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# STUDY OF POSSIBILITIES OF APPLICATION OF A THERMOPILE-BASED GAS SENSOR

DANIJELA RANDJELOVIĆ
Centre of Microelectronic Technologies, Institute of Chemistry, Technology and Metallurgy, University of Belgrade,
danijela@nanosys.ihtm.bg.ac.rs

OLGA JAKŠIĆ
Centre of Microelectronic Technologies, Institute of Chemistry, Technology and Metallurgy, University of Belgrade,
danijela@nanosys.ihtm.bg.ac.rs

MILČE M SMILJANIĆ
Centre of Microelectronic Technologies, Institute of Chemistry, Technology and Metallurgy, University of Belgrade,
danijela@nanosys.ihtm.bg.ac.rs

ŽARKO LAZIĆ
Centre of Microelectronic Technologies, Institute of Chemistry, Technology and Metallurgy, University of Belgrade,
danijela@nanosys.ihtm.bg.ac.rs

***Abstract:*** *The goal of this work is exploring the possibilities of application of a thermopile-based gas sensor. The main task was to study for which kind of gases this type of sensor would be suitable. For this purpose self-developed 1D analytical model was used. Modelling was done for multipurpose sensors developed at ICTM, but also for the same structure that would be fabricated on SOI substrate. Output signal of thermopile-based sensor depends on thermal conductivity of the surrounding gas. When this type of sensor is applied as a gas sensor, prerequisite is that the gases have different thermal conductivities so that the sensor can distinguish between them. According to simulation results, thermopile-based sensors could be applied for a number of gases which are important in industrial safety, homeland security, healthcare, domestic safety, etc. The results obtained for hydrogen detection were already presented, so in this work simulation data for other gases of interest will be given. This includes methane, ammonia, hydrogen sulfide, chlorine. Important conclusion is that thermopile-based sensor is capable to detect wide variety of gases.*

***Keywords:*** *thermopile, gas type sensor, gas thermal conductivity, analytical modelling, SOI*

## 1. INTRODUCTION

MEMS sensors based on Seebeck effect have been a subject of the long-term research at ICTM-CMT. One of the main advantages of this type of sensors is very broad range of applications (flow sensors, vacuum sensors, thermal converters, IR detectors, accelerometers, inclinometers, biological and chemical sensors, gas type sensors, binary gas mixture composition sensors, ...) [1]. Till now sensors dedicated for several applications have been developed at ICTM: 1) flow sensor [2,3], 2) vacuum sensor [4], 3) helium gas sensor [5], 4) thermal converter [2], 5) intelligent vacuum sensor [6].

Taking into account importance of portable gas sensors in areas covering the fields of defence, anti-terrorism, homeland safety, industrial safety, healthcare, etc. [7,8] the goal of this work is exploring the possibilities of wider application of a thermopile-based gas sensor. In the previous work it was shown experimentally that ICTM thermopile based sensor is suitable for Helium detection [5]. Possibility of Hydrogen detection was confirmed only theoretically and simulation data were already presented [9]. The main task of this work is to study detection of several more gases and examine how performance of thermal gas sensor could be improved.

For this purpose self-developed 1D analytical model was used. Modelling was done for multipurpose sensors developed at ICTM [2-6], but also for the same structure that would be fabricated on silicon on insulator (SOI) substrate [10]. SOI structure is considered because it offers high quality thermal isolation which improves significantly sensor performance.

