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Miniaturized Single Chip Arrangement of a Wheatstone Bridge Based Calorimetric Gas Sensor

Navas Illyaskutty, Onur Kansizoglu, Oguzhan Akdag, Binayak Ojha, Jens Knoblauch and Heinz Kohler *

Institute for Sensor and Information Systems (ISIS), Karlsruhe University of Applied Sciences,
D-76133 Karlsruhe, Germany; navasillyas@gmail.com (N.I.); onurkan61@hotmail.com (O.K.);
oguzhan_akdag@hotmail.de (O.A.); binayakojha@gmail.com (B.O.); jens.knoblauch@hs-karlsruhe.de (J.K.)
* Correspondence: heinz.kohler@hs-karlsruhe.de; Tel.: +49-721-925-1282

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Abstract: The design and fabrication of a miniaturized calorimetric-type gas sensor in a single chip arrangement is presented. Active and passive thin-film Pt meanders are integrated in a single platform (7 × 7 mm^2) together with a temperature sensor and a thin-film microheater at the reverse side. Active meanders are covered by a porous Al_2O_3/2 wt % Pt thick-film layer. The selection of substrate, position of meanders, and active catalysts (especially their concentration) play a crucial role in directing sensor performance. The presented results show that the sensor signal (Wheatstone bridge voltage) is generated by diffusion-limited exothermic reactions which point towards catalytically enhanced combustion reactions mainly inside the active porous layer. By extrapolation of the linear sensitivity curves, the sensitivity limit was estimated to be 4 ppm for propene and to be 18 ppm for CO. In general, the one-chip-sensing concept has high potential to be used as a gas sensor for analysis of combustible gases; however, further optimization of the meander design and the catalyst material as well as investigations of the sensing behavior under varying ambient temperatures are necessary before such applications shall be considered.

Keywords: calorimetric gas sensor; single chip arrangement; LTCC; catalytic activity

1. Introduction

Calorimetric-type gas sensors have been used for decades to monitor the presence of combustible gases [1,2]. Originally, they were developed for early alarming of hazardous explosive gas mixtures, for example, in coal mines [3]. The vast technological development in the past 20 years has opened up a variety of fields for applications including detection of combustible gases, e.g., from automobiles [4]; however, the analysis of the gas components of a mixture is still in question [5]. The common working principle of such sensors is based on detection of exothermic combustion of gases proceeding at a catalytically active layer which results in a temperature change [3,6]. This change of temperature is reflected as a resistance change in an embedded Pt wire in the case of the classical bead configuration or in a metallic meander microstructured beneath a catalytically active thick-film layer. The classical configuration is a pair of sensor elements, called pellistors: an active catalyst element is supplemented with an electrically matched catalytically passive reference element [3]. These two elements together with two additional fixed equal resistors constitute a Wheatstone bridge arrangement. The presence of combustible gases results in an imbalance in the bridge; correspondingly, resistance changes with temperature increase, but only on the active elements, and the output signal is a good approximation to the concentration of the target gas. In the presence of a catalyst, sufficient kinetics of a combustion reaction are probably obtained at operation temperatures in the range 300–500 °C, i.e., a permanent heating power of about 1 Watt is necessary in the case of a classical bead configuration. Nowadays, those sensors are built using microstructured chip technology as well, comprising the catalytically active layer on a microhotplate to fabricate low-power devices with a typical heating power of about 50 mW or even less to enable battery-powered mobile instrumentation. The microhotplate can be realized as a suspended thin membrane etched in silicon [5,7] or on a polyimide foil, e.g., comprising two resistive meanders with one meander covered by a catalyst [8]. In both settings the change of temperature by exothermic reaction is recorded by a change of the meander-shaped thin-film resistance layer. Alternatively, the temperature difference between the active and nonactive layer is measured by use of a thermopile. Such a thermopile-based chip was realized, for instance, in a screen-printed microstructure on Au/Pt thermocouples on LTCC substrate (LTCC: low-temperature cofired ceramics) [9]. One array of junctions of the Au/Pt thermocouple was covered by a catalytically active alumina/Pt porous layer whereas the other junctions were covered by a catalytically inactive layer. The temperature difference between both sides of the thermopile in the case of exothermic gas reaction on the catalytically active layer is measured as a thermovoltage. In all technological variations, the signal response is mainly dependent on the sum of the combustion enthalpies of the gas components multiplied with their concentrations [1,3], i.e., direct analytical information of the composition cannot be extracted from the sensor signal.

In this paper, we present a calorimetric sensor chip based on the concept of resistive temperature measurement. The chip comprises four well-separated microstructured Pt thin-film meanders; two are covered by a catalytically active layer and two by a chemically inert layer forming a Wheatstone bridge of resistances. Although the concept is similar to that described in [7], in the present study, the thin meanders are realized on an LTCC substrate and the chip is temperature controlled by means of a microstructured heating element at the reverse side and a resistive temperature sensor integrated at the front side. The advantage of this bridge configuration of sensing elements will be discussed and the sensitivities and detection limits for CO and propene gas will be highlighted.

