GAS ORGANOMETALLIC THICK FILM SENSORS

Alena Pietriková — Ján Urbančík *

This paper presents an overview of theoretical, chemical and operating principles of semiconductor gas sensors, thick film materials for gas monitoring sensors with emphasis on sensitive organometallic thick film paste and on technical realisation of a selective gas (methane) sensor. The design and topology of sensing and heater parts, selection of thick film materials, based on organometallic SnO_2 paste, the level of working temperatures, the influence of seasoning conditions on the sensor sensitivity and stability were made by sensor investigations. The authors present results of the final parameters of thick film methane sensors developed at the Department of Hybrid Microelectronics FEI TU in Košice.

K e y w o r d s: thick film, gas sensor

1 INTRODUCTION

Nowadays a general consensus has been reached in both scientific and technical communities on the need for cheap, reliable sensors and transducers for control and measuring systems. Among the various sensor technologies, thick film technology does not really offer conceptually new or sophisticated solutions but it does offer several appreciable capabilities, *eg*, flexibility in choice of materials and design, easy integration with electronic circuit and packaging. This paper illustrates some specific features of thick film technology for sensor manufacturing. Methane sensors belong to gas sensors with a wide field of application. They could be used for air pollution monitoring, indoor air conditioning, combustion control and inspection of storehouses.

In more and more sectors of work and life, law provides environmental regulations. The measurement and analysis of environmental facts is only one task of our future. Economic and ecological optimisation of many technical and chemical processes would be allowed by sensor-based control.

2 THEORY OF SEMICONDUCTOR GAS SENSOR

The design, samples production and also their testing in model conditions are based on the chemical principle and physical processes of organometallic SnO_2 gas sensors, which had to be respected in all consequent work. Generally, the chosen and used organometallic sensing layer represents a semiconductor material whose conductivity varies with changes in the surrounding atmosphere in accordance with Table 1.

Table 1. The resistivity changes in organometallic layer under the influence of surrounding agents.

Type of semiconductor	Reducing (monitored) gas	Oxidizing gas
N–type	Resistance decrease	Resistance increase
P–type	Resistance increase	Resistance decrease

The principle of gas sensing is based on reaction at effective SnO_2 surface, which has to bring more important role than spatial volume changes in semiconductor layer. This is why the specific surface, *ie*, ratio of layer volume and effective surface could be minimised. Thick film technology for sensors production cannot fully respect this demand by principle reasoning. This fact could cause increased influence of spatial reactions in compare with thin film technology manufactured sensors. However, the acquired results refer to the actuality that thick film technology could be also used in the frame of chemical and gas sensors production.

The choice of a SnO_2 layer as an N–type semiconductor material is based on its increase of resistivity after oxygen adsorption and consecutive resistance decrease after further desorption by a reduction agent. These resultant changes of the sensing layer conductivity occur after surface reactions at the semiconducting effective surface. They are caused by the following processes [1, 2]:

– Adsorbed molecules behave as donors and they influence the spatial charge.
– Oxygen vacations on the active surface can migrate a short distance into the bulk of the layer become donors. The surrounding hydrogen, methane and CO can cause wipe out of oxygen molecules from the surface lattice.

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item– Oxygen vacations on the surface can be substituted by other gas molecules, which causes a secondary decrease of spatial vacations.

– The surrounding gas reacts with adsorbed oxygen ions and affects the resultant layer conductivity.

Figure 1 shows the universal principle of chemical organometallic sensors, which is based on powder grains of an N–type semiconductor (*ie*, SnO_2) with adsorbed oxygen molecules and the distribution of energy conditions on the effective surface layer. The adsorbed oxygen molecules remove the conduction electrons from the grain surface and create a thin insulation layer around each grain surface. On the other hand, the amount of conduction electrons inside the grain cores is sufficient and these electrons create well conductive zones in the grain cores. This phenomenon goes along with the formation of positively charged ions and formation of energy barriers as a result of the equilibrium state on the surface of the effective sensor layer.

