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# Functionalized pyroelectric sensors for gas detection

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**Abstract**

A new calorimetric gas sensor based on functionalized integrated pyroelectric detector arrays was fabricated and tested. The advantages of this sensor are mainly based on its miniaturized design enabling a close-by arrangement of sensing and reference structures. The low heat capacity and high thermal isolation of the sensor elements enable in principle the application of integrated low power heating structures. Lead–zirconate–titanate (PZT)-based detector arrays were fabricated on silicon and mounted in test packages adapted to the printed circuit board (PCB) containing a simple readout circuitry. The performance of two different types of sensor surface functionalisations was studied. A polymer coating with polydimethylsiloxane (PDMS) was chosen to detect heptane absorption. A detection limit of 10 ppm heptane was found. Bacterial surface layers functionalized with small Pt clusters were applied to study catalytic oxidation of hydrogen. Within the investigated range from 0.5 up to 3.5 vol.% hydrogen, no saturation of the detection signal was observed.


*Keywords:* Calorimetric sensor; Pyroelectric detector array; S-layer; $H_2$-detection; Heptane absorption

## 1. Introduction

The capability of pyroelectric transducers to detect temperature changes which are generated by chemical reactions offers the possibility to utilize pyrochips as calorimetric chemical sensors. Generally, calorimetric sensors are widely used for the detection of combustible gases like for instance hydrocarbons, carbon monoxide and hydrogen, where the concentration-dependent thermal power of a catalyzed oxidation reaction is converted into an electrical signal by appropriate temperature sensing elements [1–6]. Furthermore, calorimetric sensors which are functionalized with gas absorbing coatings are useful for the recognition of volatile organic compounds (VOCs).

In a pellistor, which is the classical catalytic calorimetrical sensor for combustible gases, temperature sensing is performed by platinum resistance wires. Nowadays, miniaturized planar silicon devices with thin film platinum heaters and temperature sensors (micro hot plates) are more common [1,2]. Alternatively to resistive temperature detection, the importance of thermoelectric heat power transducers for calorimetric sensors is growing. Thermoelectric metal oxide sensors [3,4], fabricated in thick film technology, as well as Si or SiGe thin film thermopile sensors [5,6], prepared by conventional CMOS processes, provide, e.g. for hydrogen, detection limits in the lower ppm range. Because of the small thermal inertia of silicon thermopile sensors and the inherent reference temperature compensation effects, they can be operated in a high-speed temperature scanning regime up to 600 °C and with cycle times of a few milliseconds [5]. With respect to differences in the activation energies of the involved gas components, the shape of the signals is a characteristic of the investigated mixture, i.e. the application of pattern recognition methods should lead to an enhanced selectivity of the sensor [5].

Pyroelectric-based heat power transducers, which are mainly utilized in practice for the detection of infrared radiation, show advantages for chemical sensor applications, if fast temperature

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changes can be expected. Thus, they play an outstanding role in adsorption calorimetry, e.g. for the direct calorimetric measurement of the monolayer adsorption of metal atoms, oxygen or carbon monoxide on clean single crystal surfaces [7,8]. If the rate of a sensor recognition reaction is modulated in time in order to increase the rate of the temperature changes, which could be done, e.g. by periodic switching between analyte and reference gas flows or by temperature modulation, pyroelectric transducers should also have potentials for application as chemical sensor, as it was already demonstrated for the detection of hydrogen [9].

Here we focus on the chemical sensor application of Si-integrated pyroelectric detector arrays [10] enabling the application of different functionalisations on the same chip. The arrays were fabricated using thin film and bulk micro-machining technologies. Two kinds of sensor surface functionalizations were used to demonstrate their potentials for the detection of VOCs as well as for pellistor-similar applications. For the latter an elevated sensor temperature according to the catalytic working temperature of the particular gas of interest is necessary. Integrated low power heating structures adapted to the sensor design were successfully tested.

## 2. Sensor design and surface functionalization

### 2.1. Sensor device fabrication

The basic part of the sensor is formed by the pyroelectric detector chip carrying eight sensitive elements with an individual size of 720 μm × 360 μm. To compensate interfering signals, two elements are series connected. The functional principle of a pyroelectric sensor is given by the conversion of a change of temperature into an electrical signal as voltage or current. Originally developed for infrared applications, these sensors exhibit a specific detectivity of about $10^8$ cm Hz$^{1/2}$/W for a frequency of 1 Hz correlating with a noise equivalent power of <1 nW making them interesting also for calorimetric sensor applications.

