Paper

Silicon TCD for the methane and carbon monoxide detection

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Abstract— Analytical model, design principles, technology and test results concerning a thermal conductivity detector (TCD) are presented. Prototype TCD units fabricated using the standard silicon IC VLSI and MEMS techniques are reported. The detectors are integrated with gas separation columns and micro-valve dosing systems. Initial tests were carried out in a gas mixture containing methane, carbon monoxide, oxygen, hydrogen and nitrogen.

Keywords— detector, silicon, gas mixture.

1. Introduction

Thermal conductivity detector (TCD) prototype units were designed and fabricated within the framework of the micro total analysis systems (μTAS) project, which is focused on the hazardous gas chemical detection-recognition in the coal-mine atmosphere. The device consists of two elements – silicon chip and glass plate, which are bonded together. At the silicon-to-glass interface there are two parallel capillary channels with a system of Pt resistors overhanged across them. There are also four external gas tubing connections to the channels outlets at the device edges. Resistors are connected into a Wheatstone bridge. One channel is used for the test mixture flow, while the second one for the reference flow of pure helium. Changes of the thermodynamic parameters of the gas mixture affect the resistor temperature and the temperature profile along the TCD channel. The most advantageous features of the presented device are low geometrical dimensions of thin film resistors and extremely low thermal capacity, which makes the device very sensitive and its response fast.

2. Model

The performance of a TCD unit may be analyzed using a very simple mathematical model. Sufficiently good results were obtained with the model deriveded from the one previously described by Koch *et al.* [1–3]. The differential Eq. (1) of the thermodynamic equilibrium:

$$\frac{\mathrm{d}(P-Q)}{\mathrm{d}x} = \lambda_f A \frac{\mathrm{d}^2 T}{\mathrm{d}x^2} = \rho_f c_f A v \frac{\mathrm{d}T}{\mathrm{d}x} - 2\lambda_f \frac{l_y}{l_z} T \qquad (1)$$

was solved with several simplifying assumptions and necessary boundary conditions. The final Eqs. (2–6) of the model enable fast and easy PC calculations of the temperature distribution along the TCD channel for the given conditions:

$$T_1(x) = T_R \exp\big(\chi_1(x+L)\big) \qquad (x < -L)\,, \qquad (2)$$

$$T_2(x) = T_R \qquad (-L < x < L)\,, \qquad (3)$$

$$T_3(x) = T_R \exp\big(\chi_2(x-L)\big) \qquad (x > L)\,, \qquad (4)$$

$$\chi_{1/2} = \frac{1}{2 l_z A \lambda_f}\left(l_z v A c_f \rho_f \pm \sqrt{l_z A \big(l_z v^2 c_f^2 \rho_f^2 A + 8 l_y \lambda_f^2 \big)} \right), \qquad (5)$$

$$T_R = \frac{l_z \left(\dfrac{I^2 \rho_{met} n l_y^2}{A_{met}} + 4\lambda_{met} A_{met} T_B \right)}{\lambda_f l_y l_z A \chi_1 - \lambda_f l_y l_z A \chi_2 + 4\lambda_f l_y^2 L + 4\lambda_{met} A_{met} l_z}\,. \qquad (6)$$

Parameters applied in the analytical equation model: T – temperature, T_B – ambient temperature, T_R – resistor temperature, P – electrical power delivered to the resistor, Q – power loses caused by resistor thermal conduction, I – resistor current, n – number of the resistor meanders, w – resistor path width, g – resistor path thickness, s – separation between the resistor meanders, A_{met} – resistor cross section area = wg, $2L$ – resistor total width = $nw + (n-1)s$, ρ_{met} – metal resistivity, λ_{met} – metal thermal conductivity, v – gas flow, l_y – channel width, l_z – channel depth, A – channel cross section area = $2 l_y l_z$, λ_f – gas thermal conductivity, c_f – gas thermal capacity, ρ_f – gas specific density.

3. Design and technology

The TCD unit consist of two elements: a silicon chip (15 mm × 15 mm × 380 μm) and a glass plate (15 mm × 15 mm × 2 mm) [4–6]. The glass plate has two parallel grooves (600 μm × 600 μm × 15 mm) formed with the diamond-disc milling technique. Silicon chips were fabricated in a standard CMOS IC technological facility using several non-standard MEMS techniques. Thin film Pt resistors were patterned with the lift-off technique coupled with the application of negative photoresist (Figs. 1 and 2). After the silicon wafer dicing step, TCD chips had to come back to the "clean room" for the final chemical crystal anisotropic etching step. PECVD Si_3N_4/SiO_2 layers over the silicon substrate are sufficiently resistant to withstand the etching step in TMAH (tetra methyl ammonium hydroxide and water, $N(CH_3)_4OH + H_2O$) solution at 85°C for 200 minutes. During this etching step Pt resistors were laterally under-etched and suspended over the 400-μm wide and 100-μm deep grooves (Fig. 3). Finally, the silicon chip and the glass plate were aligned and bonded together.

