

Fabrication and Properties of a Si-based High Sensitivity Microcalorimetric Gas Sensor.

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Abstract

This paper discusses the design, fabrication, and testing in a laboratory flow-bench of a Si-based differential microcalorimeter to detect combustible gases at low concentrations. Design parameters most affecting the device sensitivity are reviewed.

Introduction

Calorimetric sensors for combustible gases, such as methane (CH_4) and carbon monoxide (CO), are commercially available in various forms [1,2]. A Pellistor, for example, consists of a small ceramic body impregnated with a noble-metal catalyst and a platinum resistor thermometer imbedded in it. This type of catalytic sensor measures the heat generated during combustion of the reactant with oxygen in the atmosphere by measuring the temperature rise induced on the ceramic element. Under appropriate conditions [1], the magnitude of the temperature rise is related to the combustible concentration. To compensate for environmental temperature fluctuations, differential structures are most commonly employed so that the reactant concentration is proportional to the temperature difference between a catalytically active element and another inactive element of (nearly) identical thermal characteristics.

Although successfully employed for years, catalytic-bead calorimeters have typical response times of several seconds because of their thermal mass and type of encapsulation, require hundreds of mW to operate, and the two elements have to be matched by sorting [1]. These devices are mainly used to detect thousands of ppm of combustible gases, such as CH_4 , although sensors with higher sensitivity but longer response time have also been reported [2].

Silicon micromachining offers the opportunity of fabricating well-matched devices with lower power consumption at potentially lower manufacturing costs. A micromachined device can also have a faster response time because the sensing element has a smaller thermal mass. On the other hand, the capability of micromachined devices to measure very low concentrations of combustible gases has not yet been established [3,4]. Devices capable of measuring 100 ppm of HC or lower are desirable for pollution monitoring applications.

This paper describes the design, fabrication, and evaluation in a laboratory flow bench of a Si-based microcalorimeter for the detection of combustible gases in the concentration range 0 to 4000 ppm. The device evaluation was

carried out under steady state conditions by externally heating the gas stream to better characterize the device behavior under well controlled conditions.

Design and Fabrication

The average temperature rise in a microcalorimeter is dictated by the balance of heat produced by the chemical reaction and the heat lost to the environment. In order to maximize the detection limit of the sensor, effects such as the reactant mass transfer, the reaction kinetics at the catalyst, the heat loss by conduction/convection to the ambient gas and by conduction to the substrate, thermal fluctuations in the environment, and the electrical characteristics of the thermometer must all be taken into account.

The key elements of a Si-based microcalorimeter are the catalyst, the temperature sensing element, the heater, and the supporting structure for all of the previous elements. The structure consists of a silicon frame with either a membrane or a more complex plate/teeter element which is obtained by

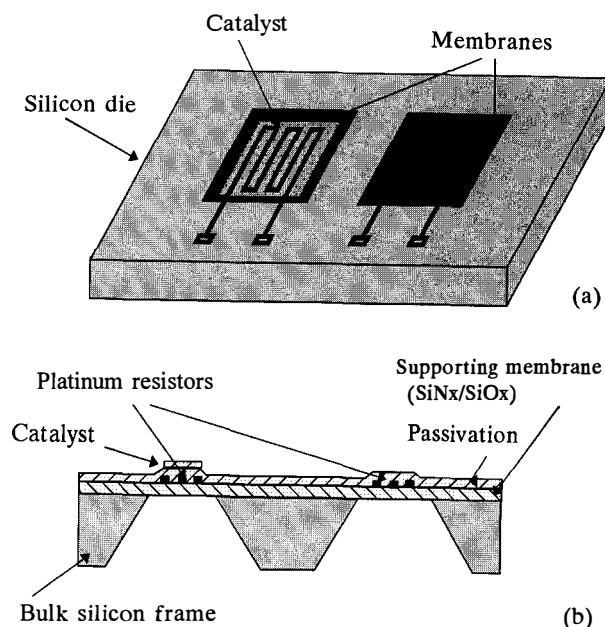


Fig. 1. (a) Perspective view and (b) schematic cross section of the microcalorimeter design used in the experiments reported in this paper.