A schematic cross section of a sensitive element of the pyroelectric detector array is depicted in Fig. 1. The array is formed by a thin film capacitor deposited on a supporting $SiO_2/Si_3N_4$-membrane. The dielectric is made of a thin film of ferroelectric lead zirconate titanate (PZT). To provide a sufficiently high thermal isolation, the underlying silicon is removed by bulk micro machining.

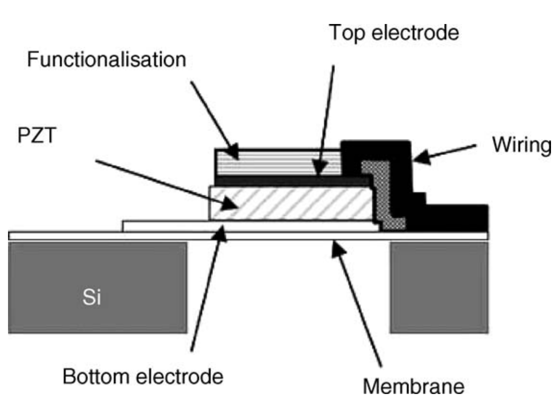


Fig. 1. Schematic sensor layout.

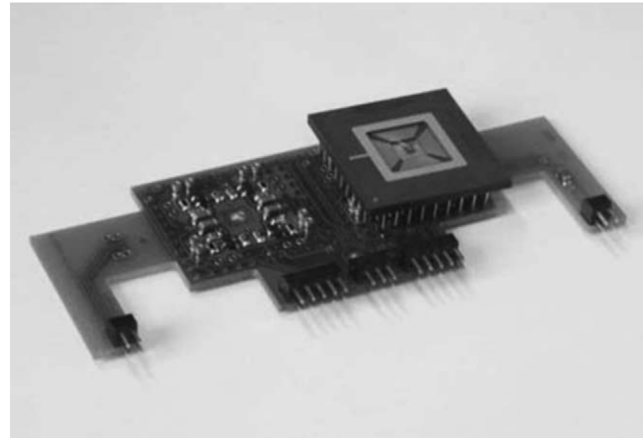

Fig. 2. Assembled gas sensor on PCB with readout circuit.

To enable elevated working temperatures a local low power thin film heater arranged on bulk-micromachined membranes and integrable with the pyroelectric sensor structure was developed and tested.

For the application as calorimetric gas sensor, the individual elements were functionalized by covering them with appropriate thin films. Heat released by interactions between analyte gas and functionalization will change the temperature of the pyroelectric element and consequently result in an electrical signal. For the test of the sensors, two types of sensor surface functionalizations were chosen as described in detail in the next section.

The detector chip is mounted in a ceramic housing adapted to the printed circuit board (PCB) carrying a simple readout circuitry with an optional voltage amplification of 10 (Fig. 2). PCB and housing are adapted to a gas flow cell enabling the supply of defined concentrations of the analyte.

### 2.2. Functionalization of the active sensor surfaces

The functionalization of active elements of the pyroelectric detector array was accomplished by coating them with a chemically sensitive layer of PDMS (polydimethylsiloxan) for the detection of VOCs or with Pt-cluster arrays grown on bacterial surface layers (S-layers) serving as catalyst for hydrogen oxidation.

For PDMS, a change of amount of gas absorbed by the functional layer causes transient heat power effects leading to temperature changes within the sensor elements. Their amplitude depends on the enthalpy and the equilibrium constant of the absorption as well on the rate of the concentration change of the analyte. A micromanipulator served for precise positioning of the polymer solution. The expected heat of absorption related to the mass of PDMS is 1.9 Ws/g at a heptane concentration of 1000 ppm [11]. Based on the specific detectivity of $10^8$ cm Hz$^{1/2}$/W at around 1 Hz and a polymer density of about 1 g/cm$^3$, a PDMS thickness of a few micrometers is estimated to be necessary for a heptane detection in the low ppm-range.