Micromachined Mercury Sensor

Kwan Schambach
Geminus e. G.
dj2dx@amsat.org

Klaus Eden
University of Applied Sciences Dortmund
eden@fh-dortmund.de

Klaus Schumacher
University of Dortmund

Gerhard Wiegleb
University of Applied Sciences Dortmund

Abstract

To allow efficient monitoring of the mercury concentration in air, a high sensitive micromachined sensor was developed. This sensor works with the so-called 'amalgam procedure'. The new idea with an integrated measuring bridge can compensate the most of the parasitic effects and double the bridge sensitivity. A heater is integrated underneath the measuring bridge on the sensor chip. The regeneration process of the sensor can be achieved by heating the mercury sensitive gold layer to approximately 150°C using this heater.

Thanks to the highly integrated form of this mercury sensor, the development of a small, compact, mobile hand held instrument with direct mercury concentration readout will become possible soon. The low current consumption of the integrated components will allow battery powered operation over several hours.

1. Introduction

It is well known that mercury and its compounds eventually cause serious poisoning. Due to its unique properties, mercury is still used in many technical fields like in fluorescent tubes, switches, batteries, rectifiers, tooth fillings, etc. Worldwide annual mercury emission is approx. 45000t into the atmosphere and approx. 4000t into the ocean [1].

Mercury is introduced into our environment and eventually find its way into the food chain through natural events (such as those related to volcanic activity) as well as through human activities such as the burning of coal, fuel oil and garbage, the smelting process and as the by-product of industrial processes. Legislation for the protection of both human beings and the environment is regulated according to the MEL-value (maximum exposure limit; for example in Germany is this value $100 \mu g/m^3$) [2]. To allow efficient monitoring of these values, a precise and high sensitive measuring instrument is required.

Actually photometric procedures based on the principle of atomic absorption are the most commonly used. However, these applications are costly, unwieldy and are not suitable for mobile use.

To fulfil the requirements mentioned, a miniaturised mercury sensor was developed that will allow quick mobile analysis. This sensor works with the so-called 'amalgam procedure'[3]. It is known that mercury forms amalgam in connection with gold. This effect can be used to determine the presence and concentration of mercury steam [4]. The formation of the amalgam causes a change in the electrical resistance of the gold layer. This change in resistance can be measured directly via a measuring bridge integrated on the sensor chip. The regeneration process can be achieved by heating the gold layer to approximately 150°C using a electrical heater underneath the gold layer. The entire design of the sensor is based upon the micromachined thin film technology. A prototype of sensor is shown in figure 1.

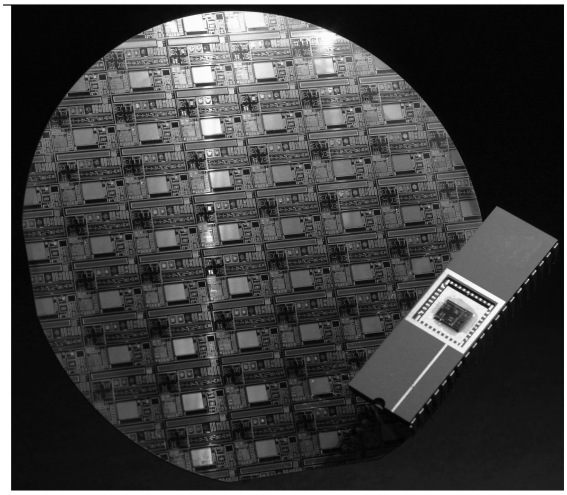

Figure 1. Sensor wafer and a prototype of sensor

2. Design of mercury sensor

The mercury sensor consists of four meander-shaped gold structures on the sensor chip, making a total size of 2mm × 2mm. All of these gold structures have a thickness of approximately 40nm. Figure 2 shows one of these gold structures. Mercury adsorption leads to an increase in the electrical resistance of the former thin gold structure. So we can call this film a Hg sensitive film. Unfortunately, the sensitive layer shows a huge cross-sensitivity to ambient temperature changes. To compensate most of the parasitic effects and double the bridge sensitivity, the gold structures are connected together electrically into a measuring bridge. Figure 3