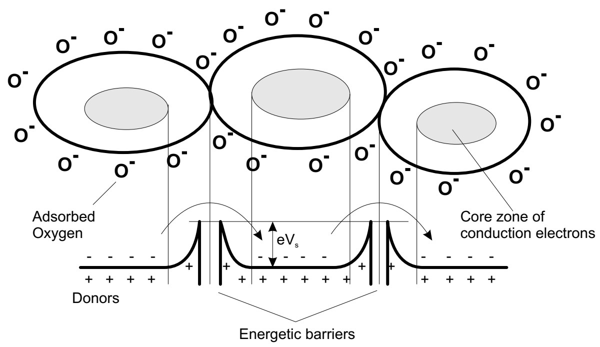

Fig. 1. Model of an N–type semiconductor with adsorbed oxygen molecules and energy barriers.

Figure 1 shows a formation of energy barriers between singular neighbouring grains as a secondary result of oxygen adsorption. The current flow across this structure must surmount these energy barriers, which manifests itself as an increase in the layer resistance. The intensity level of arisen barriers is marked as eV_s in the figure and it depends on the surrounding oxygen concentration and temperature conditions. When the active layer surface is surrounded by a reduction agent, the barriers are decreased. This is accompanied by a reduction in the layer resistance. It means that the resistivity changes in the sensing layer follow the existence of reduction agents and their concentration in the surrounding atmosphere. The printed and fired SnO_2 layer consists of grains joint to form Schottky energy barriers. Their height affects the conductivity of the SnO_2 layer. Figure 2 shows a comparison of the energy barriers in the presence of air and reducing gases. The gas presence reduces the height of the energy barrier in comparison with air because of release of electrons by oxygen ions due to their interaction with the reducing agent.

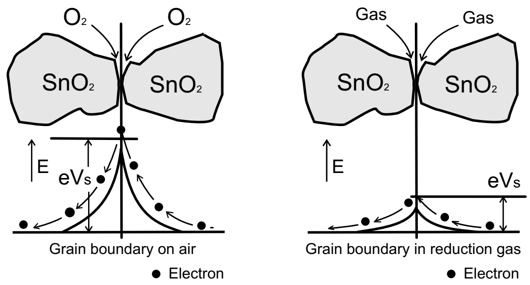

Fig. 2. Intergranular model of potential barrier. a) in air, b) in the presence of a reducing gas.

The conductivity G can be calculated as

$$G = G_0 \exp\Big(\frac{-eV_s}{kT}\Big), \tag{1}$$

where G_0 includes the bulk intergranular conductance and any geometrical effects, eV_s is the activation energy, k is Boltzmann's constant and T denotes the actual operating temperature level in Kelvin. Particular values of eV_s and G_0 can be experimentally obtained by a series of conductance measurements in exact surrounding conditions [9].

Another factor that influences the sensing characteristics is the chemical catalyser. In general, it has a two-ply function in gas sensing. First, it concentrates the reaction elements on the active surface and, second, it decreases the activation energy by changing the Fermi energy. The reduction of Fermi level causes an enhancement of barriers like a high concentration of oxygen surrounding the effective sensor surface. Also, the basic condition for this effect is that the catalyser elements have to be situated near grains interconnections for effective function. Following this fact, it is obvious that exact preparation of raw materials for the sensing organometallic layer, including the catalyser, has a crucial influence upon the sensor function [3].

In compliance with theoretical assumptions it is necessary to provide several conditions so as to achieve good gas sensing stability, sensitivity and selectivity [4]:

item– To determine and ensure the optimal working temperature. Higher temperature causes a higher reaction rate, lower temperature could cause a slow reaction, which results in changes in sensing characteristics. Both cases can influence the measurement accuracy and sensor stability. The selectivity of gas sensor can be also controlled by regulating the operating temperature.

