor layer.

The dependence of sensor resistance on O_2 concentration in the analyzed atmosphere is rather considerable in the range of small concentrations. However, the decrease of oxygen content in the human expiration by 2–3% compared with the usually detected 21% in the atmosphere is of small effect on the sensor response since this latter attains saturation in this range of concentrations.

The influence of moisture while its relative concentration is close to 100% at 20°C results in a considerable increase of sensor resistance. But the time of response to the moisture is sometimes greater than the one to acetone vapour, therefore under rapid substitution of the analyzed sampling by the clean air and a slight correction of the calibrating plot, this effect can be easily accounted.

Table 1
The sensitivity of sensors at 300°C made from different materials in acetone vapour (10 ppm)

	Fe_2O_3/RuO_2 (5 wt.%)	Fe_2O_3	Fe_2O_3/Pt thin film	SnO_2 thin film	SnO_2/Pt thin film	SnO_2/Pt thin film	CdO	CdO/RuO_2 (5 wt.%)
$S = R_a/R_g$	2.5	1.5	5.2	~1	1.4	1.2	1.2	1.5

Most difficulties in the analysis of human expiration are connected with the influence of CO_2. The presence of this impurity introduces an appreciable error in the measurements since the correction of the device indications was made over the mean value of the concentration for this gas in the human expiration. It is not measured in every test.

Thus, the influence of the hindering impurities in the analysis of human expiration has been considerably corrected using 'hardware'—we managed to introduce the calculated corrections for CO_2 so as to neglect the variation of O_2 concentration in the expiration, to align the rate of the sample pumping to discriminate the long-term response to H_2O.

The evaluation of the instrument prototype in clinic has demonstrated its satisfactory metrological parameters and confirmed the suitability and actuality of this technique in the diagnostics of saccarus diabetes. For a considerable group of patients, a correlation exists between acetone concentration in the expiration and glycaemia as well as the content of glucose and acetone in urine. It was found that for sick persons with a high level of glycaemia (glucose concentration in the blood is higher than 10 mmol/l), acetone vapour concentration in the expiration air exceeded 0.9 ppm (1.8 mg/m^3) at the concentration of glucose in urine from 0.3% to 4%. For sick persons with glucose level in the blood of 3.5 to 10 mmol/l acetone concentration in the expiration air were of 0.3–0.9 ppm (no glucose was detected in urine). There is also the necessity to adjust the sensitivity of the instrument up to 0.1 ppm of acetone in the expiration since the concentration of 1 ppm reliably measured by our instrument prototype was observed only in the cases of the mean or serious stages of the disease.

The required sensor sensitivity was achieved in laboratory conditions with the thin film samples of Fe_2O_3 of approximately 30 nm thickness surface-doped by Pt. The calculated concentration of Pt deposited on the surface of sensor layer by thermal evaporation was of 1×10^{16}–5×10^{16} atoms/cm^2 for various samples. The preparation of the sensor to the work was restrained at the temperature of 200°C under cycling between the air and 0.1% of CO in the air. This results in a sharp increase of sensitivity and resistance of the sensor (Fig. 2). The observed effect, in our mind, can be explained by the known phenomenon of dispersion of thin layers (in our case, the metal islands) of a catalyst under the multiple interaction with reactants. This results in an increase of catalytic activity of the dopant and a decrease of shunting effect of ultradispersive metal islands. Cycle ageing of Fe_2O_3/Pt sensor in the mixtures of the air–CO, air–H_2 are mostly effective in this process. The optimal working temperature of the sensor proved to be 200–250°C since higher temperature results in a decrease of its long-term stability. It is connected with an increase of surface mobility of metallic particles and their coalescence as well as with the diffusion of dopant metal into the bulk of semiconductor [2]. In spite of the high sensitivity of this system, it was not used in the instrument prototype for the analysis of acetone vapours due to its rather high resistance of about 1 GΩ. Moreover, it was demonstrated that high sensitivity to gases interfere with the measurements. For example, sensor resistivity is reduced by 25% in the analysis of the expiration air of the healthy human. This is due to the change in the composition of the gas medium compared with the atmospheric air as it was described previously. However, in spite of these drawbacks, the Fe_2O_3–Pt system seems to be the most prospective one and our further elaborations are assumed to be performed based on this system.

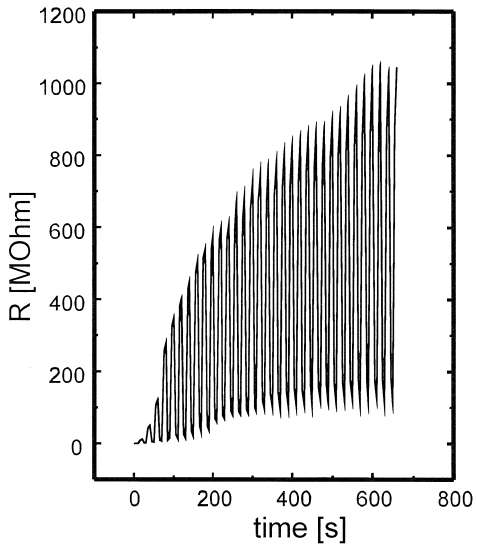

Fig. 2. Resistance and sensitivity of thin film Fe_2O_3/Pt sensor dependent on the cycle ageing between air and 0.1% of CO in the air.

4. Conclusions

Testing of the device prototype for the analysis of acetone vapours in the expiration of patients with diabetes allows to consider this diagnostic technique as a quite prospective one. Analysis of microconcentrations of the other components in the human expiration will probably allow to make a diagnosis of the other pathologic states and favour the performance of effective therapy.

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Stanislav V. Ryabtsev received his MS degree in Physics Chemistry in 1985 at Voronezh State University, Russia. Later on he worked at Karpov Institute of Physical Chemistry in Moscow. From 1994 he works as an Associate Researcher of Solid State Physics Department at Voronezh State University and is engaged with sensor properties of semiconductors.

Alexey V. Shaposhnick received his MS degree in Physics Chemistry in 1982 at Voronezh State University, Russia. In 1992 he received his PhD in chemistry. Now he works as an Assistant-Professor at the Department of Analytical Chemistry of Voronezh State University. He is studying the problems of gas mixtures analysis and their membrane separation.

Anatoliy N. Lukin received his MS degree in Physics of Semiconductors at Voronezh State University, Russia, in 1968. In 1985 he obtained his PhD degree in Solid State Physics. Now he works as an Assistant-Professor of the Solid State Physics Department of Voronezh State University and he is engaged with optical properties of semiconductors.

Evelina P. Domashevskaya received her MS degree in Physics of Semiconductors at Voronezh State University, Russia in 1957. In 1969 she received her PhD degree in Solid State Physics. And in 1979 she was granted a Dr. Science degree (Physics and Mathematics). Now she is a Professor and Head of the Solid State Physics Department at Voronezh State University. Scientific fields of interest are X-ray and electron spectroscopy, physicochemical properties of semiconductors.