Nanowire Hydrogen Gas Sensor Employing CMOS Micro-hotplate

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***Abstract*— In this paper we present a novel hydrogen gas sensor comprising a high temperature SOI-MOS micro-hotplate and employing zinc oxide nanowires as the sensing material. The micro-hotplates were fabricated at a commercial SOI foundry followed by a backside deep reactive ion etch (DRIE) at a commercial MEMS foundry. Particular care was taken in designing the heater shape using a systematic parametric approach to achieve excellent temperature uniformity (within 1-2%) as shown by both simulations and experimental infra-red imaging results. Zinc oxide nanowires were grown on these devices and show promising responses to hydrogen with a response (R_a/R_h) of 50 at 100 ppm in argon. The devices possess a low D.C. power consumption of only 16 mW at 300°C and, being CMOS compatible, offer low unit cost in high volumes and full circuit integration. We believe that these devices have potential for application as a sub-$1 hydrogen sensor with sub-1mW (pulsed mode) power consumption.**

I. INTRODUCTION

The development and increasing use of fuel cells has created an emerging demand for low cost sensors capable of detecting hydrogen leaks. Micro gas sensors with integrated electronics offer the possibility of low cost, low power gas sensing.

Typical designs of micro machined gas sensors in the literature consist of a sensing material heated by a micro-hotplate [1]. The micro-heater is thermally isolated from the substrate by means of a thin membrane. The high temperature helps improve the sensitivity and response time of the sensor. The presence and concentration of gas can be determined by the change in resistance of the sensing material. Alternatively, detection can be done by a calorimetric method where a catalyst is deposited on the micro-hotplate, and the temperature change due to combustion of the target gas detected.

Among possible sensing materials, nanomaterials are very promising for use in these devices. Nanomaterials have a large surface to volume ratio, which means that they have good sensitivity even in the small volumes that are used in micro sensors. Several materials have been reported in the literature and show good sensitivity [2-5].

However, for such devices to be produced in low cost and large volumes, they should be compatible with CMOS technology. Unfortunately most micro-hotplate designs reported in the literature employ technologies and materials (such as platinum) which are not CMOS compatible. In addition, most nanomaterial deposition/growth techniques found in the literature use conditions that are too harsh for CMOS membrane devices.

Also, since the gas sensitivity of the materials varies with temperature, for accurate sensing it is essential that the heater shape is designed such that the temperature is uniform throughout. While temperature uniformity has been studied in the literature [6-8], there appears to be no systematic approach to heater design.

In this paper we report on the hydrogen sensing results of ZnO nanowires grown on our SOI-CMOS micro-hotplates. An initial overview of the micro-hotplates is given, followed by a description of a very systematic approach adopted for the heater shape design. Finally, the gas sensing results of the ZnO nanowires for 100 ppm of hydrogen are presented.

II. SOI MICRO-HOTPLATE TECHNOLOGY

We have previously reported on the fabrication and characterization of different types of SOI micro-hotplates based on Tungsten, MOSFET and Single Crystal Silicon heaters [9-11]. The devices were fabricated by a commercial SOI-CMOS process followed by back etching by Deep Reactive Ion Etching (DRIE) to release the membrane. The

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devices have very low power consumption and can have integrated circuitry. The membrane radius of the devices is 280 µm, and the heater radius is 75 µm. Figure 1 shows the cross section of a tungsten micro-hotplate with the sensor and CMOS circuitry on the same chip.

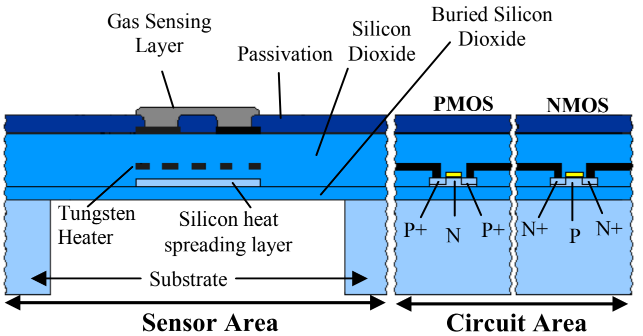

Figure 1. *Cross-section of a Tungsten based Micro-hotplate. The sensor and CMOS circutiry are on the same chip.*

Tungsten has the advantage that it can operate at very high temperatures. MOSFET heaters are easier to control through gate drive, and single crystal silicon heaters have very good long term stability.