– To achieve specific adsorption for sensing a gas by additional catalytic material which has the ability to adsorb the selected gas or to react with it.

– To use a selective filter which could avoid access of undesirable gases to the effective surface. The use of a porous platinum layer is suitable for methane detection for example.

– To have a reference resistance which could eliminate the perturbing influences of surrounding conditions including the potential operating temperature alterations and brings higher stability to resistivity measurements.

3 FABRICATION OF THICK FILM GAS SENSORS

The thick film layout design of an organometallic SnO_2 sensor and its production were performed by standard TF technology. The design philosophy goes out from a system of accumulating electrodes in combination with an active organometallic SnO_2 layer and a heater system applied to both sensor surfaces which are used as shown in Fig. 3: First, the face side for the sensing part construction, second, the back side, for realisation of the heating element.

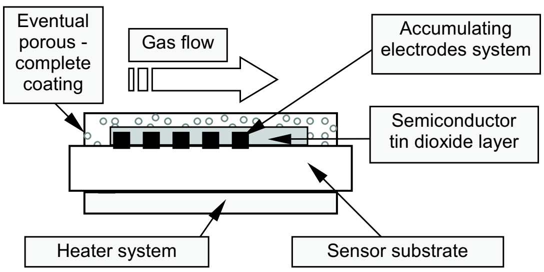

Fig. 3. The basic design for a screen-printed thick film sensor unit — cross-section.

The final version of the thick film sensor design, the choice of an optimal electrode raster, heater geometry and number of sensing layers are based on an extensive database of measured results. Schematic design of the sensor structure is shown in Fig. 4.

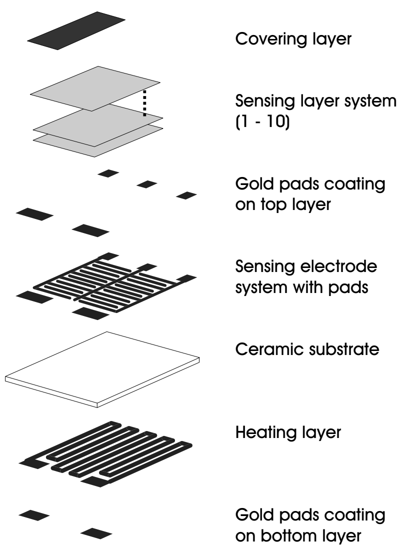

Fig. 4. The final version of organometallic sensor unit — schematic design.

3.1 Design of the sensoric part

The design of the sensoric part was focused on the layout development of the electrode system in combination with several sensing and covering layers. The choice of the most appropriate grid density was limited by resolution possibilities given by standard TF technology, the covering layer together with the number of organometallic SnO_2 layers was given by the requirements upon the sensitivity level, measurement and acquired data evaluation. The resulting outcome is shown in Fig. 5.

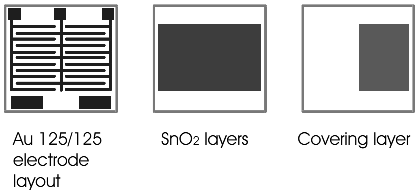

Fig. 5. Methane sensor design — sensing part

Table 2. Characteristics of materials for sensoric part of thick film gas sensors.

Substrate material	99.6 thickness 0.25 mm, substrate dimension 4.25×4.75 mm, face side
Electrode material	ESL gold paste 8880-H, fired at 980 °C, Au line/gap thickness 0.125/0.125 mm
Sensing material	Organometallic ESL paste D-3051 doped with 1 % Pt, fired at 630 °C, 1 layer is 1 μm (number of sensing layers min. 10)
Covering layer	Lanškroun glass paste TT 8010 fired at 560 °C (number of layers min. 2)

An overview of basic characteristics of the used substrate and thick film materials for the sensoric part of the methane sensor is given in Table 2:

3.2. Gas sensor heater

Generally, the heater has an important role in organometallic gas sensors because the working temperature for methane is relatively high — in the range from 420 to 470 °C. The distribution of the heating field on the substrate surface is also a very important factor for good sensor sensitivity. The heating element of a simple thick film gas sensor is usually situated on the backside of the sensor. The ceramics substrate dimensions should be very small (our dimensions are under 30 sq mm) and power consumption for 450 °C heating temperature should be low, too (our power consumption is below 2 W). The design of the thick film gas sensor and the choice of proper thick film materials for gas sensor were difficult tasks. In addition, thick film materials should be stable, reproducible and reliable.

