ROMANIAN JOURNAL OF INFORMATION SCIENCE AND TECHNOLOGY
Volume **13**, Number 4, 2010, 342–349

Emerging All-Differential Chemical Sensing

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Abstract. It is the purpose of this paper to present a novel generic concept for low drift chemical sensing which is applicable at micro and nanometer scale, based on a new, all-differential approach. At micrometer level, our principle is explained by means of surface acoustic wave (SAW) chemical sensing, while at nano level, we are using the resonant sensing principle to develop our genuine differential concept. Unlike the traditional differential approaches based on functionalized sensing layer in the sensing loop, and on a uncoated surface in the reference loop, our all differential concept provides a better response subtraction between the two paths, as the sensing loop consists of a functionalized sensing layer, as before, but, the reference loop consists of a functionalized non-sensing layer, with the same ageing and humidity behavior as the sensing layer. Twinned electronic reading is used for both loops, and thus all the common mode signals are subtracted in the differential reading, assuring the minimum base line drift of the sensor. Preliminary results of all differential sensor eliminating the effects of humidity and temperature variations are shown for the SAW sensors, with the sensor signal kept independent of their changes. Finally, the application of the novel concept for the humidity sensing with all differential resonant nanosensor is presented.

1. Introduction

The market and legislation requirements for safe industrial processes and clean environment have triggered an intensive research effort targeting miniaturized gas sensors able to detect small amount of toxic gases and to actuate the electronic system for alarming and situational corrections. Industrial process control and large area monitoring of the ambient have driven the need for small size, portable instruments with low power consumption, multi-gas sensing capabilities, without false alarms and interferences from continuous changing temperature or humidity of the ambient. To address the above requirements, the room temperature detection with low base-line drift will be an essential research direction, focused on sensing principles compatible with such future gas sensing instruments. Among the gas sensing principles which are suitable for such low-power applications, we are considering gas detection by surface acoustic wave (SAW) delay line-based micro-devices [1] [2] and, also, resonant nano-devices containing vibrating gate or vibrating body SOI-CMOSFET devices [3, 4].

In the case of SAW sensing, the chemical detection is obtained by means of an organic sensing layer which is located in the space between the two interdigital transducers (IDT) of the SAW delay line and functionalized for selective interaction with the target gas. For the envisioned resonant nanosensors, the functionalized organic layer is located either on the vibrating gate, or on the vibrating silicon body. For both principles chemical sensing is obtained by selective adsorption and reversible reaction of the gas to be detected with the functionalized sensing layer, which provides the mass loading of the sensing surface.

In the case of SAW sensing, this mass loading is further changing the SAW phase propagation velocity and this is setting the shift in the oscillation frequency of the oscillator having the sensing SAW delay line in its feed-back loop. For the resonant nanosensing, the mass loading on the functionalized surface resulted from the selective adsorption and reaction is changing the mechanical resonance frequency of the vibrating beam, and this is further changing the oscillation frequency of the detection circuit, which is thus correlated with the target gas to be measured [5]. The sensing layers are of organic nature, as they can be sensitive under such room temperature conditions and they can be functionalized for different gas targets. However, the layers present ageing of their material properties that will change their sensing properties, and for this reason, different techniques are needed for a long term stable sensor operation.

The differential sensing is one of the most applied concepts for improving the sensor response stability in the presence of temperature or humidity variation [6]. This consists of a sensing loop and a reference (non-sensing) loop, each of them having their electronic reader, while their output signals are subtracted, in order to minimize common mode signals (humidity and temperature effects). In the traditional differential approach, the sensing loop contains the functionalized sensing layer, located in the appropriate zone of the sensing device, while the reference loop is “identical or twinned” with the sensing loop, excepting the fact that the reference device is uncoated. In our paper, we shall present a novel differential principle, [7, 8] which can be applied to both SAW and resonant gas sensing, and where a functionalized reference (mono)layer is deposited on the surface of the reference device. The reference (mono) layer is having a similar ageing and similar humidity response as the sensing layer, and thus a very low baseline drift is obtained for our genuine differential sensor. An example of application of our concept to the humidity detection by all-differential resonant sensors is shown here [9].