III. Heater Design for Temperature Uniformity

The sensitivity of most sensing materials varies with temperature. Therefore, for accurate gas sensing, it is essential that the sensing material is at a uniform temperature throughout. This can be achieved by using either a heat spreading plate and/or designing the heater shape for good thermal uniformity.

A heat spreading plate is a plate within the heater region made from a material with high thermal conductivity such as silicon. This can be either embedded within the membrane's layers, or can be a thick silicon plug below the membrane. However, the thick plug requires a more complicated etching process, so an embedded silicon and tungsten plate were used in our design. These plates are very thin (around 0.2 µm) because of the fixed process parameters. Therefore, for good temperature uniformity it is important to have a good design of the heater shape in addition to the heat spreading plate.

Usually in the literature, researchers try different heater shapes and simulate them, and determine the one that gives the best temperature uniformity. However, we show here a more systematic approach to design the heater shape which was used to design the tungsten micro-hotplates. To design it, we consider the heater in two parts: an outer ring heater and an inner heater, similar to [12].

Consider first a case where there is no heat loss due to convection or radiation (i.e., only conduction losses). In such a case, a ring heater will give an ideal temperature uniformity [13], since heat loss will only flow outward of the heater, and no heat will flow within. With this ring heater, if the convection losses are now considered, the centre of the region will be cooler than the outer part of the heater region. This is because convection heat loss will also occur from the centre of the heater to the air, and to compensate for this, heat will flow from the edge of the heater to the centre. This heat flow will cause a temperature gradient within the heater.

To balance this, a heat source, such as another ring heater is needed at the centre. For perfect temperature uniformity, the heat provided by this inner ring heater should be exactly equal to the heat loss due to convection within the heater area.

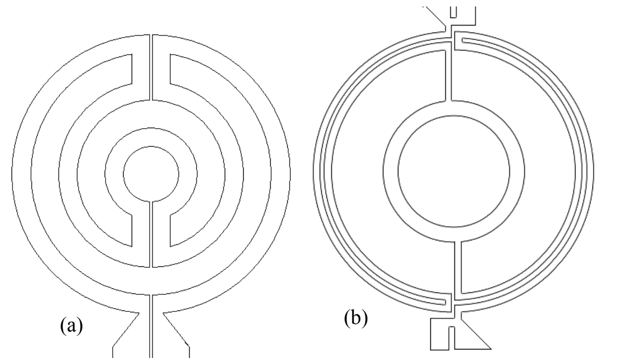

Figure 2. *(a) A simple Multi-ring Design used for the initial simulations. (b)The heater shape designed for good temperature uniformity.*

To start with, we used a simple multi-ring heater design as shown in Figure 2(a). Simulations were performed using ANSYS software for this design including conduction and convection losses and the results are shown in Figure 3. These losses can be divided into three parts: (i) conduction, (ii) convection from within the heater area and (iii) convection outside the heater region, but within the membrane. The heater should be designed such that the outer ring compensates for losses (i) and (iii), and the inner ring compensates for the loss due to (ii). This can be achieved, for example, by having the rings connected in series and having resistances proportional to the respective power required.

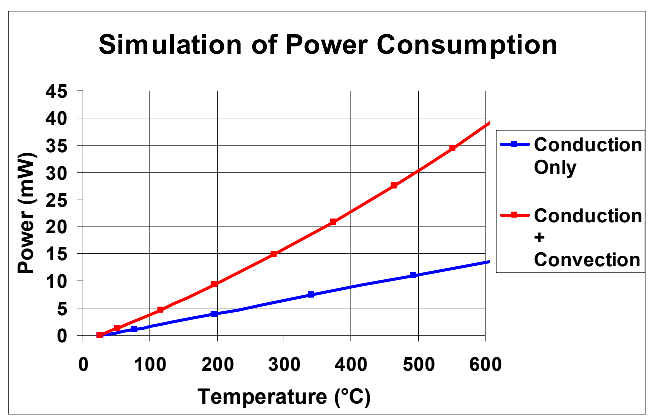

Figure 3. *The simulated power consumption of an SOI micro-hotplate.*

Consider Figure 3, at 300°C conduction losses are 6 mW and the convection losses are 10 mW. To separate out the convection losses into the parts (ii) and (iii), i.e. within the heater region and outside the heater region, consider the convection equation:

$$P_{conv} = hA(T - T_0) \qquad (1)$$

where, A is the area, T is the surface temperature, T_0 is the ambient temperature and h is the convection heat transfer coefficient. Since the temperature varies within the membrane, the convection losses per area are also different at different points on the membrane. Therefore, an estimate of the temperature at each point is required as a function of the distance from the centre.

