Sensors and Actuators A 169 (2011) 308–316

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

Measurement of reaction heats using a polysilicon-based microcalorimetric sensor

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ARTICLE INFO

Article history:
Available online 26 February 2011

Keywords:
Microcalorimeter
Hot-plate
Gas sensor
Oxidation of alkanes
Catalyst

ABSTRACT

In this work we present a low-cost, low-power, small sample volume microcalorimetric sensor for the measurement of reaction heats. The polysilicon-based microcalorimetric sensor combines several advantages: (i) complementary metal oxide semiconductor technology (CMOS) for future integration; (ii) elements of silicon micromachining (MEMS) to control thermal performance; (iii) heterogeneous catalysts for selective detection and analysis of individual gas compounds; and (iv) microfluidics for optimized control over the reaction conditions.

A comprehensive study on the electrical properties of polysilicon thin films as a potential material for temperature monitoring of highly exothermic reactions is presented. Resistive measurements were performed up to 800 °C and a temperature coefficient of resistance (TCR) of 3.24×10^{-4}/°C was derived in the quasi-linear resistive range between 300 and 500 °C. The polysilicon thin film temperature sensors show a good stability. Due to its excellent compatibility with silicon technology and chemical inertness, doped polysilicon thin films can be successfully applied in catalytic microreactors and sensor microsystems at high operating temperatures.

We demonstrate the performance of polysilicon sensors by the detection of reaction heats for a model reaction – the catalytic oxidation of propane in air at concentrations in the range of 0.01–0.8 vol.% which is below the low explosion level (LEL) of propane of 2.1% [1]. The sensor exhibits immediate and reversible response upon exposure to propane in air. By choosing a selective catalyst the specificity of the sensor can be tuned to different gases.

1. Introduction

1.1. Microcalorimetric sensors

Microcalorimetric sensors belong to the group of thermal chemical sensors and detect the heat of a reaction, released or consumed. This change in enthalpy associated with a (bio-) chemical reaction introduces a temperature change, which can be converted into an electrical signal and measured. The rate of a chemical reaction depends on temperature and concentration of target compounds. Therefore, the determination of the heat evolved provides a means of measuring the gas concentration [1,2]. One of the ways to initiate a reaction is to use a heterogeneously catalyzed system. In a typical measurement, the device is brought in contact with a solid catalyst that lowers the operating temperature of the sensor and provides a degree of control over the reaction kinetics. The basic elements of a catalytic sensor are a temperature sensor, a heater and a catalyst. The performance of a catalytic sensor is determined by each of these three elements [3].

There is a demand for microcalorimetric devices in various fields due to the simplicity and the selectivity of a microcalorimetric measurement. The detection and analysis of chemical components is vital for various industrial, commercial, research and domestic applications. Commonly, the gas reactants and by-products exhibit similar physical properties, but need to be monitored individually. Additionally, a fast response of the sensor in combination with the possibility to design a highly specific sensor are factors of main concern during the development of a gas sensing and analysis system. This counts especially for the detection of hazardous gases for environmental and automotive exhaust control [4,5], where response time and selectivity play a crucial role. Microcalorimetric sensing also has become an industrial method for measuring the flows of both gases and liquids [6]. On the application of microcalorimetry in microfluidics an informative review by Lee and co-workers was published [7]. Furthermore, microcalorimetric detection is

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doi:10.1016/j.sna.2011.02.010

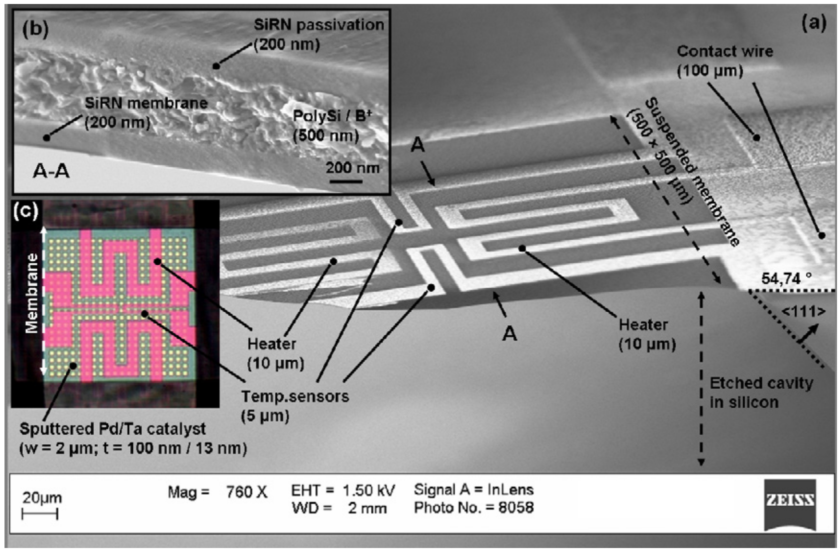

Fig. 1. HRSEM image of the sensor device after silicon etching (a), cross-sectional view on the SiRN/PolySi/SiRN membrane (b), and microscopic image made from the back side of the released membrane showing the arrangement of heaters and temperature sensors (c).