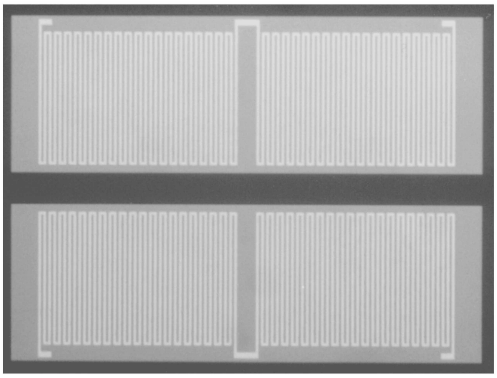

Figure 2. Gold structures

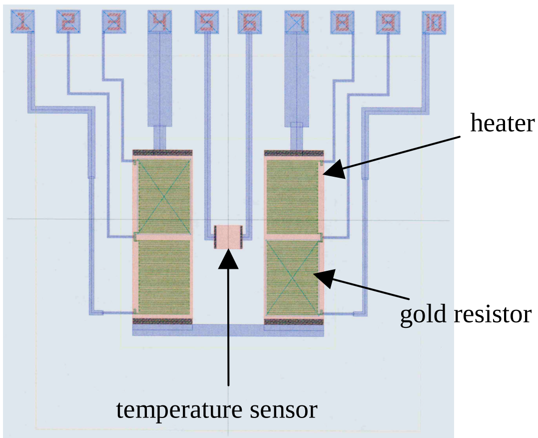

Figure 3. Design of mercury sensor

shows the design of one sensor combined with a Wheatstone bridge circuit[5]. All of the four gold structures are placed on one silicon chip very close to each other to avoid temperature differences between sensing and reference resistors, thus improving the sensor's reliability. The equivalent circuit diagram is shown in figure 4.

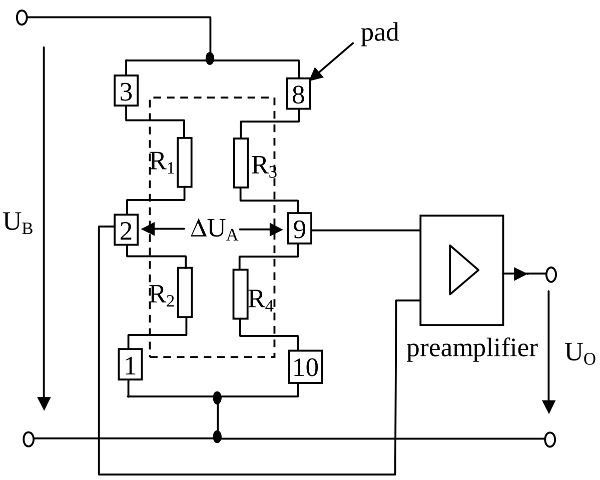

Figure 4. The equivalent circuit diagram

The reference resistors are R2 and R3. The reference resistors were placed to each other diagonally in order to double the measuring effect. The bridge voltage of the measuring bridge U_A is depended on the change of gold resistance ΔR.

$$U_A = U_B \left[\frac{R_1^{'}}{R_1^{'} + R_2} - \frac{R_3}{R_4^{'} + R_3} \right] \qquad (1)$$

with $\quad R_1^{'} = R_1 + \Delta R_1$ and $R_4^{'} = R_4 + \Delta R_4 \qquad (2)$

If the resistors have the same value R at the beginning of the measurement, then the bridge voltage will be

$$U_A = U_B \frac{\Delta R}{2R + \Delta R} \qquad (3)$$

For $\Delta R << R$ the diagonal voltage is approximately proportional to the resistance change.

$$U_A \approx \frac{1}{2} \cdot \frac{\Delta R}{R} U_B \qquad (4)$$

The heater required for the regeneration process is integrated directly under the thin gold resistors. The regeneration temperature must be monitored because the thin gold structures lose their sensitivity and will degrade at higher temperatures. Depending on the gold layer properties, the regeneration temperature will be between 150°C and 300°C. Figure 3 shows the temperature sensor located in the centre of the chip. The heater and the temperature sensor are made of polysilicon. The gold resistor, the heater and the temperature sensor are connected over Al wires with the sensor package, which is shown in figure 5.