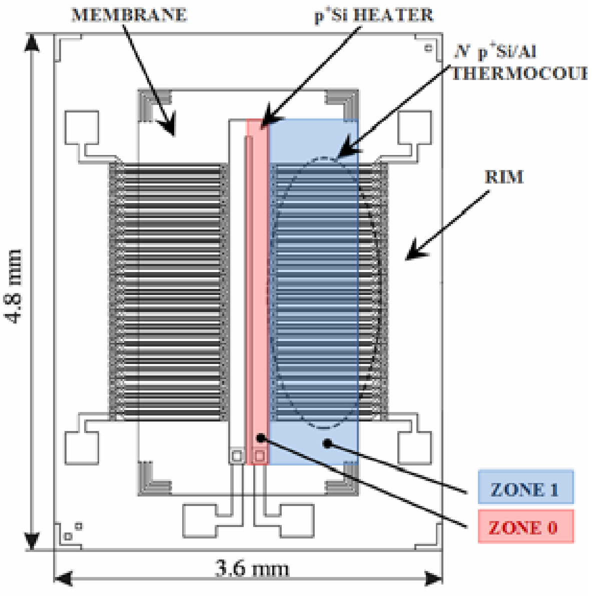
Output signal of thermopile-based sensor depends on thermal conductivity of the surrounding gas. When this type of sensor is applied as a gas sensor, fundamental prerequisite is that the gases have different thermal conductivities so that the sensor can distinguish between them. According to simulation results, thermopile-based sensors could be applied for a number of gases which are important in industrial safety, homeland security, healthcare, domestic safety, etc. This includes ammonia, carbon dioxide, chlorine, hydrogen sulfide and methane on which this work will be focused.

## 2. “N-SI” AND “SOI” THERMOPILE BASED P-TYPE SENSORS

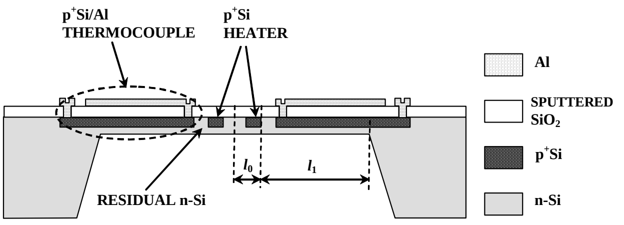
Simulations were performed for two different sensor structures, one fabricated on standard n-Si wafer, and the other one fabricated using SOI wafer. The first structure is practically identical with multipurpose sensor developed at ICTM [2]. The SOI sensor has not been realized yet but the fabrication process has been developed using the already existing technological processes developed for ICTM piezoresistive pressure sensors [10]. The advantages of SOI structure have been theoretically considered in several publications [10,11].

In both cases the sensors consist of the same elements: two independent thermopiles with $N$ $p^+$Si/Al thermocouples, $p^+$Si heater and thermally and electrically isolating membrane. The crucial difference between the two designs is that the “SOI” sensor has membrane of pure oxide 1 μm thick, while the “n-Si” sensor, apart from the oxide layer, has also residual n-Si silicon in membrane area thick $d_{\text{n-Si}} = 3$ μm.

Top view, which is the same for both sensors, is shown in Picture 1(a). Cross section of “n-Si” sensor is illustrated in Picture 1(b) and the cross section of “SOI” structure is shown in Picture 1(c). Hot thermopile junctions are situated in the vicinity of the heater, while the cold junctions are placed on the unetched part of the chip surrounding the membrane – the rim.



(a)



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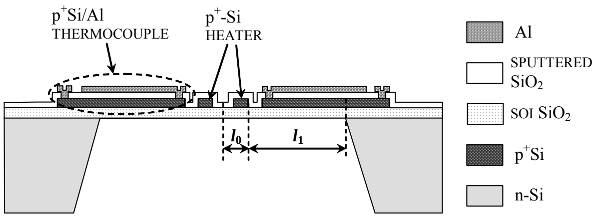

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c)

**Picture 1.** Top view of the sensor with the main elements and two zones used in 1D modelling (a), cross section of the „n-Si“ sensor (b) and of the „SOI“ sensor (c) with depicted lengths of the two zones, $l_0$ and $l_1$.

Performance of thermopile based sensors depends on sensor design. In this work structures with $N = 60$ and $N = 120$ thermocouples placed on the membrane area of the same size are studied. When $N = 60$ widths of $p^+$Si and Al stripes forming a thermocouple are $w_{p+\text{Si}} = 60$ μm and $w_{\text{Al}} = 40$ μm. For $N = 120$, $w_{p+\text{Si}} = 20$ μm and $w_{\text{Al}} = 10$ μm. In both cases length of thermocouple elements is 1090 μm.