2. Sensor Concept

As already introduced above, gas combustion reactions with environmental oxygen in almost all cases are exothermic and produce heat power P_{Chem} according to Equation (1), which is a product of the number of moles combusted per time dn/dt and the combustion enthalpy $\Delta_c H$.

$$P_{chem} = \frac{dn}{dt} \Delta_c H \tag{1}$$

At a given P_{Chem}, the temperature of the catalytically active layer will rise and the heat will transfer to the environment by thermal radiation, diffusion, and gas convection effects [10]. The quantitative rise of temperature ΔT, which may be reflected in an approximately linear resistance increase of the meander structure beneath the layer, is represented as

$$R(\Delta T) = R_0(1 + \alpha\,\Delta T). \tag{2}$$

ΔT depends mainly on P_{Chem} per unit area and on the thermal conductivity of the substrate material if the other contributions are assumed to be roughly independent. In Equation (2), R_0 represents the resistance of the meander at the operation temperature T_0 adjusted by the heater control and α is the coefficient of resistance change with temperature of the thin-film Pt meander. If two meanders covered by a chemically active layer and another two by a chemically nonactive layer constitute a Wheatstone bridge (Figure 1), the corresponding bridge voltage U_x is the sensor signal, which depends on $R(\Delta T)$ according to Equation (3).

$$U_x = U_0 \frac{\alpha\,\Delta T}{2 + \alpha\,\Delta T} \cong U_0 \frac{\alpha}{2} \Delta T \tag{3}$$

In Equation (3), U_0 is the bridge support voltage, and $\Delta T = T - T_0$ is the temperature difference between meanders covered with active and nonactive layers, respectively. The calculation is based on the assumption that without exothermal gas reaction, the resistance of all meanders R_0 is the same at the given operation temperature T_0.

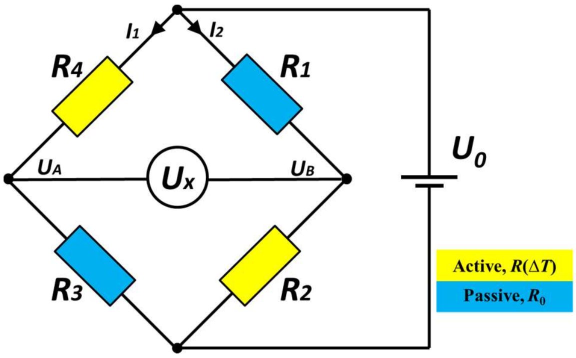

Figure 1. Arrangement of active and passive layers in a Wheatstone bridge.

According to Equation (3), the sensitivity $dU_x/d\Delta T$ is in good approximation to double the sensitivity as observed in a classical pellistor arrangement with only one gas-sensitive element [4]. For small temperature changes ΔT, in a first approximation a linear relationship between P_{chem} and ΔT is assumed and, furthermore, if dn/dt represents a transport-limited reaction rate at the porous gas-sensitive layer [10], the sensitivity $S = dU_x/dc$ should be constant, i.e., if the reaction rate is diffusion limited according to Fick's first law, a linear dependence of the bridge voltage U_x on the concentration c of the target gas is expected. Of course, this holds only in atmospheres at excess oxygen.

3. Materials and Methods

According to the considerations formulated in Section 2, it is expected that high sensitivity to combustibles is observed when P_{chem} is correlated with high ΔT. To reduce heat dissipation of the catalytically active zones of the chip by thermal conductance, i.e., to enhance ΔT between the non-active and active reaction zones, a substrate material of rather low thermal conductivity but with good thermal and chemical stability at temperatures beyond 400 °C had to be introduced. For this purpose, low-temperature co-fired ceramics (LTCC) are used as the substrate for preparing sensor chips because of their lower thermal conductivity (about 2.5 W/mK, 500 °C) compared with standard alumina substrates (10 W/mK, 500 °C) [11], which are a frequent choice for high-temperature applications beyond 300 °C. The sensor chips (Figure 2a) comprise four thin-film Pt meander structures ($R(T) \approx 30\ \Omega$ at room temperature) and a thin-film Pt resistive temperature sensor (metal line between the meanders) on one side and a thin-film Pt heater (Figure 2b) on the reverse side. Both microstructures were prepared by employing physical vapor deposition (PVD), photolithography, and plasma etching techniques [12]. Two meander structures are selected as "chemically active" and the other two as "passive". The active meanders (2 and 4, Figure 2c) are covered with a porous catalytical layer (2 wt % Pt/Al_2O_3) to promote combustion of gases. The catalytic layer was prepared by admixing of Al_2O_3 powder (CS-400/MS, Martinswerk GmbH, Bergheim, Germany) with an aqueous electrolyte of platinum nitrate (VWR GmbH, Bruchsal, Germany) by ball milling; later the result was dried and transferred to a paste by addition of an organic binder, and finally the paste was microdispensed on the sensor chip using an automized dispenser (Dotliner, Martin GmbH, Wessling, Germany). The layers were sintered at 600 °C. The passive meanders (1 and 3), the temperature sensor, and the heater were covered with a glass (Heraeus GmbH, Hanau, Germany), by microdispensing of pastes and subsequent firing, in order to limit gas reactions to the two active meanders. For further reduction of heat cross-flow from the catalytically active zones to the nonactive meanders and to the Pt resistive temperature sensor, an increased distance between active and nonactive areas (Figure 2a) was realized. This design aspect promotes further increase of ΔT and sensitivity.

