A Calorimetric Micro-Sensor for Methane Detection

Sebastian Sosin, Carmen Moldovan, Elena Manea

***Abstract*—In this work, a miniaturized pellistor for methane detection based on conventional IC fabrication is proposed and analysed. This integrated device should have several advantages over the standard design i.e. increased reproducibility, possibility to integrate read-out electronics on the same chip, reduced power consumption and possibility of making portable devices.**

The calorimetric sensor consists of a Ti-W heater (working temperature over 300°C), an insulation SiO_2 layer, a Cr-Pt temperature sensor and a catalytic layer made from Pd-doped Al_2O_3. These layers are embedded on a suspended membrane to minimize heat loss. We have realized heaters that have an average resistance of 3.5 kΩ.

The design was first simulated in IntelliSuite to find weak spots and to estimate the voltages needed to reach working temperature (7-9 Volts for 300-400°C).

***Keywords*— methane sensor, sol-gel deposition, thermal simulations, Pt resistor.**

I. INTRODUCTION

Detection of flammable gases is a vital aspect of environmental security in many application areas (domestic applications, mining industry, chemical industry, etc.). The traditional gas sensing devices which were built by covering a *platinum resistor* with a catalyst-doped ceramic *pellet* are called *pellistors*. Here the reaction takes place inside the ceramic pellet impregnated with the catalyst (heated at 300-500°C) and involves reaction between oxygen and a flammable gas. The resulting heat is detected as an imbalance of the bridge in which the sensor is connected.

In this paper, the results of our effort to improve pellistor characteristics based on application of a standard IC technology are described.

Using standard IC technology it is possible to manufacture a miniaturized pellistor that will have several advantages over the standard design i.e. increased reproducibility, possibility of co-integration of the sensing device together with electronics on the same chip, reduced power consumption and possibility of making portable systems.

II. CALORIMETRIC GAS SENSING

In general, a calorimetric sensor detects the heat. In our case, this heat is generated in a chemical reaction where the to-be-detected gas burns in a presence of oxygen and the catalyst. High efficiency of the catalytic reaction requires that the catalyst is heated to its working temperature. By heating the sensor (e.g. with Ti-W heater as shown in Fig. 1a) to the working temperature (over 300°C) the reaction between the gas (CH_4) and oxygen can take place inside the sensitive layer (porous Al_2O_3) in the presence of the catalyst (Pd). The burning reaction generates heat that leads to an increase of temperature. This variation of temperature is proportional to the concentration of methane in air and it is detected with a temperature sensor that usually is a platinum resistor (Cr-Pt resistor). The resistor is integrated in a Wheatstone bridge and each variation of gas concentration leads to an unbalanced bridge. To avoid thermal losses, the active sensor part is usually integrated on a membrane or a bridge.

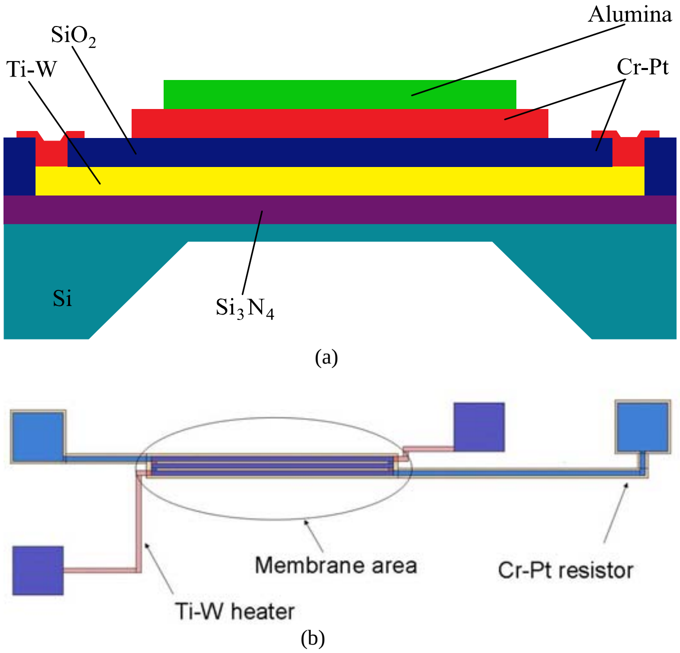


Fig. 1. Calorimetric sensor cross section (a); and sensor layout (b).