A simple estimate can be made by assuming that h is constant across the membrane and that the temperature varies linearly outside the heater region (which is not the actual case but is sufficient for a rough estimate). Taking r_1 as the heater radius, and r_2 as the membrane radius, consider the region between r_1 and r_2.The temperature at a point within this region is given by:

$$T(r) = \frac{r_2 - r}{r_2 - r_1}\left(T_1 - T_0\right) + T_0 \qquad (2)$$

where T_1 is the heater temperature, and r is the distance of a point from the centre of the membrane. Consider a ring on the membrane of radius r and thickness dr. The convection loss from this ring is:

$$dP_{conv} = h\left[\frac{r_2 - r}{r_2 - r_1}\left(T_1 - T_0\right)\right]2\pi r dr \qquad (3)$$

Integrating this from r_1 to r_2 and adding the convection loss from the heater region (assuming a uniform temperature within the heater region), the total convection loss is given by:

$$P_{conv} = \frac{h(T_1 - T_0)2\pi}{r_2 - r_1}\left[\frac{r_2^3}{6} - \frac{r_2 r_1^2}{2} + \frac{r_1^3}{3}\right] + h\pi r_1^2 (T_1 - T_0)$$

This can be solved to determine h = 326 W m^{-2} K^{-1}, which can be then used to determine the convection loss just within the heater region as 1.6 mW. Therefore, the outer ring should be able to provide 14.4 mW of power, while the inner ring should provide 1.6 mW of power. Therefore, we designed the heater as shown in Figure 2(b). For reliability purposes it was decided to use two thick outer rings instead of one thin ring to get the same resistance. The ratios of the resistances of the inner and outer rings are the same as the ratio of the power required inside and outside the heater.

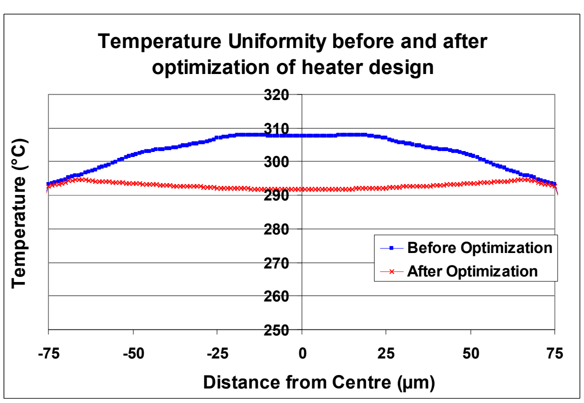

Figure 4. *Simulation of the temeprature uniformity of the heater.*

Figure 4 shows simulations of the difference in the temperature uniformity comparing the initial and final heater designs. As can be seen, the new design has almost perfect uniformity. Figure 5 shows an IR thermal image of the fabricated device, and this shows extremely good temperature uniformity (within 2%).

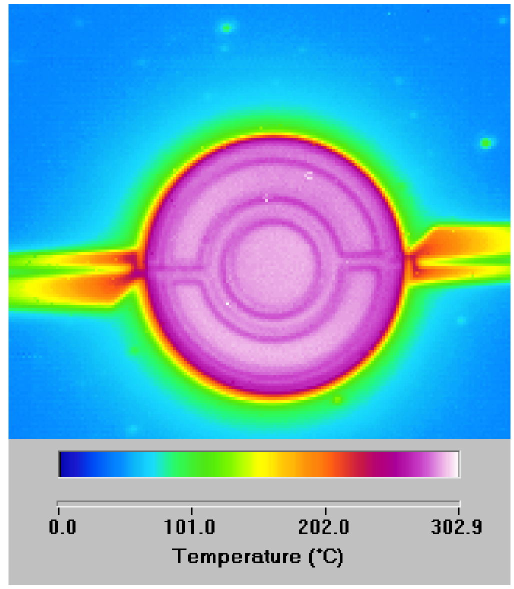

Figure 5. *IR measurement of the temperature distribution within the heater region.*

IV. Zinc Oxide Nanowires and Hydrogen Sensing

A. *ZnO Growth*

Zinc Oxide nanowires were grown on Single Crystal Silicon based micro-hotplates using a hydrothermal method [14]. This was achieved by first sputter depositing a seed layer of ZnO (~5µm) on selected areas of the chip. The devices were then dipped for 2 hours at 90°C in an equimolar (25 mM) aqueous solution of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, Sigma Aldrich) and hexamethylenetetramine (HMTA, Sigma Aldrich).

