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Magnonic sensor array based on magnetic nanoparticles to detect, discriminate and classify toxic gases

D. Matatagui [a,*], O.V. Kolokoltsev [a], N. Qureshi [a], E.V. Mejía-Uriarte [a], C.L. Ordoñez-Romero [b], A. Vázquez-Olmos [a], J.M. Saniger [a]

[a] *Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, CU, 04510 D.F. Mexico, Mexico*
[b] *Instituto de Física, Universidad Nacional Autónoma de México, CU, 04510 D.F. Mexico, Mexico*

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ABSTRACT

An array comprised of four magnonic gas sensors based on magnetic nanoparticles layers of $CuFe_2O_4$, $MnFe_2O_4$, $ZnFe_2O_4$ and $CoFe_2O_4$ was developed and tested with dymethylformamide, isopropanol, xylene and toluene. Magnonic gas sensors were composed of an yttrium iron garnet (YIG) epitaxial thin film as a magnetostatic spin waveguide combined with a spin-coated layer of magnetic nanoparticles as a sensitive layer. The magnetostatic spin waves (MSW) were very sensitive to perturbations produced in the magnetic properties of the nanoparticle layers due to interaction with gases, allowing the detection of low concentrations of gases. Finally, the sensitive layers of the magnetic nanoparticles revealed a differentiated response in regard to the gases used to test the array. Therefore, the gases could be discriminated and classified using pattern recognition techniques, such as principal component analysis and artificial neural networks.

1. Introduction

Metal oxides have been known for decades as good gas sensing materials, which have been used for environmental monitoring and industrial applications. On the other hand, nanostructured materials have been used extensively as sensitive layers in gas sensors because very large surface-to-volume ratios can significantly improve the gas sensitivity due to interaction gas-nanostructure, which primarily occurs on the surface [1–10]. Therefore, nanostructured metal oxides are shown in the literature to be among the most promising gas sensing materials.

An important group of metal oxides are ferrites, and, in recent years, many efforts have been made to synthesize nanoferrites with different morphologies, such as nanoparticles, nanorods, core–shell microspheres, thin films, etc [11–15]. Ferrites have also been used extensively as gas-sensing materials, primarily by taking advantage of their semiconducting properties [16–23]. However, to our knowledge, only a few experimental studies have been based on the perturbation of magnetic properties caused by an interaction of gases [24–26]. Main reason of the non-existence of magnetic chemical sensors is the difficulty in accurately measuring low-level magnetic variations in inexpensive systems. However, recently, a magnonic gas sensor that takes advantage of the high sensitivity of magnetostatic spin waves (MSW) to detect change in magnetic properties of nanoparticles, caused by an interaction with gases, has been developed [27].

An advantage of magnonic gas sensors is that there is an extensive variety of magnetic materials, such as ferrites, which could be used as sensitive layers. It is expected that each magnetic nanomaterial possesses a specific selectivity for each gas. In order to demonstrate this idea, an array of magnonic gas sensors with different magnetic nanoparticles as sensitive layers has been developed in this work, and specific responses of the array to different gases have been studied. The array response has been combined with patterns recognition techniques to discriminate and classify different gases.

2. Materials and methods

2.1. Magnonic device

Our magnonic devices were based on 4 mm × 2 mm rectangular ferromagnetic samples, composed of a 7.3 μm thick YIG film on a 0.5 mm thick gallium gadolinium garnet (GGG) substrate. By placing two microstrip-line antennas over the YIG film, a two-port delay line (DL) was formed. The width of the two coupling antennas

* Corresponding author. Tel.: +52 55 5622 8602x1124.
E-mail address: daniel.matatagui@ccadet.unam.mx (D. Matatagui).

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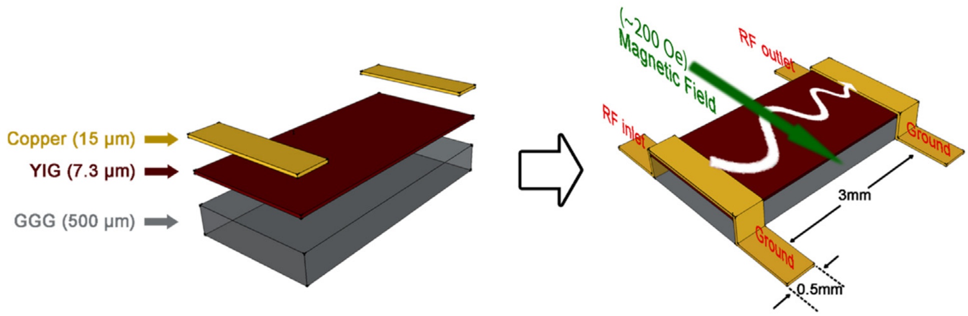

Fig. 1. Schematic of the magnonic device, showing layer configuration and magnetic field orientation in order to obtain magnetostatic surface spin wave propagation.

was 0.5 mm, and the spacing between the antennas was 3 mm. In our case, an in-plane bias magnetic field, applied perpendicularly to the wave propagation direction and parallel to the YIG film plane, gives rise to MSSW propagation along the largest dimension of the sample (Fig. 1). The typical wavelength of MSW was ~500 μm. This MSW-DL was introduced into the feedback loop of a solid-state amplifier and a directional coupler, satisfying the criteria for oscillation: the total phase shift in the loop is $2\pi n$ (n = integer), and the gain over the closed loop is 1. The coupled output from the directional coupler was used to obtain, in real time, a sample of the frequency from the oscillator without interrupting the main power flow (Fig. 2). Finally, the oscillator can be tunable by means of the bias magnetic field within a microwave frequency range from 0.2 to 3 GHz.