2. Differential sensor response

According to the above description, and in agreement with the sensing principle [6], a simple response equation of the differential sensor can be written as follows:

$$y_d(t) = (y_s(t) + \delta_s(t)) - (y_r(t) + \delta_r(t)), \tag{1}$$

where $y_d(t)$ is the response of the differential sensor, $y_s(t)$ is the output of the sensing loop, $\delta_s(t)$ is the drift signal of the sensing loop, $y_r(t)$ is the output signal of the reference loop and $\delta_r(t)$ is the drift signal of the reference loop. In the real case, the drift signal is embedded in the sensor response, but here, we have shown it separately, as we need to show the role of drift signal in the total response. If we accept that the reference loop is not sensing any signal coming from the target gas, then, $y_r(t) = \text{const.}$ and the above equation becomes :

$$y_d(t) = y_s(t) - \text{const.} + \delta_s(t) - \delta_r(t). \tag{2}$$

In the case of traditional differential sensing, as the reference element is uncoated, while the sensing element is coated, resulting in significant differences in the humidity response the ageing of the sensing layer has no corresponding layer in the reference loop, so, the traditional differential approach cannot eliminate ageing of sensing element, too. Such common mode signals which are not cancelled give sensor response drift. For an all-differential sensing approach, the functionalized reference layer has similar visco-elastic properties as the sensing layer, similar humidity and ageing behavior, and therefore we may theoretically accept that the differential sensor drift is $\delta_s(t) - \delta_r(t) \approx 0$, thus the all-differential sensor response is almost drift-free:

$$y_d(t) = y_s(t) - \text{const.} \tag{3}$$

In the case of our SAW and resonant sensors, all these above signals are response frequencies values at a given time, t, and they are provided by the associated detection circuits for the sensing loop and reference loop, respectively, which are further subtracted, as it will be shown in the next sections.

3. All differential SAW chemical sensor

More than three decades ago, the first differential sensing application for VOC detection based on SAW delay lines and sensing layer applied between the input IDT and the output IDT of the device was proposed [10]. The traditional SAW differential chemical sensing approach is shown in Fig. 1.

The sensing loop is an electronic oscillator made of amplifier A1 with the sensing SAW delay line (IDT 1, IDT 2) in the feed-back loop and the sensing layer 6 located in between IDT1 and IDT 2, while the reference loop is an electronic oscillator with the reference SAW delay line (IDT 3 and IDT 4) in the feed-back loop, and an uncoated piezoelectric surface, in-between IDT3 and IDT 4. As described in the previous section, we propose a novel differential sensing scheme, where, in the reference loop, a reference layer is deposited, as shown in Fig. 2. The visco-elastic properties of the reference layer 7 as well as its humidity and ageing behavior are similar to those of sensing layer 6, but the reference layer 7 is functionalized so that it has no sensing properties. For room temperature sensing, layers 6 and 7 are organic thin films and they can be deposited by different methods, like the direct printing processing [7]. In Fig. 3, we show our experimental results for the case of our all-differential SAW chemical sensing approach, where an organic sensing layer 6 and an organic reference layer 7 have been deposited as shown in Fig. 2 and the entire sensor was exposed to a temperature variation in the range from 20°C to 60°C.

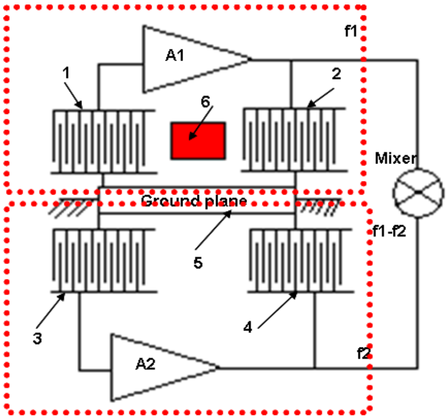


Fig. 1. Classical differential SAW chemical sensing consisting of a sensing loop (containing sensing layer 6), a reference loop and a mixer.

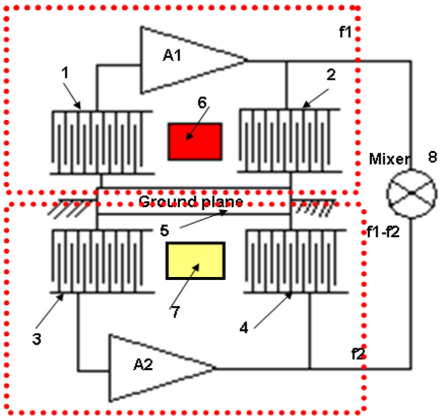
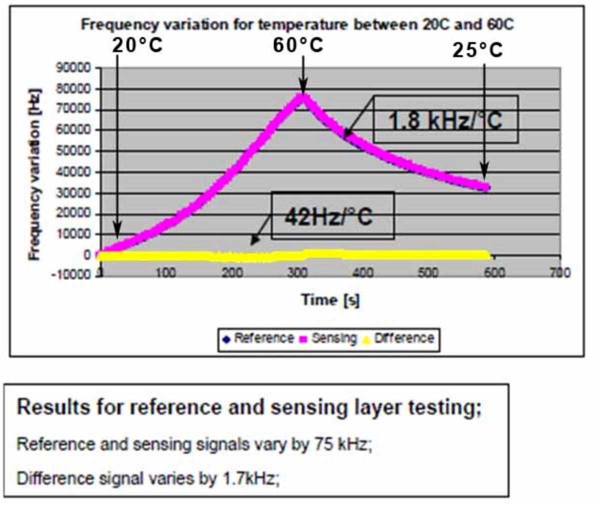


Fig. 2. Novel differential SAW chemical sensing consisting of sensing loop (containing sensing layer 6), reference loop (containing reference layer 7) and a mixer [7].