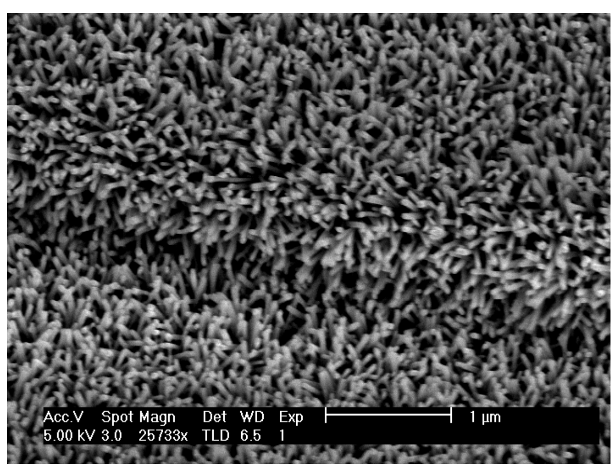

Figure 6. *An SEM of the ZnO manowires grown on a CMOS micro-hotplate.*

Not only is this method easy to use on CMOS devices with fragile membranes, but it can be used to grow on many devices (or full wafers) at the same time. Figure 6 shows an SEM picture of the ZnO nanowires grown on the micro-hotplates.

B. Hydrogen Sensing

The ZnO nanowires were then tested for response to 100 ppm of hydrogen in argon. The micro-hotplate was used to heat the material to a high temperature, and the resistance of the material was measured with and without the presence of hydrogen. Figure 7 shows the gas sensing results for three different micro-hotplate temperatures. The gas response is extremely high, with the resistance dropping from 1400 to 26 Ω, an (Ra/Rh) value of 50, and the response time improves significantly at high temperatures.

Figure 8 shows the response to hydrogen at a micro-hotplate temperature of 300°C. The recovery time of the sensor is initially slow, but it greatly speeds up when heating to 380°C.

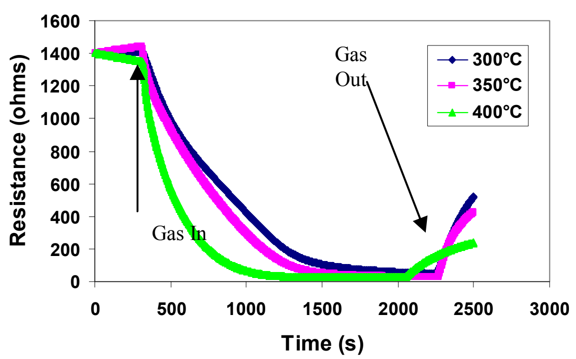

Figure 7. *Gas Sensing measurements for 100 ppm of hydrogen in argon. The micro-heater is used to heat up the ZnO nanowires to different temperatures and the film resistance is measured.*

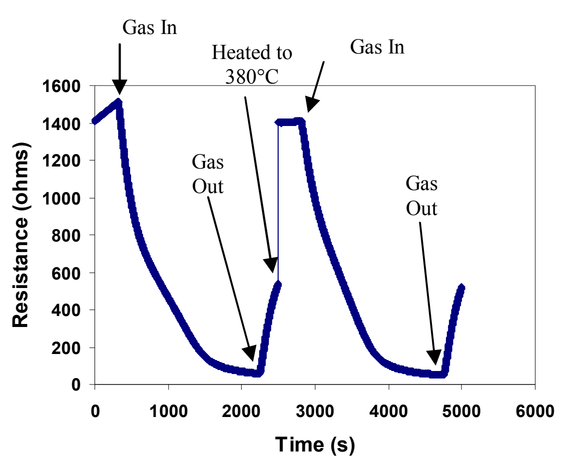

Figure 8. *Gas sensing measurement at 300°C with improved recovery time by overheating.*

V. CONCLUSIONS

In this paper, we have reported on the temperature uniformity of our CMOS micro-hotplates and on the hydrogen sensing results of ZnO nanowires grown on our devices. Instead of a trial and error method, we have adopted a systematic approach to the design of the heater shape and achieved excellent temperature uniformity. We have also reported the gas sensing results of ZnO nanowires grown on our devices, which show very good sensitivity. The devices have low D.C. power consumption, (16 mW at 300°C), are CMOS compatible and have good response to hydrogen, and so have the potential to be used as a low cost, low power hydrogen gas sensor.

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