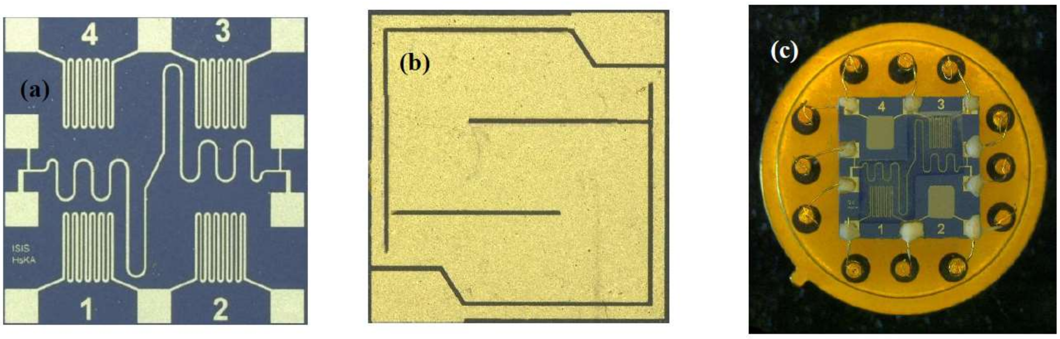

Figure 2. (**a**) Calorimetric sensor in single chip arrangement on a low-temperature co-fired ceramics (LTCC) substrate of 7 × 7 mm^2; (**b**) Pt heater structure on the reverse side; (**c**) Sensor chip with active layers (2% Pt/Al_2O_3) and passive meanders/temperature sensor covered by glass paste.

The response of the sensor (Figure 3) to different concentrations of CO and propene was measured in an automized gas sensor test station [13] under a constant flow (100 mL/min) of the model gas mixture. During operation, the sensor chip was heated at 500 °C.

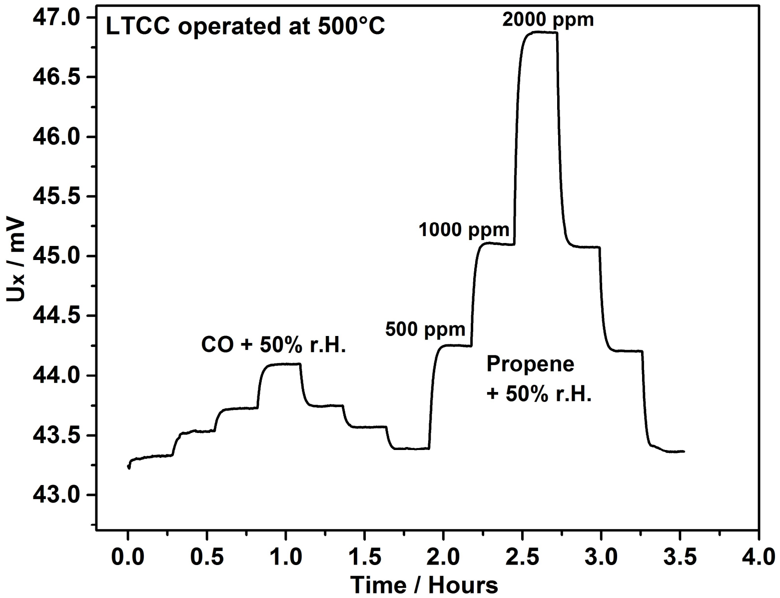

Figure 3. Bridge voltage U_x when the sensor chip was exposed to CO and propene at different concentrations but constant humidity (50% RH, 21 °C). The concentration steps at both gas exposures were set the same.