The frequency response of sensing loop f1, of reference loop f2 and of the mixer 8 from Fig. 2, as a function of the temperature variation is set by the temperature dependence of the SAW device. As shown in Fig.3, the response frequencies of the sensing oscillator and the reference oscillator have similar (high) variations with temperature variation while the differential response (f1–f2) is almost equal to zero. In Fig. 4, we show the response of all-differential SAW sensor to humidity variation in the range from 15% to 50% RH, and here one can easily notice the humidity cancelling effect in the final sensor response due to the presence of the reference layer with the same humidity behavior.

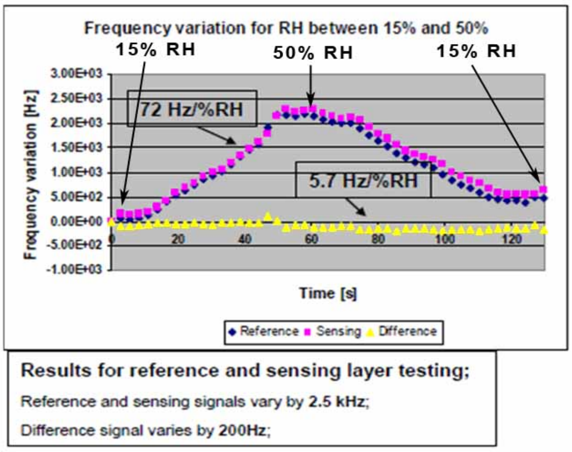


Results for reference and sensing layer testing;

Reference and sensing signals vary by 75 kHz;

Difference signal varies by 1.7kHz;

Fig. 3. Response of the sensing oscillator, reference oscillator and mixer of the all-differential SAW sensor to the temperature variation.



Results for reference and sensing layer testing;

Reference and sensing signals vary by **2.5 kHz**;

Difference signal varies by **200Hz**;

Fig. 4. Response of the sensing and reference oscillator and of the mixer to the RH variation, in the RH range from 15% to 50%.

4. All differential resonant nanosensor

As described above, the resonant nanosensing is expected to show high gas sensitivity due to low inertial mass of the vibrating beams and enhanced mass loading effect of the adsorbed gases on such elements [5]. The benefit of using organic sensing layer to perform gas detection at room temperature is of high interest for the chemical nanosensing domain. However, the baseline drift issues are still of major concern for the nanosensing process. In this context, we have proposed the all-differential sensing concept for the improvement of the baseline drift response of these resonant nanosensors. The concept is applicable to any kind of electronics used in the sensing and reference loop. In Fig. 5, we show an example of all-differential chemical resonant nanosensor, where twins sensing reference loops and output mixer for frequency subtraction are used, with the only difference between them coming from the fact that in the sensing loop we are using sensing functionalized organic (mono) layer deposited on the surface of vibrating gate (or silicon body) of the sensing SOI-CMOSFET device, while in the reference loop we are using reference (non-sensing) functionalized (mono) layer on the surface of the reference vibrating SOI-CMOSFET device. The reference (mono) layer has similar ageing and humidity response as the sensing (mono) layer.

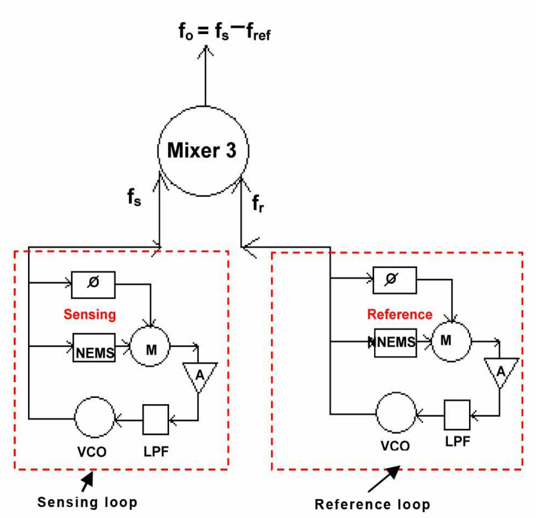


Fig. 5. All differential resonant nanosensor with vibrating gate or silicon body SOI-CMOSFET [8].