For the purposes of analytical modelling membrane area is divided in two rectangular zones as illustrated in Picture 1 (a). Length of the first zone is $l_0 = 180$ μm, while $l_1$ depends on thickness of the residual silicon and equals $l_1 = 790$ μm in SOI sensor and $l_1 = 793$ in n-Si sensor.

## 3. ANALYTICAL MODEL AND SIMULATION PROCEDURE

Binary mixture is formed of two gases with fraction of the monitored gas – $x$, and fraction of the “carrier” gas – (1-$x$). Expression for thermal conductivity of a binary gas mixture given in [12] will be used

$$\lambda_{mix}^{bin} = \frac{x\lambda_{gas1}}{x+(1-x)F_{12}} + \frac{(1-x)\lambda_{gas2}}{(1-x)+xF_{21}}, \qquad (1)$$

where $\lambda_{gas}$ is gas thermal conductivity, while $F_{12}$ and $F_{21}$ are parameters depending on molecular weights, $M$, and dynamic viscosities of the gases, μ.

Formula for calculating parameters $F_{ij}$ is

$$F_{ij} = \frac{\left[1+\left(\frac{\mu_{gas(i)}}{\mu_{gas(j)}}\right)^{0.5}\left(\frac{M_{gas(j)}}{M_{gas(i)}}\right)^{0.25}\right]}{\left[8\left(1+\frac{M_{gas(j)}}{M_{gas(i)}}\right)\right]^{0.5}}, \ \{i, j\}=\{1, 2\}. \quad (2)$$

We will consider here binary gas mixture of air and the following 5 gases: ammonia, carbon dioxide, chlorine, hydrogen sulfide and methane. Relevant parameters for all gases are listed in Table 1 [13,14].

**Table 1.** Gas parameters used in simulations

| GAS | $\lambda$ [W/mK] | $M$ [u] | $\mu$ [μPa·s] |
|---|---|---|---|
| Air ($N_2$) | 0.0259 | 28.0134 | 17.82 |
| Ammonia ($NH_3$) | 0.0247 | 17.2 | 10.15 |
| Carbon dioxide ($CO_2$) | 0.01655 | 44.01 | 14.9 |
| Chlorine ($Cl_2$) | 0.0081 | 70.906 | 13.27 |
| Hydrogen sulfide ($H_2S$) | 0.0146 | 34.076 | 12.8 |
| Methane ($CH_4$) | 0.0341 | 16.044 | 11.18 |

General analytical model for binary gas mixture detection using thermopile based MEMS sensors is presented in detail in [5]. This model is based on core 1D analytical model with two zones given in [2].

Voltage generated at the thermopile is chosen to be the parameter of interest. It is assumed that the output signal equals the sum of voltages at both thermopiles. General formula for Seebeck voltage is

$$U(x, p, T) = N\alpha_{p+\mathrm{Si/Al}}\Delta T\left(x, p, T\right) \quad (3)$$

Where $N$ is total number of thermocouples in both thermopiles, $\alpha_{p+\mathrm{Si/Al}} = 300$ μV/K is the Seebeck coefficient of $p^+$Si/Al thermocouples and $\Delta T$ is temperature difference between the hot and cold thermocouple junctions. Both the thermopile voltage and temperature difference depend on fraction $x$, ambient pressure – $p$, and temperature - $T$.

Based on the brief theory given in [9], and general expression for the temperature difference established on the chip for given power generated at the heater at constant ambient pressure and temperature, expression (3) can be written as

$$U\left(x\right) = N\alpha_{p+\mathrm{Si/Al}}\Delta T\left(N, \lambda_{mix}^{bin}\left(x\right), \varepsilon_{iu}, \varepsilon_{il}, R_H I_{const}\right), \quad (4)$$

where electrical resistance of the heater is $R_H = 5.8$ kΩ, current supplied at the heater is $I_{\mathrm{const}} = 3$ mA, while $\varepsilon_{\mathrm{iu}}$ and $\varepsilon_{\mathrm{il}}$ are emissivities of the upper and lower surface of the zone "$i$" ($i = 0, 1$) depicted in Picture 1(a).

