Response of a SAW Sensor Array based on Nanoparticles for Measuring Ammonia in the Environment

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Keywords: Sensor Array, Surface Acoustic Wave, Ammonia, Nanoparticles, Gas Sensors, Environment.

Abstract: Four surface acoustic waves (SAW) sensors based on sensitive layers of Fe_2O_3 nanoparticles, pure and combined with noble metals nanoparticles, composed an array sensor to measure ammonia in the environment. The sensor array was tested with nanostructured sensitive layers, which detected the changes of the elastic properties induced by ammonia interaction. The sensor with pure Fe_2O_3 nanoparticles exposed to 50 ppm of ammonia showed no significant effect, however the sensors with Fe_2O_3 nanoparticles combined with Au, Pt and Pd nanoparticles responded to these concentrations of this gas, which is so dangerous for the environment and the health, with a high sensitivity.

1 INTRODUCTION

The ammonia is mainly an industrial gas with tremendous effects for the environment and for the health, above all to high concentrations. With respect to environment, due to its acidity, this compound is one of the most important acid pollutants, since its deposit can cause great damage to natural ecosystems sensitive to acidification: fauna, flora and quality of air.

Ammonia is a precursor compound of particulate material, and therefore contributes to the health effects caused by PM10 and PM2.5 particles.

High concentrations of ammonia are a great damage to the human health. The lower limit of human ammonia perception by smell is tabulated to be around 50 ppm (Budarvari, 1996). However, even below this concentration, ammonia is irritating to the respiratory system, skin and eyes. Immediate and severe irritation of the nose and throat occurs at 500 ppm. High ammonia concentrations, 1000 ppm or more, could cause pulmonary edema; and higher concentrations, 5000-10000 ppm, could be already lethal within 5-10 min (Timmer, 2005).

The Occupational Safety and Health Administration (OSHA) established an exposure limit of 25 ppm for ammonia in workplace air during an 8-hour day and a 35 ppm limit for a short period of 15 minutes. The National Institute for Occupational Safety and Health (NIOSH) recommends that the ammonia level in the workplace air should not exceed 50 ppm during a 5-minute exposure period.

Therefore, efficient, reliable, low cost, sensitive, small sensors and easy to handle are need to control the air pollution and to replace the conventional techniques of gas analysis. There are many works where the efficiency of SAW sensors for gas sensing at room temperature has been demonstrated in the last decades, but in almost all of them, the sensitive layers used have been polymers deposited by drop or spray coating, being therefore difficult to get repeatability and homogeneity of the sensitive layers (Reibel, 2000, Bender, 2003; Sunil, 2015). In addition, the polymer coatings are degraded and suffer the swelling effect over time (Matatagui, 2005), due to the gas exposures and this leads to a great loss of stability and sensitivity to the gases. To cover these disadvantages, for some years, it has begun to work with thin coatings of metal oxides, and more recent with nanostructured coatings of these materials (Grate, 1994), since in addition to offering a great long-term stability they also have a much greater surface area for sensing, and therefore the sensitivity to gases is increased.

In this work, coatings of iron oxide nanoparticles have been prepared by spin coating and besides have been functionalized with Au, Pd and Pt in order to

Matatagui, D., Gràcia, I. and Horrillo, M.
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DOI: 10.5220/0008918600930096
In *Proceedings of the 9th International Conference on Sensor Networks (SENSORNETS 2020)*, pages 93-96
ISBN: 978-989-758-403-9; ISSN: 2184-4380

compare the sensitivity to low concentrations of ammonia through Love wave devices.

2 MATERIALS AND METHODS

2.1 Surface Acoustic Wave Sensor Array

The group of micro-electromechanical systems (MEMS) includes SAW devices, which consist essentially of a piezoelectric substrate with two interdigital transducers (IDT) used to generate and receive the acoustic waves, obtaining a two-port delay line (DL). The type of the propagated wave depends on the selected configuration of the device. In the present work shear horizontal (SH) guided waves were used that are called Love wave (LW).

Our LW device was based quartz substrate with 200 nm thick of aluminium IDTs. The wavelength (λ) was 28 µm, the center-to-center separation between both IDTs (Lcc) was 150λ and the acoustic aperture (W) was 75λ that is the length of the IDT strips (Fig. 1a). A film of SiO_2 with a thickness of 3.5 µm was deposited on the piezoelectric by plasma enhanced chemical vapour deposition (PECVD). The synchronous frequency of the Love wave multi-guiding layer was around 160 MHz (Fig. 1).

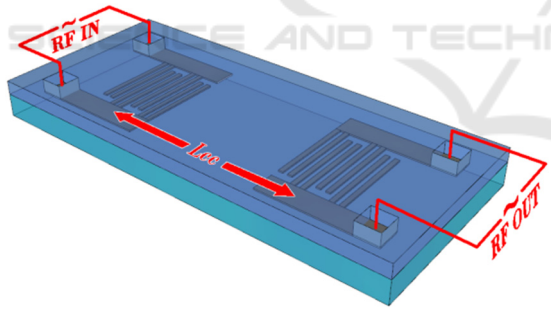

Figure 1: 3D scheme representing Love-wave device.