2.2. Array sensitive layers

The operational principle of the system is based on the shift in the oscillator frequency caused by changes in magnetic properties of nanoparticles, deposited on YIG film, due to the adsorption of gas molecules. Therefore, different ferrite nanoparticles were used as sensitive layers to form the gas sensor array: $CuFe_2O_4$, $ZnFe_2O_4$, $MnFe_2O_4$ and $CoFe_2O_4$. Nanopowders were dispersed in isopropanol by means of sonication for 1 h and deposited by spin coating on the YIG at a rate of 2000 rpm. Then a 30-min postbake at 100 °C was carried out in order to fix the nanoparticles on YIG and eliminate the isopropanol.

2.3. Gas sensing measurements

The volatile compounds used in the experiment were: dimethylformamide, isopropanol, toluene and xylene. The vapour concentration was calculated using Antoine's Equation. The volatiles were extracted and diluted with synthetic air, which was controlled by a mass flow controller in order to provide the desired concentration. The volume of the liquid samples was 5 ml. They were kept at a constant temperature of 3 °C in a thermal bath for 30 min (headspace time) before being carried to the chamber. Airflow in the chamber was 100 ml min^{-1} and the exposition and purge times were of 1 min each. The experimental control and data acquisition in real time were implemented with a PC using custom made software.

2.4. Statistical treatment

Principal component analysis (PCA) is a statistical method for reducing the number of dimensions of numerical dataset. Mathematically, PCA projects the data onto a new coordinate base formed by orthogonal directions with data of great variance. The principal components are ordered, thus the greatest variance is on the first coordinate (called first principal component, PC1), and the second

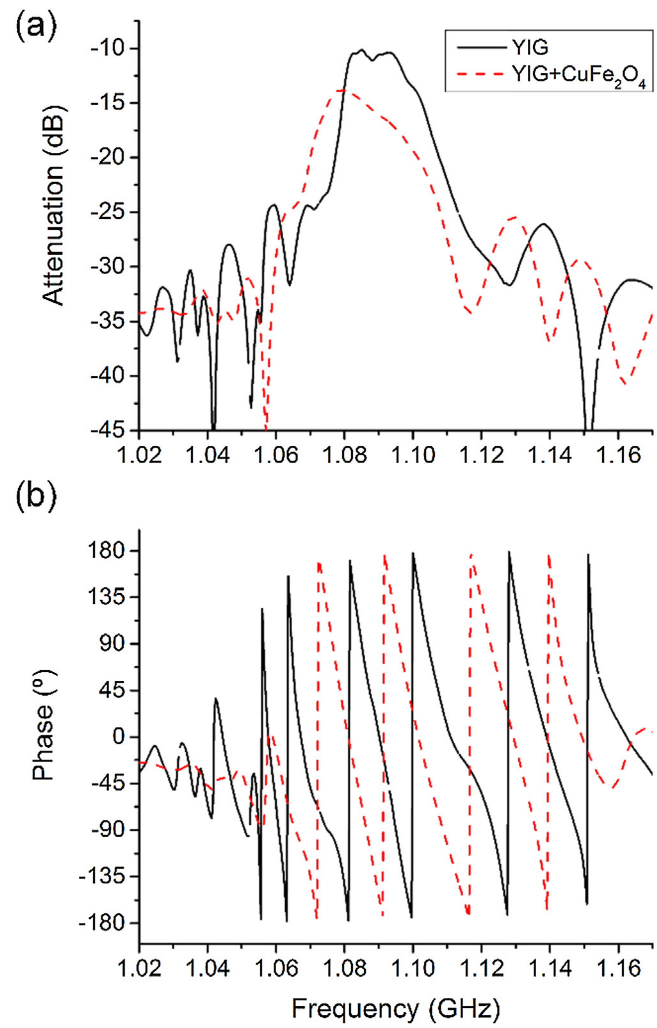

Fig. 2. Frequency response of the Magnonic device before and after being coated with $CuFe_2O_4$ nanoparticles.

greatest variance is on the second coordinate, PC2, and so on. PC1, PC2 and PC3 allow the visualization of dataset's main information in a 2-D and 3-D representation.

A probabilistic neural network (PNN) was applied to the PC1, PC2 and PC3 in order to recognize the type of gases 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