For gas detection it is important to monitor the change of thermopile voltage due to variation of the parameter $x$. If "reference voltage"is the thermopile voltage value in pure air, that is when x = 0, then the expression for the voltage change is

$$\Delta U(x) = U\left(x\right) - U\left(x = 0\right), \quad (5)$$

assuming constant pressure and temperature.

Dependence of the voltage change on the binary gas mixture composition and on the number of thermocouples was studied.

**Table 2.** Material properties and corresponding values used in simulations

| MATERIAL/ PARAMETER | $n$-Si | $p^+$Si | $SiO_2$ | Al |
|---|---|---|---|---|
| Thermal conductivity $\lambda$ [W/(mK)] | 150 | 75 | 1.2 | 218 |
| Thickness $t$ [μm] | 3 | 0.3 | 1 | 0.7 |
| Emissivity ε | 0.5 | 0.5 | 0.2 | 0.8 |
| Density $\rho$ [kg/m$^3$] | 2330 | 2420 | 2220 | 2702 |

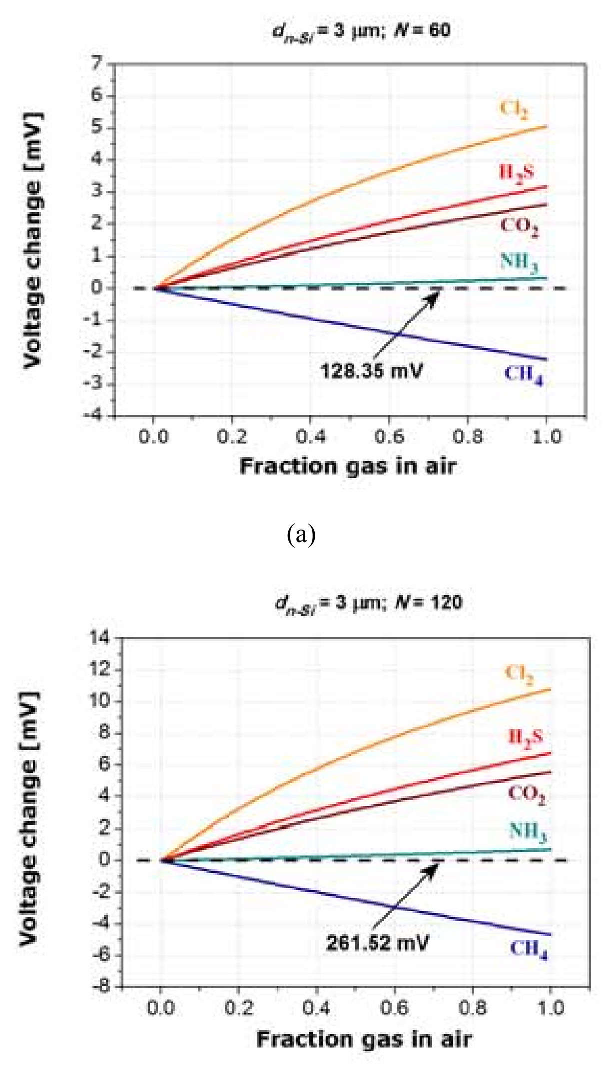
## 4. SIMULATION RESULTS

Simulations were performed for the "$n$-Si" and "SOI" structures assuming that the sensors are operating at atmospheric pressure ($10^5$ Pa) and constant ambient temperature of 20 °C.

Picture 2 shows simulation results obtained for "n-Si" sensor with $d_{n\text{-Si}} = 3$ μm. We considered two different designs. In the first one, $N = 60$ thermocouples was placed on the chip (Picture 2(a)), while in the second one, number of thermocouples was doubled, $N = 120$ (Picture 2(b)).

Picture is showing voltage difference as a function of fraction of the chosen gas in air. For 60 thermocouples, the „reference“ value of voltage equals to 128.35 mV. As gas content is increasing, voltage difference increases with positive sign for chlorine, hydrogen sulfide, carbon dioxide and ammonia, while it also increases but with the negative sign for methane. If we double number of thermocouples, it can be seen that the voltage difference will also be a little bit more than doubled.