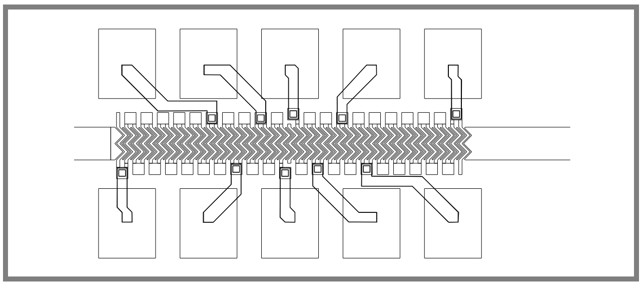

Fig. 1. Fragment of the TCD mask layout.

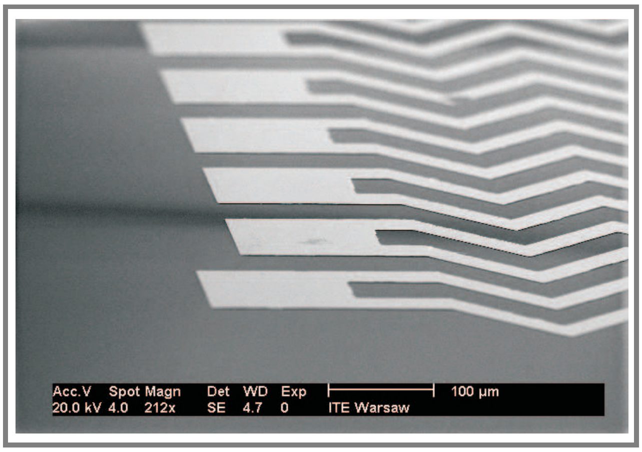

Fig. 2. Pt resistors before the channel photolithography and etching steps.

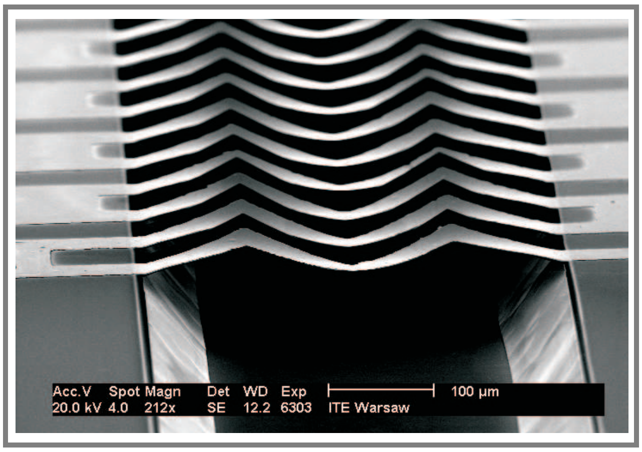

Fig. 3. Pt resistors after the channel photolithography and etching steps.

4. Results

Thermal conductivity detector units were tested as elements of a micro total gas analysis system (Figs. 4 and 5). The resistors were connected to form a fully active Wheatstone bridge, which was operated in the cooling mode. One pair of the resistors, located at the opposite bridge positions, was cooled by the pure carrier gas (helium) flowing through the reference channel. The other pair of the resistors was placed inside the stream of the carrier gas containing separated components of the gas mixture under test, flowing through the second TCD channel. The Wheatstone bridge was supplied from a standard battery source 9 V DC.

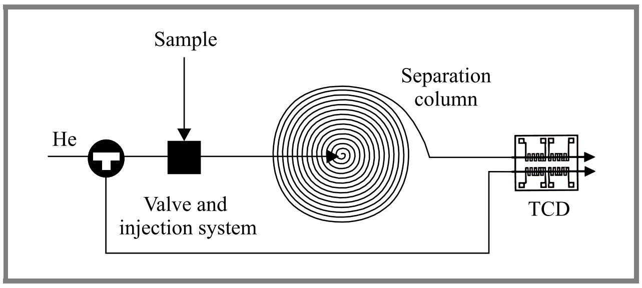

Fig. 4. TCD unit in the micro total analysis system.

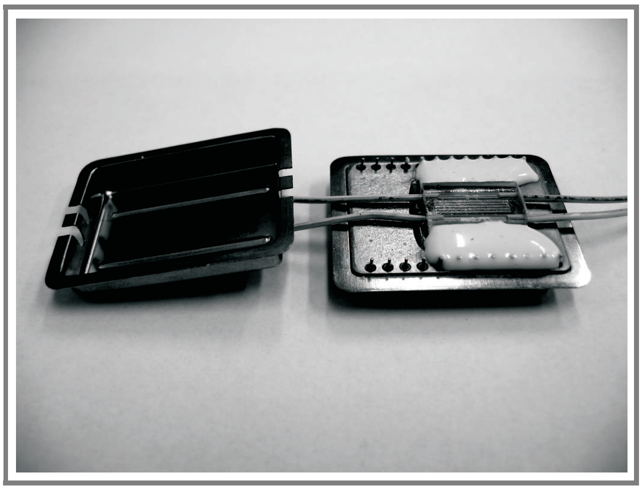

Fig. 5. TCD unit in the open package.