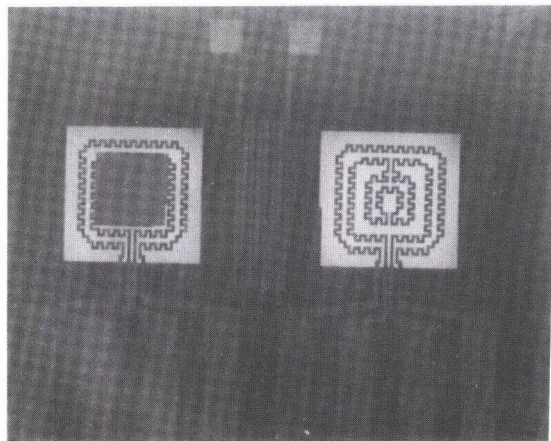


Fig. 2 The photograph shows another type of microcalorimeter with separate Pt resistors for the heater and the thermometer. A Pd film catalyst covers part of the membrane on the left.

etching the underlying bulk silicon. The membrane should have a small thermal mass for fast response time, but must be mechanically robust to support the thermometer and the catalyst and survive temperature cycling, pressure shocks, water mist and small particles impingement. It should also be configured in such a way as to minimize the heat loss to the silicon frame and to the ambient gas for increased sensitivity. The catalyst should have a large specific surface area for the device to operate in mass-transport limited regime. In this case, some catalyst aging can be tolerated without causing the sensor output to change. Good thermal contact between the catalyst and the underlying temperature sensing element is also important for increased sensitivity. The catalytic layer should not substantially change the thermal characteristics of the membrane otherwise the sensor temperature compensation may be compromised. For greater sensitivity, the thermometer should mainly sense the central region of the substrate where the temperature rise due to the reaction is the greatest, without substantially contributing to conductive heat loss. A thin-film resistor with stable resistance and temperature coefficient of resistance (TCR) is desirable as the temperature sensing element. The film resistor is patterned as a winding element to increase its resistance (i.e., the output signal) and distribute the stress induced by the thermal mismatch with the substrate.

The microcalorimetric devices studied in this work utilize thin dielectric membranes. Similar structures have been recently reported by other authors [3,4]. However, the membranes of devices that we have investigated are much larger, ranging from 1 to 4 mm² to facilitate various deposition techniques for a variety of catalysts. The larger size is achieved by using low residual-stress dielectric films. Our simplest design, shown in Figs. 1a and 1b, uses a 1.2x1.2 mm² membrane. The die includes two identical membranes separated by 1 mm on the silicon frame to minimize thermal cross-talk. The membranes are kept relatively thick (up to 1 μm total thickness) for robustness, in order to support thick catalytic layers (up to a few μm) and to withstand stress induced by mismatch in thermal expansion coefficients. The temperature sensor is a Pt-film in a serpentine pattern that covers approximately 50% of the

membrane area. Another design shown in Fig. 2 uses double element (heater/thermometer combination) with a wave-like pattern in order to distribute thermal stresses. A thermopile-based device, using Pt and Pt/Chromel, was also fabricated to evaluate the advantages of this alternate temperature sensing method. This paper, however, reports only results obtained on devices as depicted in Fig. 1a.