Basic characteristics of thick film materials used for the construction of the heating part of the methane sensor based on a conducting thick film are given in Table 3.

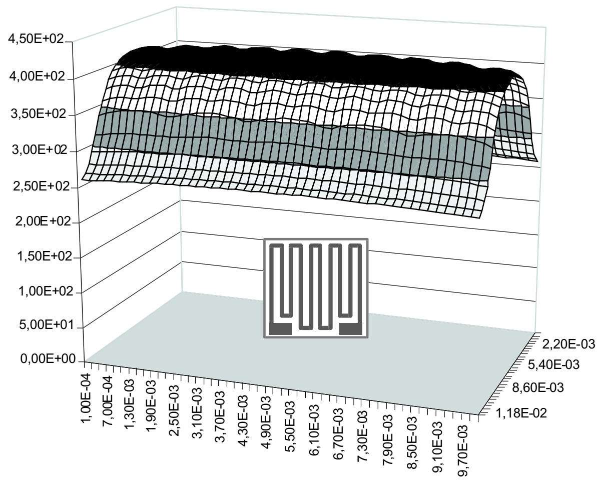

Fig. 6. Final version of heaters and temperature field collocation.

The heating concept based on a conductive thick film brings, beside high stability of the operating temperature, also the possibility of topical temperature evaluation.

Table 3. Material characteristics for the heating part of thick film gas sensors.

Substrate material	99.6 % $Al_2\vee_3$ Kyocera, thickness 0.25 mm, substrate dimension 4.25.75 mm, back side
Electrode material	Pt conductor composition DuPont 9141 fired at 980 °C, Pt line/gap thickness 0.175/0.250 mm

The resultant temperature field (Fig. 6) collocation is satisfactory due to sensor dimensions, which also brought the expected effect to power consumption saving. Furthermore, the small sensors dimensions and low weight provide an improvement in reliability with regards to mechanical fixation in the sensor carrier frame. It is based on Low Temperature Cofired Ceramics by wire bonds technology. On the other hand, substrate dimensions influence the resistance values of the sensing layer. Figure 6 shows the final version of the heater design based on a conductive layer and the actual temperature field collocation.

4 THE MEASURING PRINCIPLE AND RESULTS OF SENSING CHARACTERISTICS

Testing of the organometallic thick film environmental gas sensors is an exacting complex work and that is why the measurements were carried out in a fully computer-aided system that allows simulation of the electronic evaluation circuits. The designed and implemented measurement system allows to perform and store complex measurement series of up to five autonomous sensors or sensor arrays, up to five outputs. This fact allows testing of several sensor substrates in the same working conditions such as surrounding temperature, humidity, atmospheric pressure and gas concentration. It also allows to monitor and control the influence of the sensor operating temperature upon the sensing characteristics in the range up to 500 °C.

The ceramic sensor substrates were fixed, by wire bonding technology, in a special frame based on LTCC, considering the high levels of operation temperatures. The carrier frame for sensor assembly with a sensing unit is shown in Fig. 7 and it was situated inside a glass bulb with a known volume for testing and measurement purposes.

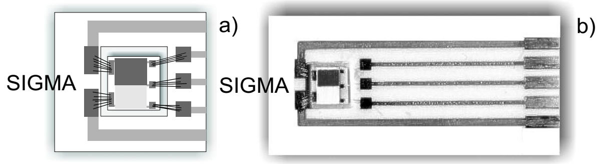

Fig. 7. Detail of the sensor assembly (a) and a carrier frame based on LTCC (b) with the gas sensor unit.