Manuscript received September 26, 2005. This work was supported by the Romanian National Research Program MATNANTECH and by IntelliSense (providing their software tools).

S. Sosin was till May 15, 2005 with IMT Bucharest and is now with the Delft University of Technology, Lab. of HiTeC / Dimes (Mekelweg 4, 2628 CD Delft, the Netherlands, phone: +31-15-2786468; fax: +31-15-2623271; e-mail: s.sosin@ ewi.tudelft.nl).

C. Moldovan is with IMT Bucharest, The Laboratory for Microsystems in Biomedical and Environmental Applications (32B, Erou Iancu Nicolae street, 077190, Bucharest, Romania, e-mail: cmoldovan@imt.ro).

E. Manea is with IMT Bucharest (32B, Erou Iancu Nicolae street, 077190, Bucharest, Romania, e-mail: elenam@imt.ro).

III. DESIGN

Our design tries to respect two main criteria: low power consumption and compatibility with conventional IC technology. The device consists of a thin metal (Ti/W) heater and a platinum temperature sensor built on top of a suspended silicon nitride membrane (dimensions of 500µm x 50µm). The Pd-doped alumina layer is deposited by spin coating of a sol-gel solution that after thermal treatment becomes doped Al_2O_3. Building the sensor on a suspended membrane reduces heat loss through the substrate thus minimizing power consumption. The membrane is released using back-side anisotropic etching leaving the membrane suspended over a ~400µm deep air cavity. Both the heater and the sensing resistor have a similar design consisting of three 500 µm long by 10µm wide metal lines; Ti-W for the heater and Cr-Pt for the temperature sensor (see Figure 1a and 1b).

IV. MODELING

A. *Introduction*

After designing the layout, finite element analysis (FEA) simulations were performed in order to determine if the design has flaws and if the device is going to perform close to our expectations. Simulations were performed for a device with polysilicon heater on a suspended bridge.

For FEA, a model is created based on the layout and the fabrication steps. In Figure 2 the 3D model mesh used for simulating the sensor with the integrated heater is shown. The bottom of the device was fixed and had a constant temperature of 27°C. The mesh has greater detail along the resistors and the bridge since this is the area of the sensor where higher accuracy of the thermal profile and mechanical behaviour of the structure is required.

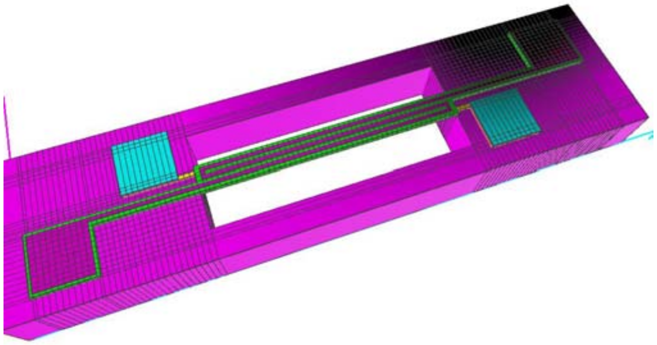
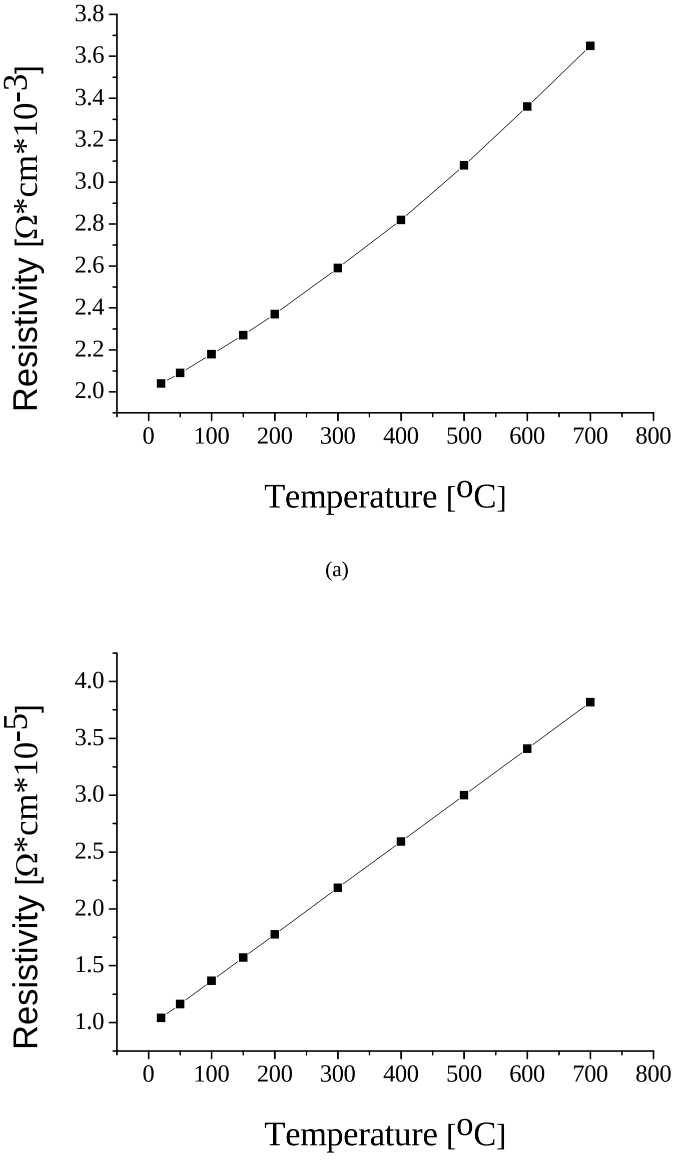