As schematically shown in the device cross-section of Fig. 1b, the supporting membrane is deposited first on a silicon wafer, 100 mm in diameter, 400 μm thick. We have used either a 0.6 μm thick layer of low-stress LPCVD silicon nitride, or a composite of PECVD silicon oxide/nitride layers (about 0.5 μm and 0.1 μm, respectively) deposited over 0.1 μm of LPCVD nitride. After annealing at 600 °C, the latter composite layer, has a small residual stress (tensile) of about 6×10^{-8} dynes/cm², the compressive state of the oxide being compensated by the tensile nitride. A Pt film, 100 nm thick, is then sputter deposited in argon after an ion-milling step, which removes approximately 20 nm of the top silicon nitride film, to improve the adhesion of Pt to the substrate. Alternatively, a film of Ti/Pt, consisting of a 10 nm Ti layer and a 100 nm Pt layer, is prepared by e-beam deposition. The film resistors, acting as temperature sensors and/or heaters, are delineated by lithography and wet etching. After annealing the Pt resistors at 500 °C in nitrogen to stabilize their resistance and temperature coefficient of resistance (TCR), the wafers are coated with 0.2-0.3 μm of PECVD silicon nitride for passivation and annealed at 500 °C. The passivation is then removed on the contact pads with plasma etching. While defining the opening for the contact pads, an etch-mask pattern is also defined on the back side of the wafer using a double-sided aligner. A 30% aqueous solution of KOH at 80 °C is used to completely etch the silicon underneath the membranes. The membranes have sufficient mechanical strength to allow the wafer to be diced with a diamond saw. For ease of handling, a die size of 7x7 mm² is used, although only a 3.5x3.5 mm² area is needed for the device with the smallest membranes. For maximum flexibility, the catalyst is deposited after dicing on single devices, either by sputtering through a shadow mask (mainly Pt and Pd) or using solutions/slurries impregnated with the appropriate catalytic material.

Microcalorimeter Thermal Sensitivity

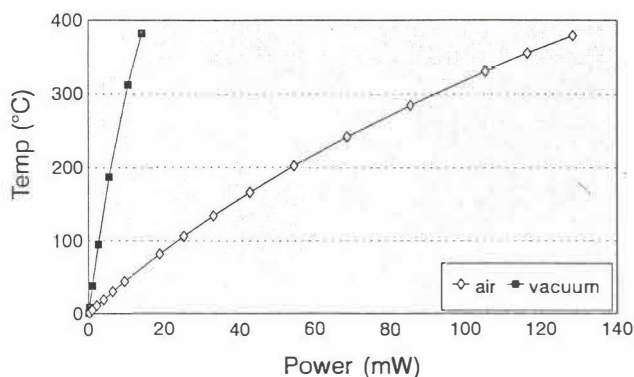


Fig. 3. Thermal sensitivity of the device measured in stagnant air and in vacuum.

Catalytic Differential Microcalorimeter Sensitivity

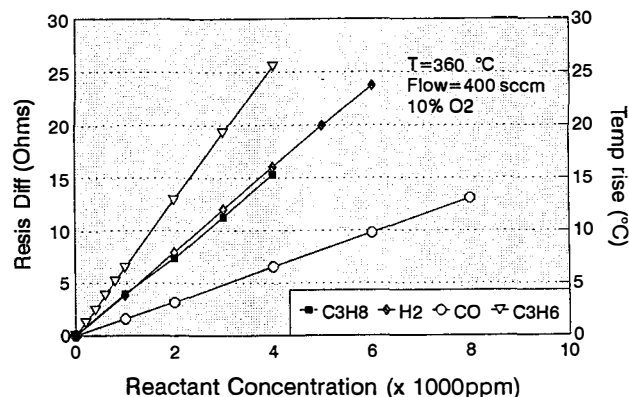


Fig. 4. The resistance difference between the active and the reference temperature sensing elements of the microcalorimeter (left vertical axis) is plotted as a function of propylene, propane, hydrogen, and carbon monoxide concentration by volume. The right axis shows the corresponding average temperature rise produced by the reaction on the membrane.