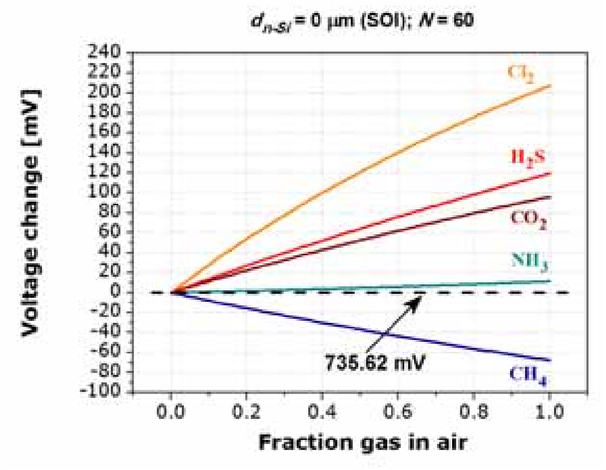
Similar behaviour is observed for the „SOI“ sensors (Picture 3), only in this case it is obvious that a much higher voltage level is reached. For $N = 60$, „reference“ voltage is about 735 mV, while for $N = 120$, it is almost 2V. Voltage differences now reach more than 200 mV for chlorine, for example, while they are also much higher for all other gases compared with relevant data in the case of „n-Si“ sensor.



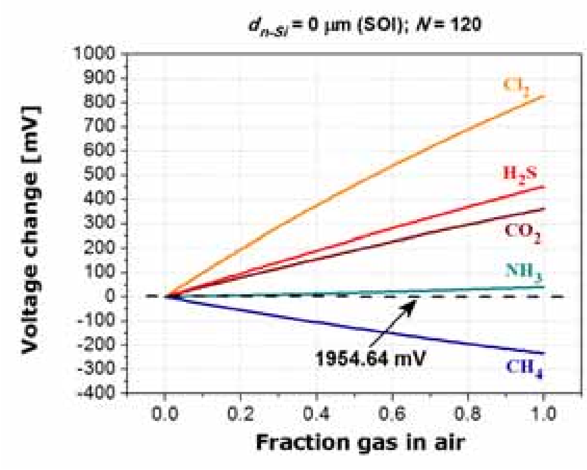
(a)

(b)

**Picture 2.** Simulation results obtained for „n-Si“ sensor with $d_{n\text{-Si}}$ = 3 μm for $N$ = 60 (a) and $N$ = 120 (b).



(a)



(b)

**Picture 3.** Simulation results obtained for „SOI“ sensor for $N$ = 60 (a) and $N$ = 120 (b).

## 5. CONCLUSION

Analytical model was applied to study behaviour of “n-Si” and “SOI” sensors in binary gas mixtures formed by adding chlorine, hydrogen sulfide, carbon dioxide, ammonia and methane to air. Calculations were performed at room temperature and atmospheric pressure. When increasing selected gas content in the air, voltage change was observed for all gases leading to conclusion that the examined thermopile based sensors could be applied for detection of presence of these gases in air.

Further, it was concluded that gas senor response could be improved by increasing number of thermocouples. In the case of “n-Si” sensor, the output voltage is more than doubled for twice as many thermocouples. On the other hand, the same increase in number of thermocouples gives almost 4 times higher voltage difference in “SOI” sensors.

When comparing “n-Si” sensor with some residual silicon and “SOI” sensor with membrane of pure oxide one can conclude that “SOI” structure has superior performance. If we observe results obtained for chlorine, which has the most prominent change, for 60 thermocouples voltage difference is about 40 times higher in “SOI” sensor than in “n-Si” sensor for the respective chlorine fractions in air. In the structures with 120 thermocouples this factor increases up to 70.

This is a consequence of practically ideal thermal isolation between the hot and cold thermocouple junctioncs achieved in “SOI” structure with oxide membrane. On the other hand, in “n-Si” structure heat transfer via conduction through the residual n-Si is the dominant mechanism.