Fig. 2. Meshed FEM model of a calorimetric sensor.

B. *Device simulations*

Because the device operates at high temperature it is necessary to use a temperature dependant resistivity for the electro thermal simulations. For the heater layers polycrystalline silicon and platinum were considered. Their temperature variable resistivity between 20°C and 700°C is shown in Figs. 3a and 3b.



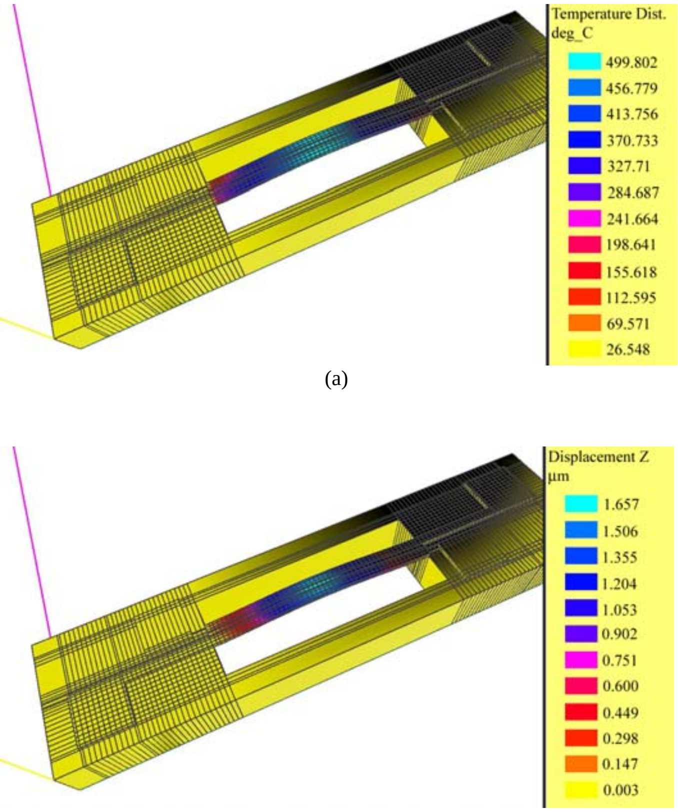
(a)

(b)

Fig. 3. (a) Polysilicon resistivity; (b) Platinum resistivity vs. temperature.

Two types of results were obtained from electro-thermal simulations of the sensor model: z-axis displacement and temperature distribution. The device needs higher voltages to heat at temperatures higher than 300°C, because of higher heat losses at higher temperatures. Figure 4a shows the thermal profile of the sensor at 10.5 Volts.

In Table 1 the results obtained from three simulations are presented. The results indicate that operating voltage of 7.5-9 V should be sufficient to achieve the required working temperature of 300-400°C for the Pd catalyst. However, confirmation of these results on fabricated samples is required.