The following gas mixture of typical components of a coal-mine atmosphere has been used in the TCD tests: 20% CH_4, 8% CO, 15% O_2, 4% H_2, 55% N_2. The first

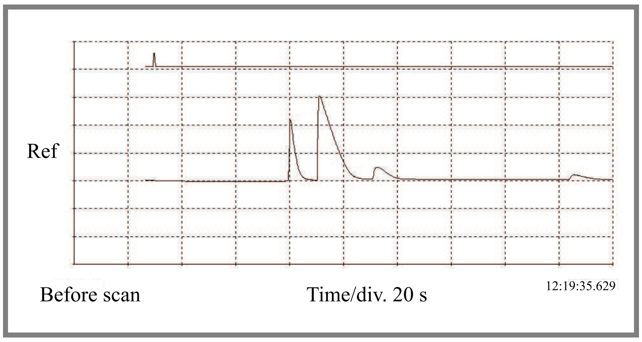

Fig. 6. TCD $U_{OUT}(t)$ plot in conditions of 26 cm/s (1.2 ml/min) carrier gas flow, upper line – sample injection, lower line TCD response: [O_2] peak 45 mV $\approx$ 50 s from the injection, [N_2] peak 60 mV $\approx$ 60 s from the injection, [CH_4] peak 10 mV $\approx$ 80 s from the injection, [CO] peak 5 mV $\approx$ 155 s from the injection.

experiment (Fig. 6) has been carried out with the helium carrier gas flow of 26 cm/s (1.2 ml/min). The reference flow rate chosen for the second experiment (Fig. 7) was 60 cm/s (2.8 ml/min). The output voltages of the Wheatstone bridge were plotted as a function of time. The horizontal axis scale was 20 s/div, while that of the vertical axis 20 mV DC/div. Pneumatically activated microvalve dosing system has been used for precise sample volume injection into the carrier gas stream – in both experiments 14 μl volume samples were used. The outlet of the dosing system was connected with the capillary separation column several meters long. Inside this column the gas mixture sample was diluted in the helium carrier gas and separated into the individual components, which were diluted in the carrier gas only. Every chemical component requires a specific time period to pass the separation column and reach the detector. It depends mainly on the carrier gas velocity and the internal surface coating of the capillary. Under stable thermodynamic stable the timing between the sample injection and electrical signals is used for the chemical identification of the mixture composition. The column, the tubing and the internal diameters of the TCD channel have to be very close to reduce gas stream disturbances and flow resistance.

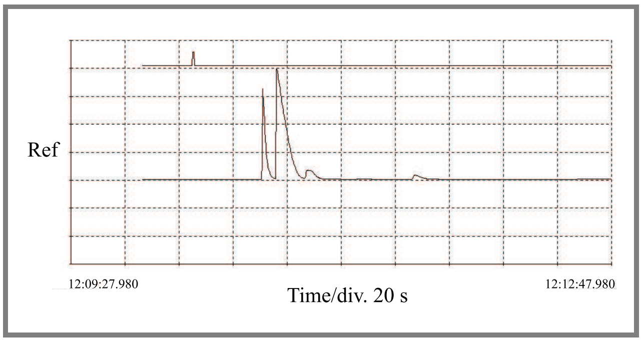

Fig. 7. TCD $U_{OUT}(t)$ plot in conditions of 60 cm/s (2.8 ml/min) carrier gas flow, upper line – sample injection, lower line TCD response: [O_2] peak 60 mV $\approx$ 25 s from the injection, [N_2] peak 80 mV $\approx$ 30 s from the injection, [CH_4] peak 10 mV $\approx$ 40 s from the injection, [CO] peak 5 mV $\approx$ 80 s from the injection.

A change in the chemical composition of the gas inside the TCD channel affects the thermodynamic properties of the system (mixture thermal conductivity, thermal capacity, specific density). The detector transforms these changes into a temperature profile shift along the TCD channel axis. In the cooling mode, decreased/increased heat transfer from the resistor to the gas stream results in an in-creased/decreased resistor temperature. The resultant material resistivity changes are registered by the Wheatstone bridge output voltage ΔU_{OUT}.

5. Conclusions

Thermal conductivity detector devices were successfully designed and fabricated. Test results in a well defined gas mixture of hazardous components of a coal-mine atmosphere were satisfactory. Further improvements of device sensitivity are possible if the Wheatstone bridge supply voltage is increased and the geometrical dimensions of the resistors are reduced. Using poly-Si resistors doped with P, As or B insted of Pt resistors seems to be a very promising idea seems to be implementation instead of the Pt resistors, because the latter ones are supposed to be chemically active in contact with the hydrocarbons.

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