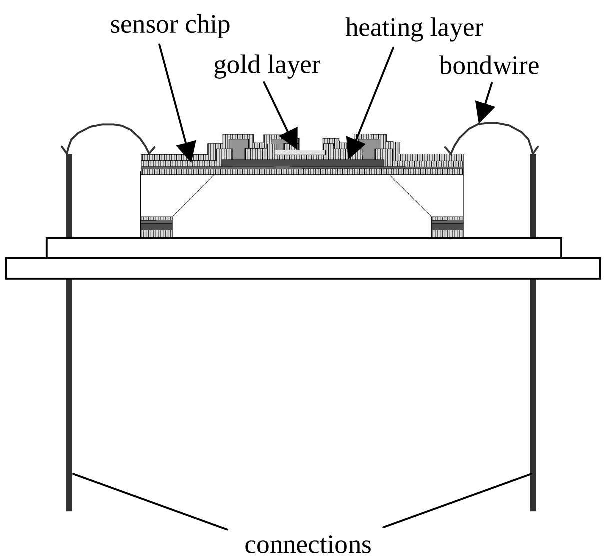

Figure 5. Mercury sensor (cross section)

3. Measurement

In order to examine the reaction of the sensor in contact with mercury and the regeneration, the sensor is put into a measuring system. A commercial MAK-monitor was used for reference [6] to determine the concentration of the mercury in the gas stream. Figure 6 shows the measurement setup and the gas flow path. The flow rate of the air stream is regulated by a mass flow controller. The mercury cell contains a drop liquid mercury in a glass tube. The mercury atoms diffuse through a ceramics filter over this tube. The air stream takes the mercury atoms to the sensor. The mercury concentration can be controlled either via the mercury cell temperature or via the air flow rate. In the laboratory setup, control was performed using the "Labview" software package [7].

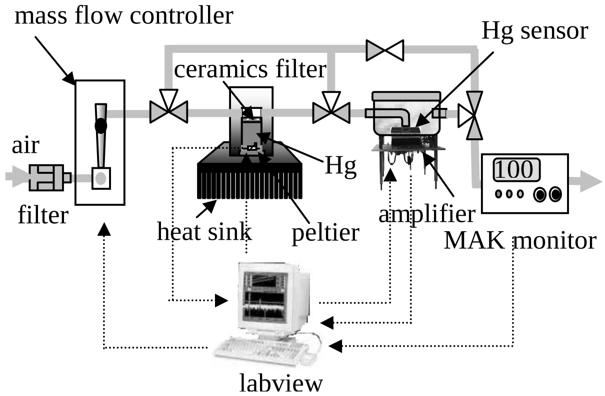

Figure 6. Measuring system

The changes of the electrical resistance of mercury sensor can be detected with help of a preamplifier. This preamplifier is an instrumentation amplifier, which has very low offset voltage (50µV), drift (0.5µV/K) and high common-mode rejection (120dB at G>100). To preserve a good signal-to-noise ratio, the electrical connection between sensor and preamplifier must be as short as possible.

4. Results and discussion

During the contact of the sensor with mercury vapour, the electric resistance of the gold changes due to the amalgam formation. The total resistance of the gold can be described with a parallel circuit of the Hg sensitive resistor R_{Hg} and the unaffected resistor of the gold layer R_{Au}. Figure 7 shows the equivalent circuit diagram. The total resistance will change continuously with increasing mercury concentration in gold. The gold layer must be made very thin to achieve a reasonable sensitivity. The gold layer must be regenerated for repeated measurements. This regeneration process is realised by a heater directly beneath the gold layer. The resistance of the heater depends on the chip temperature. During the regeneration the heater is connected to a power supply. The current, which flows through the heat resistor, changes the temperature of the sensor. The gold layers are regenerated, when the mercury atoms are completely driven out from the sensor. After the regeneration the original condition of the sensor is restored.

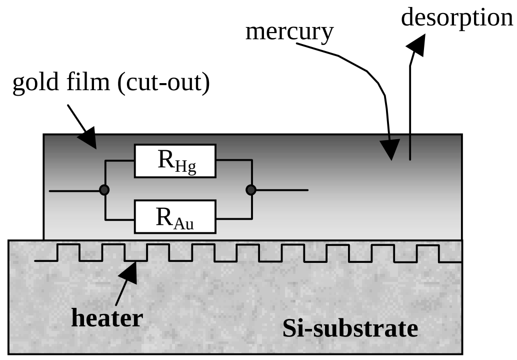

Figure 7. Gold film

The data have been collected separately for measurement and for regeneration. During the measurement an air stream with constant mercury concentration flows over the sensor. The change of the gold resistance increases continuously with time until it reaches its final value, which shows the saturation of the gold surface with mercury atoms. The formation of amalgam is a very slow chemical process. The slope of the change in the gold resistance depends on the mercury concentration. The change of the gold resistance climbs more quickly, if the concentration is bigger. The change of gold resistance over time is shown in figure 8 with a mercury concentration of $100µg/m^3$. The signal rises quickly at the beginning of the measurement, then slowly turns to saturation. After approximately five hours the saturation is reached. The maximum change of resistance is approximately 3,4%.