(a)

(b)

Fig. 4. (a) Temperature distribution, and (b) z-axis displacement at 10.5 Volts.

TABLE 1. Simulations results of sensor at different voltages.

Simulation Nr.	Voltage (Volts)	T_{max} (^oC)	maximum z-axis displacement (microns)
1	4	113	0.31
2	7.5	301	0.96
3	10.5	499	1.65

V. FABRICATION

Fabrication sequence of the proposed calorimetric sensor is shown schematically in Fig. 5. After wafer cleaning, a thin thermal oxide is grown on the wafers. Silicon nitride (0.5 µm) is deposited on both sides of the wafers: on the top side it will form the membrane and on the back side it will act as mask for the final anisotropic etch (Fig.5b).

Before depositing the thin layers of metal for the heater another cleaning is done and after drying the wafers are coated with 0.02µmTi/0.1µmW (Fig.5c). The heater is then defined through a photolithographic process. The metals are easily etched in 34 g KH_2PO_4-13g KOH-33g $K_3Fe(CN)_4$ -11g H_2O with an etch rate of 1600Å/min.

Before covering the heater with an electrical insulating layer of SiO_2 the heater electrical resistance is measured on random structures across the wafer. The measurement shown that the average resistance is 3.5kΩ with a 10% variation across the wafer.

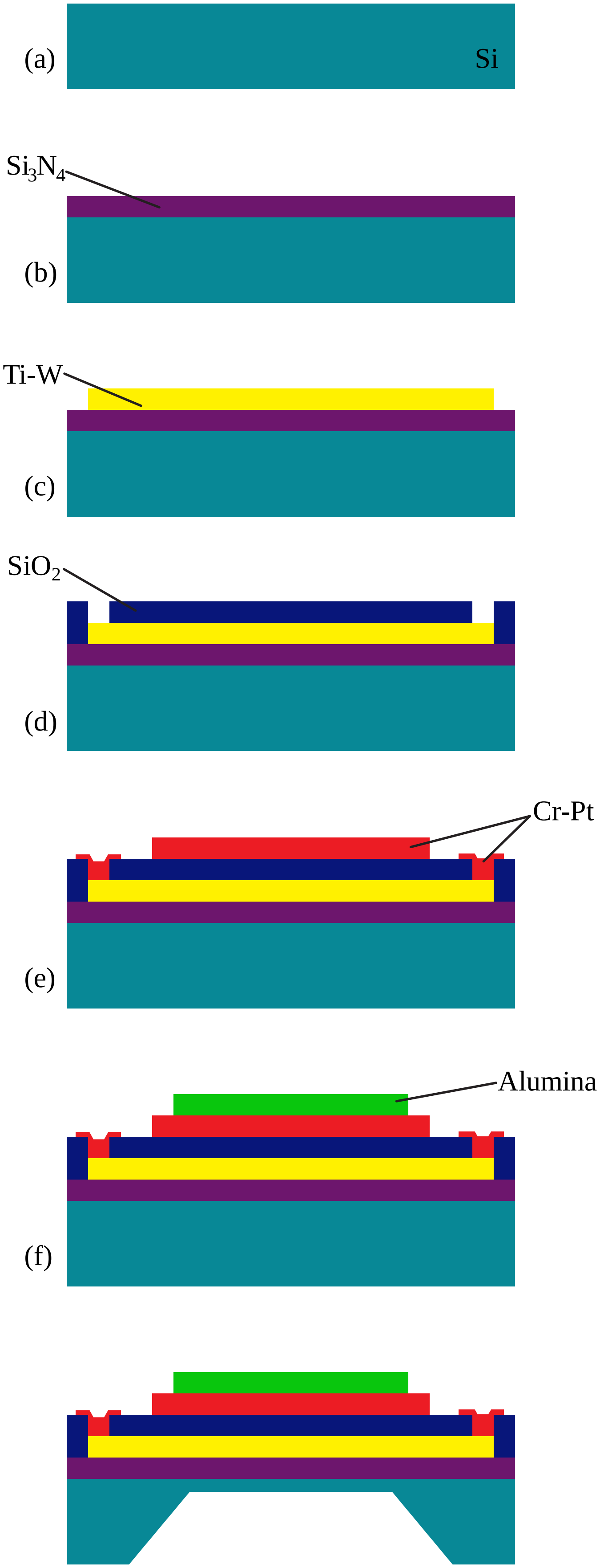


Fig. 5. Schematic fabrication sequence of the calorimetric sensor.