Characterization

The devices were characterized both for their thermal and chemical response. The thermal sensitivity of the device was determined from the temperature rise detected by the Pt thermometer when 1mW electrical power was dissipated through it. The chemical sensitivity for a given combustible gas is defined as the average temperature difference between the two membranes when the device is exposed to 1000 ppm of reactant at a given temperature. In both cases, the temperature change was determined from the change in resistance of the Pt thermometer and its previously measured TCR. Since the temperature rise generated on the catalyst at the gas concentrations of interest was less than 30°C, a linear relation between resistance R (ohms) and temperature T (degrees Celsius) was assumed as given by

$$R(T) = R(0)[1 + \alpha T]$$

Typical values for α (TCR), as measured in a furnace under steady-state conditions between room temperature and 400°C, are 2500 ppm/°C for the Ti/Pt resistors and 3000 ppm/°C for the Pt resistors. Fig. 3 shows the temperature rise observed on the device as a function of power input, both in air, under stagnant conditions, and in vacuum. The thermal sensitivity in air is 5°C/mW and 38°C/mW in vacuum, demonstrating that the major heat loss mechanism for these micromachined "hot plates" is conduction to the ambient gas.

The device response to different gases was measured in a steady-state flow reactor in which the gas stream was kept at constant temperature by an external heater. The tubular flow chamber was made of quartz and the sample was positioned in the center by an alumina rod axially inserted in the tube opposite to the end where the gas stream entered the flow chamber. The silicon die was cemented to an alumina plate and

wire-bonded to screen-printed interconnects on the substrate. The devices were usually mounted several millimeters away from the leading edge of the substrate. The gas stream was prepared by mixing nitrogen and oxygen with one or more reactants using mass-flow-controllers. The flow rates were varied between 100 and 1000 sccm. The cross section of the reactor was approximately 10 cm², and the average flow velocity in the quartz chamber could be changed from about 0.2 to 2.0 cm/s. The volume of the chamber was approximately 2000 cm³.

Hydrogen (H₂), carbon monoxide (CO), propane (C₃H₈), and propylene (C₃H₆) were used for the characterization. Typical reactant concentrations were in the range 0 to 4000 ppm. The tests were run with excess oxygen, either 2% or 10% by volume. The flow stand was controlled by computer which was also used for recording the device output as a function of time. In a typical run, the gas concentration was changed stepwise every 5 minutes, while the flow and temperature of the gas stream were kept constant. In other runs, the reactant concentration was kept constant and the flow rate was changed.

The sensor output was measured in two different modes. In one case, a constant current of 1mA was passed through the two resistors connected in series and the voltage drop across each one was recorded and converted to a resistance difference by the computer. In the other case, the active and the reference elements were connected in a Wheatstone bridge configuration to two external resistors, approximately equal in value to the reference resistor at the temperature of the measurement. The voltage difference across the reference and active resistor and the bridge offset voltage were recorded and converted by the computer to resistance values. The sensor output was sampled with a 180 ms integration time every 20 s, or faster, with the average of the last 10 points used to generate the response vs. concentration curves, as shown in Fig. 4. The standard deviation of the same 10 data points was taken as a measure of the signal variability. The gas concentration in the large-volume flow chamber could not be changed fast enough at the flow rates allowed by the equipment to measure the true chemical response time of the device. Characterization at higher flow rates is under way.

Results and Discussion

Fig. 4 shows typical results on the sensitivity of a device which uses a small-mass agglomerate of fine powders as a catalyst, the same material used in a macroscopic commercial device [2]. The catalyst covered about 80% of the area defined by the thermometer. Fig. 4 plots the device output, measured as a resistance difference, as a function of the concentration for four different gases. The average temperature rise is shown on the right axis. The data were collected at a gas temperature of 360 °C. The device sensitivity to C₃H₆ is 6.2 °C/1000 ppm, while the relative sensitivities to C₃H₈, C₃H₈, H₂, and CO shown in Fig. 4 are 3.9 : 2.3 : 2.4 and 1. For diffusion-limited operation, it is expected that the device sensitivities to different gases scale as the product of the enthalpy of combustion and the diffusion coefficient of the reactants. The respective enthalpies of combustion for these gases are 458, 486, 57, and 67 Kcal/mole, while the binary diffusion coefficient at 350 °C are 0.56, 0.54, 0.75, and 2.7 cm²/s, respectively. The products of

