



## Detection limit for an adsorption-based mercury sensor

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### ABSTRACT

A novel readout procedure for the determination of detection limit at an adsorption-based mercury sensor is described. The procedure is based on the evaluation of the initial voltage slope in time evolution of adsorbed elementary mercury. The Langmuir time-dependent adsorption theory is utilized to derive it. This procedure gives the theoretical minimum for the detection for this type of the sensor, which is estimated at 180 ng/m<sup>3</sup>. This is five times lower than the best previously reported results. This procedure can also be used for regular sensor readout. This work describes the experimental procedure for mercury sensor fabrication as well as its measurement cycle. The sensor is working in the cycles of mercury adsorption and evaporation induced by heating. It is shown that every part of the cycle can be monitored by measuring output voltage of the sensor without any additional measurements like surface temperature or rate of the evaporation.

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## 1. Introduction

The awareness of mercury pollution became very prominent since the famous Minamata disease case [1]. During the last decades, many of the regulations across the world limited or totally prohibited the use of the mercury containing devices [2,3]. Still, the most important source of the anthropogenic pollution are coal-fired power plants where huge amounts of coal are burned in the process of electrical energy production, releasing a number of pollutants including elementary mercury [4].

A number of methods for mercury detection have been described in the literature [5]. One of the attempts to make a small and portable device for mercury vapor detection has been presented by Mattoli et al. [6]. Their work is based on the principle described by McNerney et al. [7]. Schambach et al. use the same principle for mercury vapor detection [8], while Toda et al. use the same sensor for nitrogen oxide detection [9]. In this type of sensor the resistivity of a thin gold film is modified by adsorption of mercury on its surface. The key practical question is what is the detection limit of this type of mercury vapor sensor. The direct output from the sensor is voltage and it takes an additional mathematical procedure to calculate the concentration of mercury vapor to which the sensor was exposed. Mattoli et al. [6] developed the formula based on the diffusive sampling [10]. They determined a detection limit [6] of about 1 µg/m<sup>3</sup>.

This work is an attempt to show that a proper choice of the readout procedure can improve the detection limit of a given sensor. A readout procedure based on the Langmuir time-dependent adsorption theory is demonstrated. This procedure can be used not only for the detection limit considerations but also for the regular readout in the working conditions. The only drawback in the latter case is that the readout is integrated over the period of the mercury vapor adsorption and thus it gives an averaged value over the period of adsorption.

## 2. Fabrication of sensor

A single crystal silicon wafer was thermally oxidized for 10 h at a temperature of 1200 °C in the presence of water vapor in order to grow a 2 µm thick layer of surface oxide. The parameters of the wafer are given in Table 1. A layer of chromium was sputtered as an underlayer for a gold thin film by RF magnetron sputtering with base pressure 6.67 × 10<sup>-4</sup> Pa (5 µtorr), argon pressure 0.667 Pa (5 mtorr), power 0.5 kW, turret voltage 110 V and duration 30 s. Subsequently, a 150 nm thick layer of gold was deposited by RF sputtering, base pressure 6.67 × 10<sup>-4</sup> Pa (5 µtorr), argon pressure 0.93 Pa (7 mtorr), power 1 kW, turret voltage 3100 V and duration 60 s. There was a particular advantage in using this specific thickness for the gold film. The sensitivity of this type of sensor increases as the thickness of the gold film reduces. On the other hand, the same thin gold layer is used to form wire bonding pads. It was proven that a 150 nm thickness was the minimum for adequate wire bonding. A thinner film would result in a more

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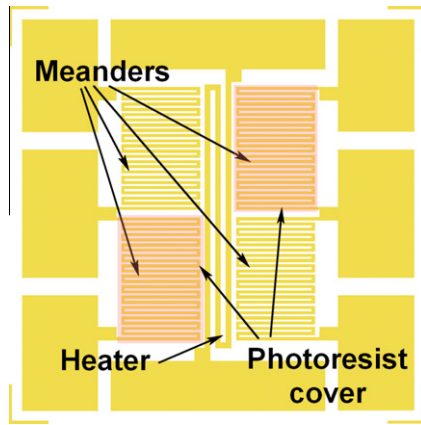
E-mail address: [milijas@nanosys.ihtm.bg.ac.rs](mailto:milijas@nanosys.ihtm.bg.ac.rs) (M. Sarajlić).