also widely applied in bioanalytical chemistry [8]. An overview of various designs of microcalorimeters for (bio-) chemical analysis was given by van Herwaarden [9]. Finally, microcalorimetric sensors have been successfully applied in the process control of integrated microreactors for gas-phase catalytic reactions [10–12]. An important issue in this application is the possibility of maintaining similar reaction conditions in various channels during scale-up and automation.

This work focuses on microcalorimetry as a detection method. It is the only method providing a direct indication of the reaction kinetics by absolute measurement of reaction heats. The ultimate goal of this study is to develop a microfluidic system in which microcalorimetry is applied for catalytic detection of gases, kinetics studies, but also for catalyst screening, study of catalyst deactivation processes and measurement of reaction, adsorption or desorption heats. We use a solid catalyst immobilized on a transducer surface. The catalytic oxidation of various hydrocarbons (methane, ethane, propane, etc.) occurring at elevated temperatures was selected as a target reaction. Furthermore, high temperature handling within 100–450 °C is required for on-a-chip activation and regeneration of catalysts. For these reasons it is important that resistive characteristics of functional material do not degrade under the influence of temperature.

As a proof of concept we study the oxidation of propane in air for concentrations of propane within 0.01–0.8 vol.% using a CMOS compatible, low-power micro hot plate based sensor. The oxidation reaction is exothermic and the released reaction heat is directly proportional to the gas concentration. This is used for calibration. The actuating temperature of the catalytic oxidation (typically up to 550 °C [13,14]) and the measured total reaction heats are parameters which are specific for individual gas compounds. In this way an effective differentiation between compounds of common nature may be achieved by using one single chip.

1.2. Feasibility of polysilicon integration

In this study we implement thin films of doped polycrystalline silicon (polysilicon) as resistive heaters and temperature sensors. Polysilicon is a widely studied material and its implementation in microsensor technology was investigated extensively [15]. However, its properties still find new and exiting applications in CMOS/MEMS design, e.g. thermoelectric power generators [16], temperature sensors on a chip for study of polymerase chain reaction (PCR) [17] or micromachined neural probes [18]. This demand for polysilicon as a material for high temperature sensing and microreactor applications is justified by its excellent compatibility with standard CMOS and MEMS technologies, its stability and chemical inertness at high temperatures.

Platinum (Pt) is a preferred material for high-temperature sensing applications [19]. Polysilicon, unlike commonly used Pt thin films, does not catalyze any (undesired) reactions. In microsystems comprising catalysts and applied for the synthesis or analysis of fine chemicals it is of special importance that all elements except the catalyst exhibit zero catalytic activity. Although it is possible to circumvent this problem for Pt resistors, by encapsulating it between catalytically inactive passivation layers [20], reliable use of Pt requires a stable adhesion layer. Most of the issues related to a Pt reliability are due to a degradation of this adhesion layer at temperatures above ca. 550 °C. Polysilicon thin films do not require such adhesion layers.

Processing of polysilicon has some advantages compared to metal thin films. It enables high temperature operations and, can, therefore, be easily passivated with high quality thermal oxide or nitride to prolong the life-time of a resistor. Ehmann and co-workers investigated the properties of polysilicon in harsh temperature environments and demonstrated its reliable operation for temperatures up to 1200 K [21].

Furthermore, polysilicon can be used not only as a material for heating and sensing, but also as a thermopile, a piezoresistive component or as a mechanical support in bulk micromachining. This is especially important for the construction of smart sensor systems comprising devices of various functionalities.

In addition, as a part of the global trend, silicon-based sensors and microreactors need to be technologically merged with MEMS/NEMS. In this view, polysilicon-based microdevices easily enable high temperature post-CMOS processing steps, such as temperature-assisted anodic bonding.

2. Experimental

2.1. Design overview

The prototype calorimetric sensor consisted of heavily boron doped polysilicon heaters, temperature sensors and a patterned