The isolation oxide is deposited and patterned by lift-off because the heater is easily etched in HF (0.5µm thick, Fig.5d). This layer covers the whole chip, leaving only contact openings for the heater.

Another lift-off step is used for patterning the platinum heat sensor (Cr/Pt, 0.02µm/0.2µm, Fig.5e) since platinum is hard to wet etch (in Aqua Regia). In Figure 6 two sensors (from an array of four) are shown just before sol-gel deposition. The two resistors are isolated by a layer of SiO_2 and the pad openings for the heater can be easily seen.

The wafers are then cleaned and the silicon nitride on the wafer backside is plasma etched to open windows for KOH etch step (Fig.5g). Since the sensitive layer is spin coated (Fig.5e), the membrane should be released only after coating the wafers with the sol-gel.

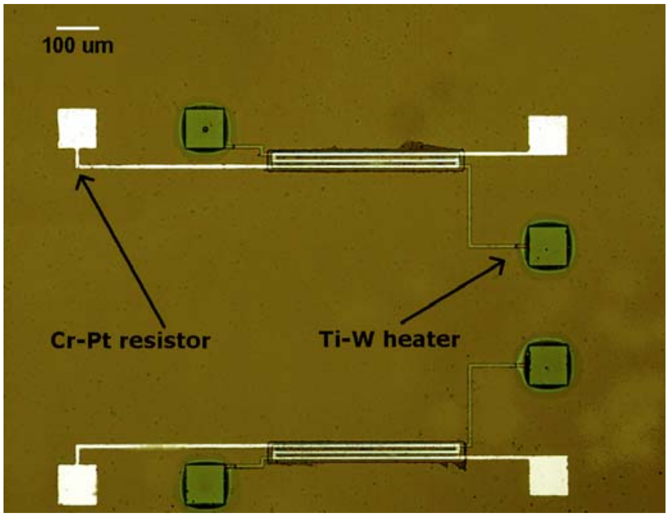


Fig. 6. Photography of fabricated heater and sensing resistor.

VI. CONCLUSIONS

We have designed and simulated a calorimetric gas sensor fabricated on a suspended membrane. The fabrication of the sensor is almost finished and on-wafer measurements seem to agree with the simulations.

The purpose of the simulations was to determine if the device would operate with low power consumption and also if this design could work at the temperatures higher than 300°C needed for the catalytic reaction to take place. Before running the simulations the membrane (bridge) was supposed to be released by using a sacrificial layer leaving the membrane suspended over a one micron gap. This design was modified since the maximum z-axis displacement of the beam is greater than one micron and also finding the right masking material for the front side release of the wafer was too complicated. Using a back side anisotropic etch release of a membrane instead of a bridge solves many of the initial problems caused by the sacrificial layer design.

Although no simulations were done for the membrane design we expect that heat loss will be bigger than in the suspended bridge design. By combining simulations and measurement we hope to solve the problems and improve the design of a second generation of this sensor.

Most of the measurements showed a value of the heater resistance around 3.5 kΩ, with small variations from wafer to wafer. We also found several wafers that had heater resistances around 2.7 kΩ and we suppose this is caused by old equipment.

Problems were encountered with adhesion of the sol-gel during one test on dummy wafers. The problems could have been caused by dirty wafers and humidity level in the lab. Further tests are required in order to find the proper viscosity of the sol-gel.

REFERENCES

[1] J.W. Gardner, P.N. Bartlett; Electronic Noses - Principles and Applications, Oxford University Press, 1999, pp 67-110.
[2] R.F. Taylor, J.S. Schultz; Handbook of Chemical and Biological Sensors, Institute of Physics Publishing Bristol and Philadelphia, 1996, pp. 371-394.
[3] S. Sosin, C. Moldovan, R. Iosub; Designing and manufacturing of a calorimetric micro-sensor for methane detection, CAS International Semiconductor Conference Proceedings, Vol. 2, 2004, pp. 381 – 384.
[4] IntelliSuite User Manual.