**Table 1**  
Parameters of the silicon wafer.

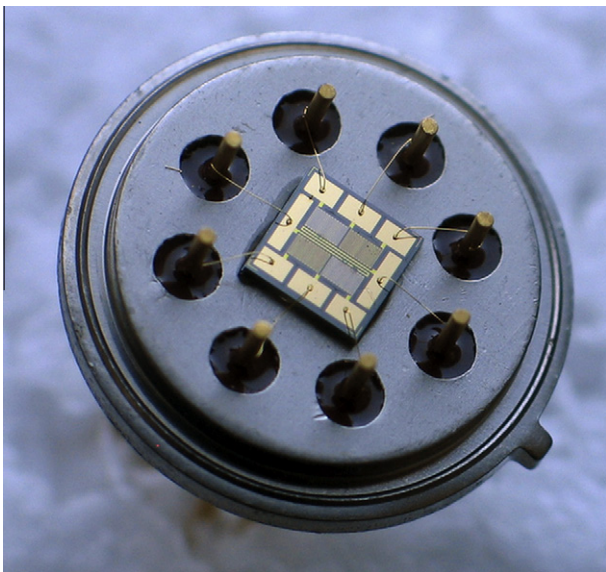
Polishing	Single side polished (SSP)
Diameter	3 in
Thickness	380 $\mu\text{m}$
Orientation	{100}
Type	n
Resistivity	3–5 $\Omega\text{cm}$

sensitive device but at the cost of an additional fabrication step to make thicker wire bond pads.

The thin gold film was formed by optical lithography into four meanders, one heater in the middle of the sensor and eight wire bonding pads, Fig. 1. The smallest features in the sensor were the meander conductive lines having a width of 20  $\mu\text{m}$ . The width of the conductive line of the heater is 40  $\mu\text{m}$ . The total size of the chip is 3.2 mm by 3.2 mm. According to the Wheatstone bridge theory [11], the highest sensitivity of the bridge is achieved if two of the diagonal resistors are fixed and the other two are variable. In this respect, two of the diagonal meanders were covered by a thin



**Fig. 1.** Scheme of the front side of the sensor after the Au–Cr etch process.



**Fig. 2.** Adsorption-based mercury sensor chip bonded on the surface of a Kovar housing.

photoresist film while the other two were left open, Fig. 1. Photoresist AZ 1505, (MicroChemicals, Germany) was deposited by spin coating for 30 s at 4000 rpm. The thickness of the photoresist was 0.5  $\mu\text{m}$  after drying for 15 min at 100  $^{\circ}\text{C}$ . Photoresist was further processed by optical lithography by exposing it through a patterned mask to UV lamp for 2 s, then developed for 25 s at room temperature, and finally baked for 30 min at 100  $^{\circ}\text{C}$ . The finished wafer was sawed and the best dies were placed on the housing and wire bonded, Fig. 2.

### 3. Results and discussion

#### 3.1. Theory

According to the Langmuir theory, the mass of gas adsorbed on a solid surface in time is given by [12,13]:

$$m = m_{\text{sat}} \left( 1 - \exp\left(-\frac{t}{\tau}\right) \right) \quad (1)$$

where  $m$  is the mass of the adsorbed gas,  $t$  is the time, and  $m_{\text{sat}}$  is the mass of the gas at the surface saturation [12]:

$$m_{\text{sat}} = m_0 \frac{\sigma_1 \mu}{1 + \sigma_1 \mu} \quad (2)$$

where  $m_0$  is the mass adsorbed in the case of a very high gas concentration, theoretically infinite,  $\sigma_1$  is a constant,  $\mu$  is the number of atoms that hit a square meter of the surface per second and is given by [12]:

$$\mu = p(2\pi MRT)^{-1/2} \quad (3)$$

where  $p$  is the gas partial pressure,  $M$  is the molar mass of the gas,  $R$  is the universal gas constant and  $T$  is the absolute temperature. The parameter  $\sigma_1$  from Eq. (2) is [12]:

$$\sigma_1 \cdot v_1 = \alpha \quad (4)$$

where  $\sigma_1$  is the gas evaporation rate in the case of a surface completely covered by adsorbent,  $\alpha$  is the fraction of the atoms that condense on the surface with respect to the number of atoms impinging on the same surface and  $\tau$  is a time constant defined by [12]:

$$\tau = \frac{N_0}{N \cdot v_1 (1 + \sigma_1 \cdot \mu)} \quad (5)$$

where  $N$  is the Avogadro number and  $N_0$  is the number of adsorption centers.

The well-known equation for the Wheatstone bridge with four equal resistors and a small deviation of measured resistivity gives [11]:

$$U_{\text{out}} = \frac{1}{2} \frac{\Delta R}{R} U_{\text{in}} \quad (6)$$

where  $U_{\text{out}}$  is the Wheatstone bridge output voltage,  $U_{\text{in}}$  is the Wheatstone bridge input voltage,  $R$  is the balanced total resistivity of the Wheatstone bridge and at the same time the resistivity of each separate resistor, and  $\Delta R$  is the resistivity change of the unbalanced Wheatstone bridge.

It was assumed that mercury adsorption would linearly shift thin gold film resistivity:

$$\Delta R = \text{const} \cdot m. \quad (7)$$

This assumption was motivated by the shape of the experimental curve during mercury adsorption and sensor saturation, Fig. 3, which is similar to the analytical curve for mass versus time given

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