The measurement series and testing of the produced methane sensor were conducted under standard conditions (surrounding temperature was in the range from 25 to 35 °C, 65 % humidity) and at various ageing and various humidity condition units for verification of their sensing properties. The measuring principle consists in resistivity changes in the organometallic layer based on the reaction at the effective SnO_2 surface. The sensitivity, *ie*, the $R_{\mathrm{air}}/R_{\mathrm{gas}}$ ratio dependence of the N–type semiconductor layer based on the organometallic thick film in the presence of the reducing gas is represented by a linear increasing behaviour (Fig. 8).

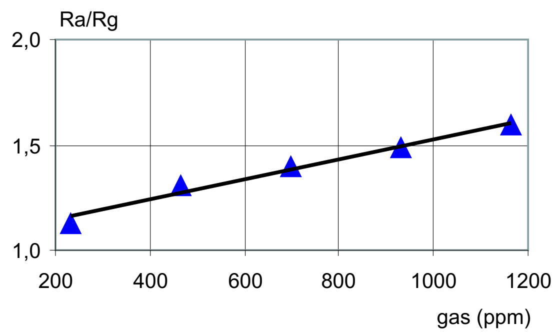

Fig. 8. Representative results of sensing characteristics for the methane sensor unit.

Figure 9 shows the test results after sensor ageing during 3 hours at 350 °C and at 65 % humidity. The results proved and demonstrated that ageing can positively affect the sensibility of electrochemical gas sensors.

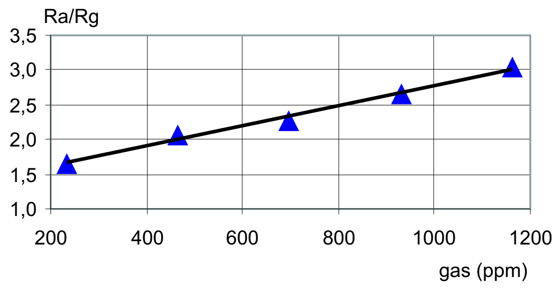

Fig. 9. Representative results of sensing characteristics for the methane sensor unit.

Other tests were focused on the verification of the humidity influence on the sensing properties. Several measurement series were performed and the results indicated that the influence of humidity was negligible.

5 CONCLUSION

Selective gas sensors based on standard thick film technology are looking forward to being more popular in response to the demand for higher reliability and better cost. The organometallic methane sensor can connect this technology and electrochemical based sensors. The shown results demonstrate that the gas sensor based on an organometallic thick film has good reliability in various environmental conditions such as different humidity levels or various modes of ageing. Table 4 shows the acquired basic specifications of a methane sensor prototype based on organometallic SnO_2 thick film.

Table 4. Final sensor specification.

Sensor type		Thick film gas sensor based on organometallic SnO_2 paste
Target gas		Methane
Typical operating temperature		450 °C
Typical ambient test condition		22–25 °C at 65–75 % humidity
Typical detection range		100–5 000 ppm
Electrical characteristic under standard test conditions	Heater Voltage	10 V DC
	Heater Resistance	15–20 Ω at 20 °C 44–50 Ω at 450 °C
	Heater Current	< 0.2 A
	Heater Power Consumption	< 2 W
	Resistance of SnO_2	300–75 kΩ in 100–5000 ppm
Sensitivity Ratio R_{air}/R_{gas}		1.1–2.2 in 100–5000 ppm

The authors continue their research work in the field of thick film gas sensors in order to make them easily applicable in industrial batch production. Continuation of the research work will be also focused on ageing, accelerated ageing and reliability tests with emphasis on improving the sensor characteristics stability and failure prediction. Finally, the continuous research work could contribute to a development of a thick film based sensor array in the near future.

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