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Propagation of acoustic waves in metal oxide nanoparticle layers with catalytic metals for selective gas detection

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ABSTRACT

A novel array comprised of six Love-wave sensors based on metal oxide nanoparticles layers (ZnO and TiO_2) mixed with different metals (Co and Pt) was developed to detect, discriminate and classify toxic gases. The metal oxide nanoparticles worked as guiding and sensitive layers at the same time for every sensor. The properties of the different layers of nanoparticles change due to that interaction with the gases, and consequently each sensor suffers a different frequency shift. The array has been tested with different concentrations of ammonia, toluene and xylene. Very low concentrations of these samples have been detected and discriminated by principal component analysis, such as 10 ppm of ammonia, 5 ppm of toluene and 10 ppm of xylene. A correct classification of the measurements has been carried out by means of probabilistic neural network.

1. Introduction

Due in large part to the growing use and widespread availability of chemicals in industry and everyday life, the exposition to hazardous gases has become a serious problem, which is harmful to human health and safety. Therefore, over the last decades, the development of low cost gas sensing devices for the detection of toxic chemical agents has gained an increasing attention.

Many of the low cost sensors that have been developed for specific applications in toxic chemical agent detections, have been based on metal oxides. Metal oxides have been, in most cases, sensitive layers used for development of resistive sensors, such as WO_3 [1], NiO [2], SnO_2 [3], In_2O_3 [4], TiO_2 [5], ZnO [6], CuO_2 and CuO [7], which have a great sensitivity at high temperature but a poor sensitivity at room temperature.

On the other hand, the efficiency of the devices based on surface acoustic waves (SAW) as gravimetric sensors for gases detection at room temperature has been proved in the last decades [8–10]. In literature, many reports proposed the use of polymers as sensitive layers [11–20]. However, recent reports showed that the oxide thin films used as sensitive layers of SAW devices have advantages such as their long-term reliability and stability [21–23].

A novel idea has been the use of layers of nanoparticles of metal oxides, as guide and sensitive layers for Love sensors, due to their high specific surface area.

In addition these layers of nanoparticles have been mixed with different metals to improve the selectivity to the gases. Thus the array of sensors was combined with patterns recognition techniques to detect, discriminate and classify different toxic chemical agents at room temperature [23,24].

2. Experimental

2.1. SH-SAW device

The SAW devices used in this work were based on a shear horizontal surface acoustic wave (SH-SAW) propagated on piezoelectric. In our case the piezoelectric was the ST-cut quartz substrate and the propagation direction of the wave was perpendicular to the *x* crystallographic axis. This SH-SAW, with a wavelength of $\lambda = 28\ \mu m$, was generated and detected by interdigital transducers (IDTs) which transform the RF signals in mechanical waves by means of the piezoelectricity of the substrate. The IDTs were made using standard lithographic techniques, depositing an aluminium layer with a thickness of 200 nm through RF sputtering and forming

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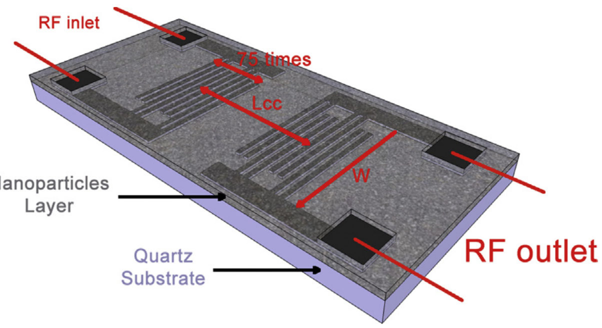

Fig. 1. 3D scheme representing a Love-wave sensor with two RF ports, layer composition, and geometrical parameters.

Table 1
Sensor array composition.

Sensor	S1	S2	S3	S4	S5	S6
Metal oxide	ZnO	TiO_2	ZnO	TiO_2	ZnO	TiO_2
Metals	–	–	Co	Co	Pt	Pt

a delay line (DL). A double finger electrode was designed to obtain destructive interference of the wave reflection that occurs in the IDT, repeating this structure 75 times to form each IDT. The spacing, centre to centre between IDTs (Lcc) was 225 λ and the acoustic aperture (W) was 75 λ. Finally, a device of 4 mm × 9 mm × 0.5 mm (Fig. 1) is obtained.