Four different dispersions of iron oxide (Fe_2O_3) nanoparticles (Sigma 544884, average size smaller than 50 nm) were prepared. One of them, S1, was prepared exclusively from (Fe_2O_3) nanoparticles dispersed in water. The other three were decorated with noble metal nanoparticles of Au, S2, (Metrohm-Dropsens AUNP-COL), Pt, S3, (Metrohm-Dropsens PTNP-COL), and Pd, S4, (Metrohm-Dropsens PDNP-COL). The prepared dispersions were deposited on the LW device as films at a spin rate of 4000 rpm, and then a 30 min postbake at 150 °C was carried out in order to fix the nanoparticles on the surface. In this way, an array of sensors with four different sensitive layers was obtained (Table 1).

2.2 Experimental Setup

The detection system consisted of the test chamber with the four Love-wave sensors and a reference LW device that form the array inside. Each Love-wave sensor was integrated in an oscillator circuit that leads the oscillation with a specific frequency, which was used as an output signal (Fig. 2).

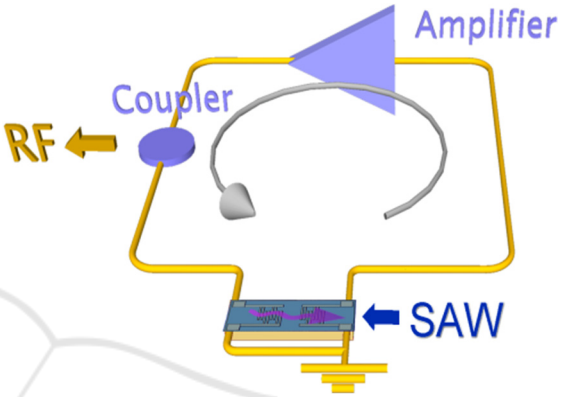

Figure 2: Scheme of the oscillator controlled by the LW-DL.

The acquisition signal is based on a heterodyne configuration; each of the four sensor-oscillator signals is mixed with the signal from the oscillator based on a reference LW device, obtaining a new signal from the difference of the two original frequencies. The sensors worked at room temperature (24 ºC). The experiment control and data acquisition in real time were implemented with a PC by means of software made at home. A scheme of the experimental setup is shown in Fig. 3.

The sensor array was tested using 50 ppm of ammonia, which was diluted in synthetic dry air and stored in a commercial bottle (Praxair). A computerized flow controller system was used to obtain the final flow, by mixing the flow of the samples of the bottles and the synthetic dry air. This was achieved by using mass flow controllers, connected to the PC by Modbus protocol, that provide the desired concentrations. The total constant flow of the gas was kept at 200 $mL \cdot min^{-1}$ and the exposure and the purge times were 5 and 10 min, respectively. The responses were displayed in real time and saved for processing and analyzing.

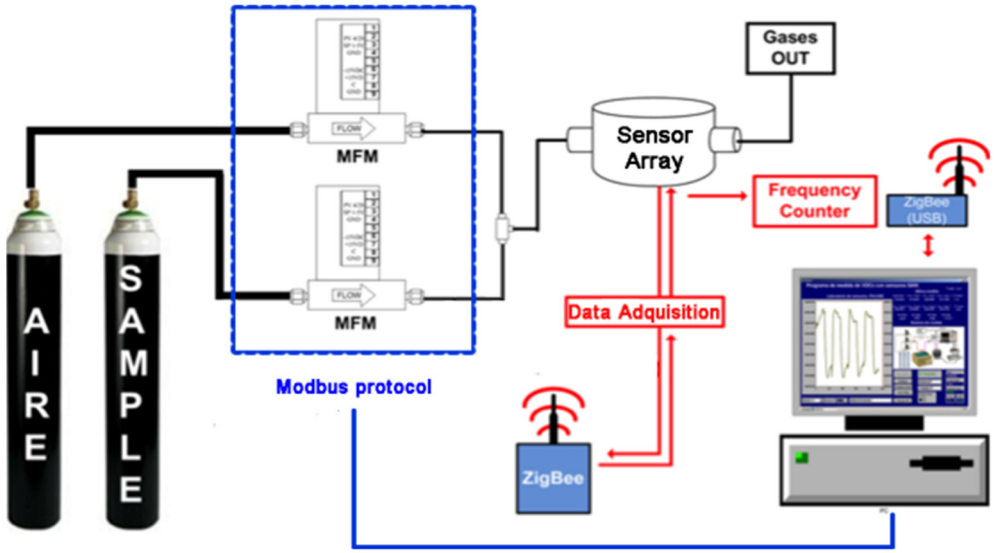

Figure 3: Scheme of the instrumentation and experimental set up used for the data acquisition in real time.

3 RESULTS AND DISCUSSION

3.1 Electrical Characterisation

The sensors were electrically characterized by means of the vector network analyser which measured the frequency response. Fig. 4 is an example of the frequency response (a LW device without sensitive layer, reference) that shows an attenuation around 18 dB and at the operating frequency around 160 MHz.