A schematic view of the silicon chip containing the functionalized sensing nanobeam and the functionalized reference nanobeam, both of them vibrating at their mechanical resonance frequency is shown in Fig. 6.

An appropriate example could be detection of humidity with these types of resonant devices, for which we propose different approaches.

In all these approaches we take into account two types of layer: a hydrophilic sensing layer which is sensitive to water molecules and the reference layer which is almost similar with the sensing layer regarding the chemical and physical properties, but is hydrophobic and thus, insensitive. Below, we show such hydrophilic/hydrophobic tandems of sensing and reference layers, respectively.

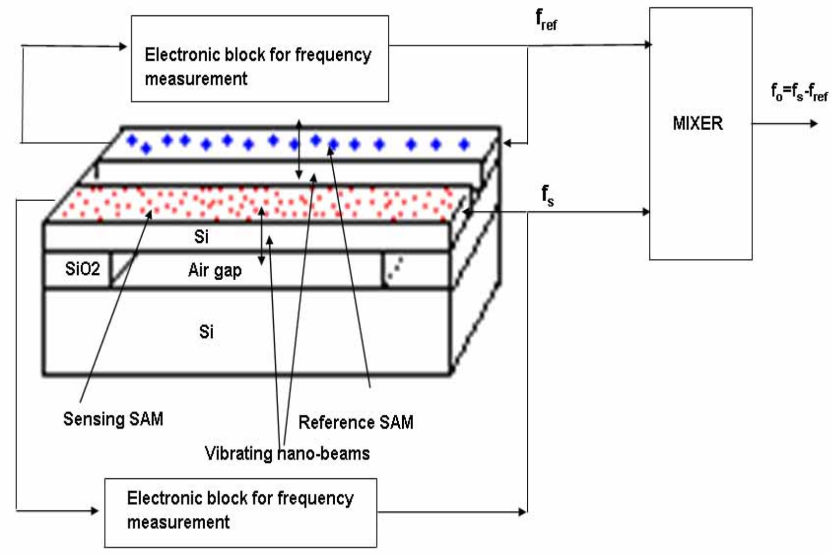


Fig. 6. A schematic view of the all-differential resonant nanosensor showing functionalized sensing and reference beams, the twinning electronic blocks for frequency measurement, as well as the output mixer, where subtraction of frequency is done [8].

- The hydrophilic sensitive layer is sodium poly-styrene sulfonate and the hydrophobic reference layer is polystyrene.
- The hydrophilic sensitive layer is sulfonated carbon nanotubes which is synthesized from carbon nanotubes and sulphuric acid at 300°C. The reference layer is unfunctionalized hydrophobic carbon nanotubes.
- The sensitive layer is a hydrophilic matrix nanocomposite based on poly sodium(p-styrene) sulfonate and sulfonated carbon nanotubes. This matrix nanocomposites is deposited as thin film onto the surface of carbon nanotubes. The reference layer is a hydrophobic matrix nanocomposites based on polystyrene and carbon nanotubes.
- The sensitive layer is a hydrophilic polyacrylic acid as sodium salt deposited as thin film onto the surface of carbon nanotubes. The reference layer is made of the hydrophobic carbon nanotubes.
- The sensitive layer is a hydrophilic matrix of poly(sodium p- styrene) sulfonate and a polyacrylic acid as sodium salt deposited as thin film onto the surface of carbon nanotubes. The reference layer is made of hydrophobic carbon nanotubes.
- The sensitive layer is a matrix nanocomposite based on sulfonated carbon nanotubes and titania and the reference layer is made of carbon nanotubes.

In all above mentioned approaches, carbon nanotubes can be single, double or multi-walls.

5. Conclusions

The traditional differential sensing concept based on sensing loop and reference loop, where the sensing layer is present in the sensing device, while a bare surface is present in the reference device does not eliminate the drift coming from the ageing of the sensing layer and the humidity response of the coated and uncoated surfaces. These are very important issues for organic sensing layers. This paper presents a novel concept for improved chemical sensing, called all-differential, where a reference layer with similar ageing and humidity behavior is introduced in the reference loop, and thus the effect of all common mode signals (temperature, humidity, ageing) on the baseline drift can be significantly reduced. The concept was exemplified for SAW and resonant differential sensing. The experimental results have shown an output sensor signal which did not change while the temperature varied from 20 to 60°C, or the humidity was changed from 15 to 50 RH%. As an example of application of our concept at nanometer scale, we show how to make the functionalization of the beams for the all differential resonant nanosensor which is used for relative humidity detection, and, where the sensing layer and reference layers have similar visco-elastic properties, but the sensing layer is hydrophilic while the reference layer is hydrophobic.

Acknowledgements. This work was co-funded by the EU FP7 STREP NEMS-IC project and Honeywell International.

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