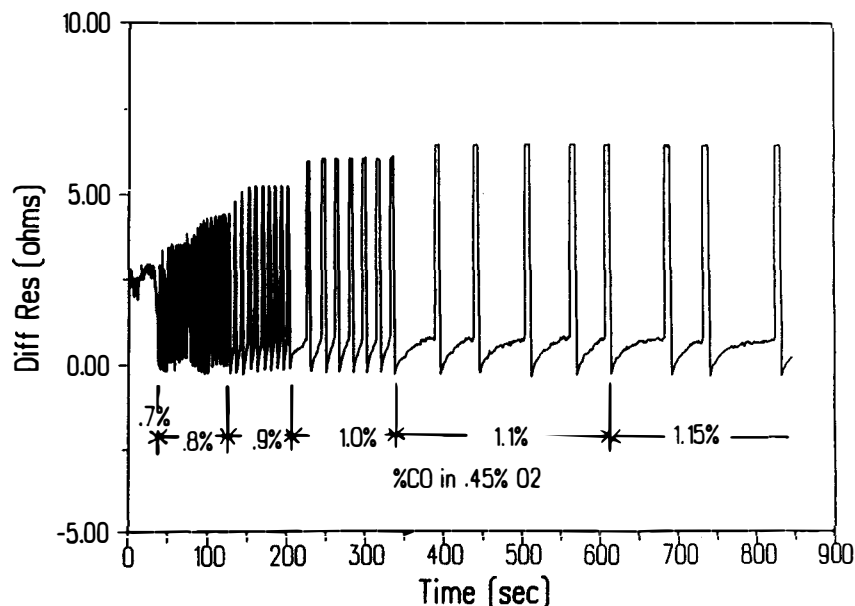


Fig. 5. Oscillatory reactions observed for the oxidation of carbon monoxide on the surface of a microcalorimeter using a Pd film catalyst.

the diffusion coefficient and enthalpy for the different gases scale as 5.1 : 5.2 : 3.1 : 1. These values are close to the measured relative sensitivities but not in the right order. The discrepancies may signify that the device response depends on the reaction rate at the catalyst surface, at least for some of the gases. However, the device output is nearly temperature independent above certain values (for H_2 and C_3H_6 , about 150 and 300 °C, respectively), which supports the model that the device is mass-transport limited above certain temperatures. Further studies are being carried out to clarify these discrepancies.

The detection limit for this device is defined here as the standard deviation of ten successive measurements carried out with short integration time (180 ms). For propylene, a maximum standard deviation value of 53 mΩ was measured, corresponding to a detection limit of 8 ppm. The standard deviation of the sensor output measured in a bridge configuration was found to be about a factor of five smaller.

Similar results were obtained for devices having a 400 nm Pd film as the catalyst, covering an area slightly larger than that occupied by the thermometer. The output signal, normalized to a temperature rise, was approximately 30% less than that found for an equivalent device with the commercial catalyst. In addition, the response to propane was very small and saturated quickly by increasing the reactant concentration.

A thermal response time of 20 ms was measured for the devices used in the measurements described in this paper. In another flow stand capable of higher flow rates, the chemical response time was found to be of the order of 1 s.

Oscillatory reactions for CO and C_3H_6 were observed for the device using a Pd film catalyst at 300 °C. Fig 5 shows the device output changing from low to high in less than 1s. Notice that the period of the oscillations is affected by the reactant concentration, as expected for chemical oscillatory phenomena [5].

Some devices were also evaluated in the self-heated mode by passing current through the thermometer. The results of these measurements were similar to the data reported above. Almost no convective cooling was detected for flow velocities comparable to those used in the previous experiments.

CONCLUSIONS

The present results show that the detection limit of a Si-based differential microcalorimeter can be, under laboratory conditions, of the order of 2 ppm of propylene and that response times of the order of 1 s can be achieved. The device sensitivity to different gases depends on the catalyst used. The device output is relatively insensitive to temperature and flow, consistent with mass-transport limited behavior. This is the desirable operating mode for a calorimetric device to minimize changes induced by catalyst aging. However, we have found some discrepancies between the measured values for the relative sensitivities to various gases and the values calculated for a simple diffusion model.

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