2.2. Sensitive layers

Two different nanoparticles, ZnO (Sigma 721077) of average size 35 nm and 25 wt% dispersed in H_2O, and TiO_2 (Sigma 700347) of average size 21 nm and 35 wt% dispersed in H_2O, were deposited on the SH-SAW device as films with a thickness of approximately 0.6 μm at a spin rate of 4000 rpm and 8000 rpm, respectively, and then a 30 min postbake at 150 °C was carried out in order to fix the nanoparticles on the SH-SAW device and eliminate the humidity. Thereby, on the one hand the layers of nanoparticles obtained were also used as guiding layers of the devices. Therefore the velocity of the SH-SAW has to be lower in the nanoparticle layers (ZnO and TiO_2) than in the substrate (Quartz), to be able to be used as guiding layers of the SH-SAW generated in the piezoelectric substrate, and in this way to produce the propagation of Love-waves. It implies the concentration of the energy of the wave in the layer of nanoparticles, and consequently the acoustic wave properties are very sensitive to the configuration and physical properties of the nanoparticles layer [25]. On the other hand, the layer of nanoparticles also perform the functions of sensing layer, due to the change of its mechanical and electrical properties when the nanoparticles interact with the chemical agents and consequently the wave propagation velocity changes, and therefore the frequency when the Love-wave Delay Line is used as controller of an oscillating device. Once the layers of nanoparticles were deposited, two different catalysts, Co and Pt were incorporated in order to obtain different responses of each sensor by means of the different catalytic processes. Co and Pt were added by means of chloroplatinic acid hexahydrate (Sigma 206083) and cobaltous nitrate hexahydrate (Sigma 239267) respectively, which were diluted to 2 wt% in deionized H_2O water and deposited by spin coating over layer of nanoparticles at a spin rate of 4000 rpm. Then a thermal treatment at 380 °C and ambient atmosphere for 4 h using a tube furnace with a temperature ramp of 4 °C min^{-1} was carried out in order to disperse the metals in the layer of nanoparticles. In this way, an array of six sensors with six different sensitive layers has been fabricated and assembled (Table 1).

2.3. Setup of gas sensor array

The detection system consisted of the test chamber with the six Love-wave devices 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 output signal. The different signals from array sensor were connected to a microwave switch system (Keithley S46) in order to alternate the different signals, making possible their measurement in a unique channel of the frequency counter (Agilent 53131A). Both, microwave switch system and frequency counter, were controlled by a GPIB protocol. The temperature of the sensors was kept at 25 °C, similar at room temperature, using a PID system, in such a way that the temperature was measured with a Platinum resistance sensor (Pt100) and controlled by a Peltier device. The sensor of temperature, and the Peltier device were communicated with a computer by a ZigBee protocol. 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. 2.

As far as the toxic gases are concerned, the sensor array was tested using different concentrations of ammonia, toluene and xylene, which were diluted in synthetic dry air and stored in commercial bottles (Praxair) A computerized flowcontroller system was used to vary the concentration of 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 min^{-1} and the exposure and the purge times were 10 and 20 min, respectively. The responses were displayed in real time and saved for processing and analyzing.

2.4. Statistical treatment

Principal component analysis (PCA) and probabilistic neural network (PNN) were used for data analysis.

Principal component analysis (PCA) is a chemometric linear, unsupervised and pattern recognition technique for reducing the number of dimensions of a numerical dataset in a multivariable problem. Mathematically, this method applies a linear transformation to the data and result in a new space of variables called principal components. The principal components are ordered, thus the greatest variance is on the first coordinate (called first principal component, PC1), the second greatest variance is on the second coordinate, PC2, and so on. PC1, PC2 and PC3 allow the visualization of dataset main information in 2-D and 3-D representation. The scores plot is usually used for studying the distribution of the data clusters. This method extracts the principal components, but also extracts information of the contribution (load) of each sensor to the components. In the loading plot sensors with similar contributions will be close together. Sensors close to the origin have comparably small contribution.

A probabilistic neural network (PNN) was applied to the PC1, PC2 and PC3 in order to recognize the type of VOCs patterns under study. Neural networks are mathematical models that process information by means of an adaptive system that changes its structure based on external or internal information that flows through the network during the learning phase. Thus, a neural network creates a function to capture and represent complex input/output relationships. The PNN is a type of neural network with radial basis transfer functions that measures the distance between input vector and the training vectors. A PNN was trained, and the performance was evaluated with leave-one-out validation method. This method consists of training N distinct nets (in this case, N is the number of the measurements) by using the remaining vector, excluded from