4. Results & Discussion

The response (bridge voltage measurement U_x) versus time (Figure 3) demonstrates that the signals are highly stable and reproducible at the repeated concentration steps by maintaining similar baselines and good reproducibility of the signals. However, U_x is not zero when synthetic air at 50% RH is exposed. This means that the bridge is not balanced at this condition and indicates inhomogeneous temperature distribution over the chip and, perhaps, limited resistive symmetry of the meanders forming the Wheatstone bridge. Inhomogeneity of the temperature was confirmed by a high-resolution IR camera (DIAS Proview 380 L, DIAS Infrared GmbH, Dresden, Germany).

Despite the temperature inhomogeneity, the change of the bridge voltage ΔU depends strongly linearly on concentration (Figure 4). This strengthens the assumption of a transport-limited reaction by diffusion perhaps at the geometrical surface and at the inner, porous surface of the active layer, as already discussed in Section 2. The ratio of sensitivities for propene and CO was estimated at S(propene)/S(CO) = 5.8. This value is significantly lower than the ratio of enthalpies Δ_cH(propene)/Δ_cH(CO) = 7.8, where Δ_cH(propene) = −2220 kJ/mol and Δ_cH(CO) = −283 kJ/mol were used for calculation. This means that there is no strong relation between enthalpies of combustion and sensitivities, and this may be explained by a higher diffusion coefficient of CO gas molecules in the porous gas-sensing layer ($D_{CO} > D_{propene}$).

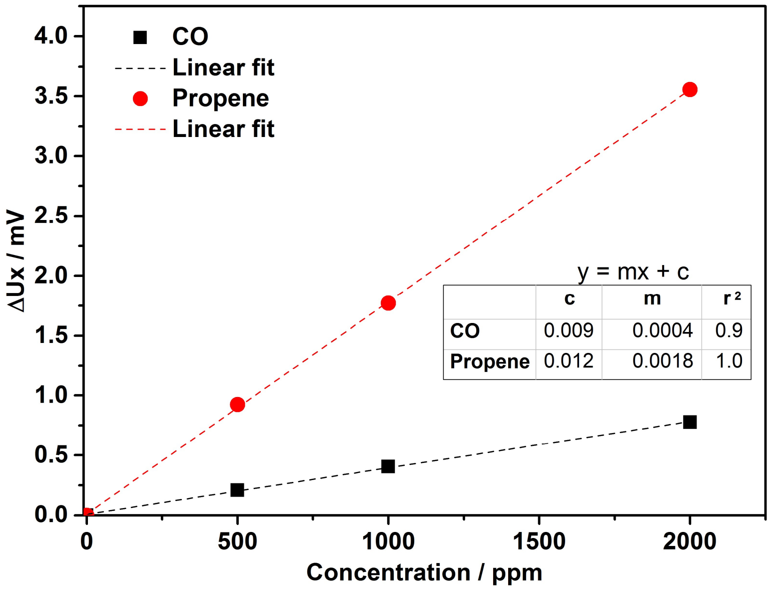

Figure 4. Response of the sensor (ΔU_x) vs concentrations of CO and propene.

Another important point related to application potential of the sensor concept is the limit of detection of this small one-chip sensor design. The noise of measurement of U_x, δ, has been analyzed at synthetic air conditions and the lower limit of measurement was defined to be significant if the signal is not lower than 3δ. Extrapolating the linear curves ΔU_x versus concentration (Figure 4) to the 3δ-value yields concentration limits of detection of about 4 ppm and 19 ppm for propene and CO, respectively. Although these values can be only rough estimations due to the wide concentration range of extrapolation, the results demonstrate that high gas sensitivity is possible even at this rather small chip design.

5. Conclusions and Outlook

A Wheatstone bridge based self-heated microstructured calorimetric-type gas sensor has been realized in a single chip design on an LTCC substrate. The sensitivities at different concentrations of CO and propene in 50% humid air have been obtained. The linear dependence of the sensor signals on gas concentration confirms a diffusion-limited combustion reaction, which indicates that the catalytical reaction proceeds less at the geometric surface but mainly inside the porous layer.

Under laboratory conditions, very stable and reproducible sensor signals were recorded and the lower limits of detection were estimated by the extrapolation method to be 4 ppm and 19 ppm for propene and CO, respectively.

These stimulating results open new options for fabrication of economic calorimetric gas sensors and applications for detection of hazardous, explosive gas mixtures and, perhaps, for analysis of partly and uncombusted gas components in the flue gas of biomass combustion systems. However, further optimization of the chip design, dependency of the sensitivity on layer thickness and catalyst concentration, and behavior of the temperature-controlled chip at varying ambient temperatures are still open and will be investigated in future work.

Author Contributions: H.K. conceived the idea; H.K. and N.I. designed the experiments; O.K. and O.A. performed the experiments; N.I., J.K., B.O. and H.K. analyzed the data; J.K. and B.O. contributed reagents/materials/analysis tools; N.I. and H.K. wrote the paper.

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Conflicts of Interest: The authors declare no conflict of interest.

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