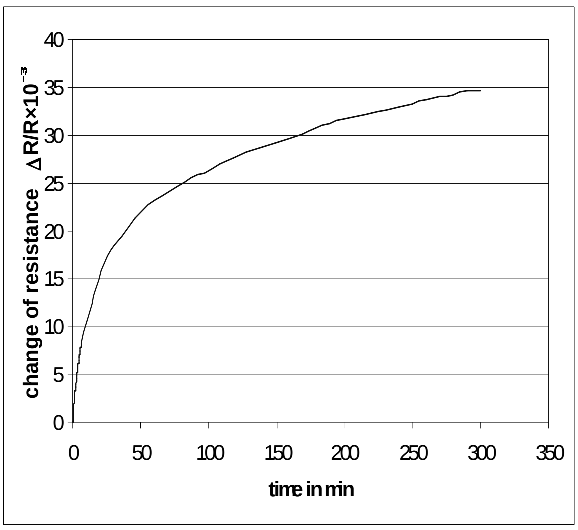

Figure 8. Change of resistance at $100µg/m^{3}$³

After the measurement the regeneration of the sensor takes place at approximately 150°C. Fresh air streams over the sensor at a constant flow rate of about 700ml/min. The concentration of the mercury, which is driven out from the gold layer during the heating procedure, can be measured with the MAK monitor. The regeneration is finished, when the mercury concentration reaches zero. Figure 9 shows a regeneration procedure. The mercury concentration shown by the MAK monitor is printed over time of regeneration. Before regeneration, no mercury was detectable in the airflow at room temperature. At temperatures above 150°C, the amalgam connection in gold is broken and the concentration of mercury at the output increases. The mercury concentration drops gradually, showing that the amount of amalgam compound decreases in the gold. After approximately one hour the gold layer is free from amalgam again. The sensor is reusable for the next measurement. The value of the inflection point and the duration of the regeneration depend not only on the quantity of adsorbed mercury atoms but also on the thickness of the gold layer and the regeneration temperature. The fact is, that regeneration time decreases with higher temperature or thinner gold layers.

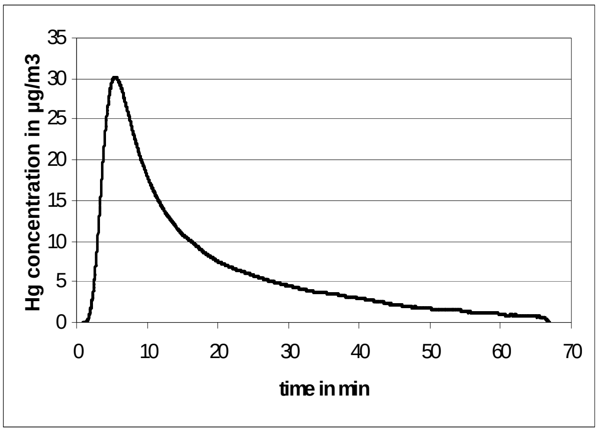

Figure 9. Regeneration of the sensor

5. Conclusion

The results have shown that the mercury sensor described here is suitable for a measurement in air. With a mercury concentration around the MEL value, the sensor shows reproducable output signals. It was noticed that the sensor responds quite quickly to changes of the mercury concentration in air. In practice, it is not reasonable to continue measurement until saturation is achieved. This shortens the regeneration time as well!

The extremely thin structure of the gold prevents a possible memory effect during multiple measurement and regeneration processes. With the compact construction of the sensor, the heating process in the regeneration can be achieved with minimal energy consumption. This is the basis for a handheld mercury concentration meter and for portable applications.

6. References

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[6] From Seefelder messtechnik

[7] From National Instruments