The sensitive layers introduced in the new device insertion losses, reaching up to 30 dB in the case of the guiding layer based on the combination of iron oxide and Pd nanoparticles. However, the electronic nose was made to support SAW sensors with attenuations up to 38 dB.

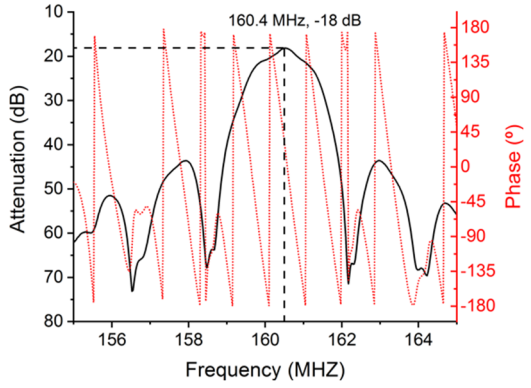

Figure 4: Frequency response (attenuation and phase) of a LW device without sensitive layer.

3.2 Ammonia Characterization

The sensor was characterized in ammonia environments for concentration of 50 ppm (Fig. 5). Experimental measurements for gas characterization showed that sensor response is clearly dependent on the composition of nanostructured guiding layer. Therefore, the sensor with pure iron oxide nanoparticles did not show any evidence of response for ammonia exposition. On the other hand, the sensor with sensitive layer based on the combination of iron oxide and Au nanoparticles showed maximum response, followed by the sensor with combination of the sensor with combination of iron oxide and Pt nanoparticles, and finally by the sensor with combination of iron oxide and Pd nanoparticles.

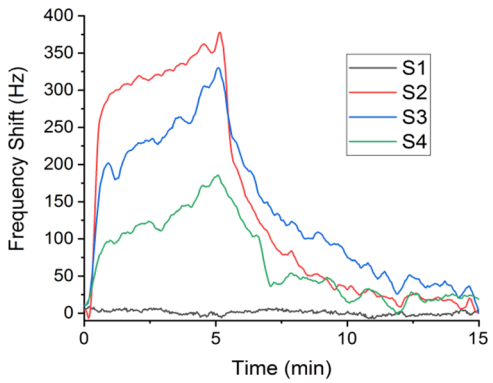

Figure 5: Real time response of a LW sensor array based on iron oxide nanoparticles for a concentration of 50 ppm of ammonia.

The measurement reproducibility was tested measuring 50 ppm of ammonia in three continuous exposure-purge cycles, during which a similar frequency shift was obtained (Fig. 6).

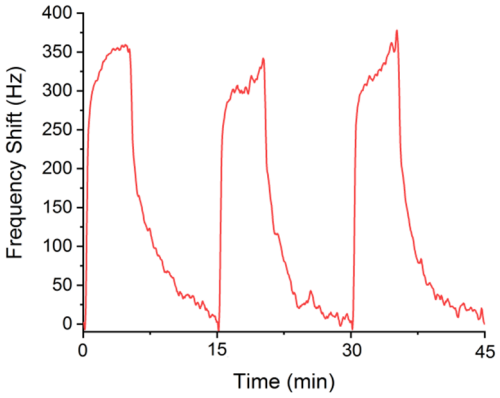

Figure 6: Real time response and recovery of a LW sensor with senstive layer based on combination of iron oxide and Au nanoparticles for a concentration of 50 ppm of ammonia (three exposures and purgue process).

According to the theory (Raj, 2017, Fragoso-Mora, 2018), the fact that the frequency increased with gas interaction implied that the velocity of the wave was highly affected by the elastic properties of nanoparticle layer, resulting high sensitive to the gas interaction.

Table 1 shows the stadistic of the response, sensitivity, standard deviation and limit of detection (LOD) of the triplicates exposures of the sensors to 50 ppm of ammonia.

Table 1: Sensor Array.

Sensor	***S1***	***S2***	***S3***	***S4***
Noble Metal NP	---	Au	Pt	Pd
Response (Hz)	0	359	314	203
Sensitivity (Hz/ppm)	0	7.19	6.28	4.06
Standard deviation	0	18.5	26	16
LOD (ppm)	---	4.17	4.77	7.37

4 CONCLUSIONS

The combination of the iron oxide nanoparticles with noble metal nanoparticles induced an elastic sensitivity for ammonia.

The results showed that the sensor array was highly effective in detecting ammonia with high sensitivity (50 ppm). The nanostructured sensors of the array showed different sensitivities at room temperature, good repeatability, fast response and reversibility, and therefore they are good candidates to get a wireless sensor network for environmental applications.

ACKNOWLEDGEMENTS

This work has been supported by the Fundación General CSIC via Program ComFuturo and the Spanish Ministry of Science, Innovation and Universities under the projects RTI2018-095856-B-C22 (AEI/FEDER) and TEC2016-79898-C6 (AEI/FEDER). This research has used the Spanish ICTS Network MICRONANOFABS (partially funded by MINECO).

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