It is worth mentioning that since sensors response depends on the thermal conductivity of the detected gas even better performance was observed for mixtures of helium [5] and hydrogen [9] with air and these results were already presented elsewhere. Important conclusion is that thermopile-based sensor is capable to detect wide variety of gases.

Finally, we can conclude that in terms of gas sensing "SOI" structures have better perspective than the conventional "n-Si" sensors. For the same top-view layout "SOI" sensors provide much higher output voltage and give much higher voltage difference when increasing selected gas fraction in air.

## REFERENCES

[1] Meijer,G.C.M., Herwaarden,A.W.: *Thermal Sensors*, IOP Publishing, Bristol, 1994

[2] Randjelović,D., Petropoulos,A., Kaltsas,G., Stojanović,M., Lazić,Ž., Djurić,Z., Matić,M.: *Multipurpose MEMS Thermal Sensor Based on Thermopiles*, Sensors and Actuators A, 141 (2008) 404-413.

[3] Randjelović,D., Djurić,Z., Petropoulos,A., Kaltsas, G., Lazić, Ž., Popović, M.: *Analytical modelling of thermopile based flow sensor and verification with experimental results*, Microelectronic Engineering, 86 (2009) 1293-1296.

[4] Randjelović,D., Jovanov,V., Lazić,Ž., Djurić,Z., Matić,M.: *Vacuum MEMS Sensor Based on Thermopiles – Simple Model and Experimental Results*, in Proc. 26th Int. Conf. on Microelectronics MIEL 2008, Niš, Serbia, May 11-14, 2 (2008) 367-370.

[5] Randjelović,D., Lazić,Ž., Popović,M., Matić,M.: *Helium Sensing Using Multipurpose Thermopile-Based MEMS devices*, Proc. 28th Int. Conf. on Microelectronics MIEL 2012, Niš, Serbia, May 13-16 (2012) 147-150.

[6] Randjelović,D.V., Frantlović,M.P., Miljković,B.L., Popović,B.M., Jakšić,Z.S.: *Intelligent Thermal Vacuum Sensors Based on Multipurpose Thermopile MEMS Chips*, Vacuum, 101 (2014) 118-124.

[7] Bogue, R., "Terrorism and military actions pose the ultimate challenge to gas sensing", *Sensor Review, 31* (2011) 6-12.

[8] MNT Network News Bulletin: MNT Gas Sensors Roadmap, Issue 14, January 15 2007, http://208.254.39.65/mntnetwork/e_article000729863.cfm

[9] Randjelović,D., Lazić,Ž., Jakšić,O., Vasiljević-Radović,D.: *Analytical Modelling of Hydrogen Sensing Using IHTM Thermopile Based MEMS Multipurpose Sensors*, in Proc. 5th International Scientific Conference on Defensive Technologies OTEH 2012, Belgrade, Serbia, September 18-19 (2012) 662-667.

[10] Randjelović,D., Smiljanić,M.M., Lazić,Ž., Popović,M.: *Enhancement of the Performance of Multipurpose Thermopilče-Based Sensor Using Proprietary MEMS Technology for SOI Piezoresistive Pressure Sensors Fabrication*, in Proc. 56th Conf. for Electronics, Telecommunications, Computers, Automation and Nuclear Engineering *ETRAN 2012*, Zlatibor, Serbia, June 11-14 (2012) MO3.3-1-4.

[11] Randjelović,D., Kozlov,A., Jakšić,O.: *Vacuum Sensing Based on the Influence of Gas Pressure on Thermal Time Constant*, Proc. 29th Int. Conf. on Microelectronics MIEL 2014, Belgrade, Serbia, May 12-15 (2014) 179-182.

[12] Xensor Integration, http://www.xensor.nl/txtfiles/hfdfiles/prodstan.htm.

[13] Matheson https://www.mathesongas.com

[14] Incropera,F.P., DeWitt,D.P.: *Fundamentals of Heat and Mass Transfer*, John Wiley & Sons, Hoboken, 2002