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Gas sensors based on elasticity changes of nanoparticle layers

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ABSTRACT

In this paper, propagation of shear horizontal surface acoustic waves (SH-SAW) in nanoparticle layers was studied by means of dispersion acoustic theory in waveguides. These studies have allowed to obtainment of properties of nanoparticles layers, such as shear stiffness modulus. In addition, the numerical analysis of multi-guiding layers have allowed for the design of an innovative, simple and inexpensive gas sensor based on elastic properties variation of the nanoparticles layers due to their interaction with gases. Each sensor has been prepared by coating a uniform layer of nanostructured indium tin oxide (ITO) nanoparticle layer on a piezoelectric material (quartz), working as a guiding layer by confining SH-SAW energy and obtaining a Love-wave sensor. The perturbation produced in the elastic properties of the nanoparticle layer due to its interaction with gases induced a change in wave velocity that was detected by the frequency shift of an oscillator, working as a sensitive layer. Therefore, the Love-wave sensor was optimized with multi-guiding layers containing an intermediate guiding layer of SiO_2. The Love-wave multi-guiding layer sensor was tested to different concentrations of toluene and benzene, measurements showed high sensitivity, short response time, and good reproducibility, and ability to detect very low concentrations of test gases, such 1 ppm of toluene and 25 ppm of benzene.

1. Introduction

In recent years, there is serious growing concern about the volatile organic compounds (VOCs) impact on health, in particular for gases such as toluene and benzene, because they are usually associated with the occurrence of cancer and other adverse health effects. Consequently, new regulations to control the exposure to VOCs have been established [1–4], with the aim of preventing diseases. In order to efficiently comply with VOCs regulations, their concentrations should be monitored in real time and in situ. Powerful analytical techniques can be used to detect the VOCs concentrations, such as gas chromatography/mass spectrometry [5,6] or ion mobility spectroscopy [7,8], among others. However, these techniques require expensive equipment and specialized personnel for their operation. With the goal to obtain miniaturized, low-cost and easy to use alternative systems to detect VOCs there is increasing research in the wide field of solid-state chemical sensors. At nanoscale, materials and their advanced-design features have led to a new generation of chemical sensors with enhanced sensitivity and response time [9–14], mainly because nanomaterials provides high surface-to-volume ratio, which promotes chemical activity.

Inside the vast field of solid-state chemical sensors, traditionally surface acoustic wave (SAW) sensors are known as gravimetric sensors, since they can measure very low change in surface mass density [15–18]. Among SAW sensors, Love-wave devices have gained importance due to their potential to confine the wave energy in a thin guiding layer, provided that the velocity of the acoustic wave in the guiding layer is slower than that in the substrate, obtaining a very high mass sensitivity. Commonly, a thin sensitive layer on the top of the structure is used as an active medium that interacts with the environment but energy is not confined in this layer. Recent research has shown how Love-wave devices can confine the energy of the wave in metal oxide nanoparticle layer, being both guiding and sensitive layer. These Love-wave devices are promising chemical sensors due to they work at room temperature [19], have a high surface-to-volume ratio and metal oxides present high long-term stability.

In 1992, Grate et al. [20] demonstrated that the gases could significantly affect to the elastic properties of sensitive layer of

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SAW sensor, showing it in the velocity of the propagated wave. Then, some studies used viscoelastic polymers to develop SAW gas sensors [16]. Recent published works proposed that gases, such as ammonia, could affect elastic properties of nanoparticle layer [21–24]. Both mass or elastic sensitivity and attenuation of the Love-wave for a determined guiding layer are related to its thickness. In many cases the highest sensitivity required a thickness, for which the attenuation is so high that the wave can be not transmitted.

For this reason, analysis methods have been developed for studying Love-wave propagation in multiple elastic layers [25–28]. Liu et al. [27], presented a method for N elastic, isotropic, dielectric and nonpiezoelectric layers deposited on a piezoelectric substrate, including expressions for important parameters as dispersion equation, mass sensitivity and electromechanical coupling. Love-wave devices with multilayered structures have demonstrated to improve mass sensitivity, insertion loss, frequency stability and temperature stability [29].

Therefore, a multi-guiding layer could be used to obtain high sensitivity with appropriate attenuation of the wave, which, in the case of mass sensitivity, was studied by different authors [30], however in the case of the elastic sensitivity it has never been studied.

In the present work, we have studied the elastic sensitivity of Love-wave sensors based on an Indium tin oxide (ITO) nanoparticle layer with multi-guiding structure (SiO_2-ITO). Resulting Love-wave sensors were tested with toluene and benzene.

2. Materials and methods

2.1. Love-wave device

The basic principle in a Love-wave sensor is the change in the propagation velocity of the surface acoustic waves which are caused by perturbations on the active surface of the device. The velocity changes are performed indirectly, using the device as the resonating element in a delay line (DL) oscillator circuit that allows to measure the velocity changes by means of the oscillation frequency changes. Since, the shift in the wave velocity are proportional to shift in the oscillation frequency.

Love-wave sensors researched in this work were composed of a piezoelectric substrate and two guiding layers. To generate and receive the acoustic waves two port delay lines (DL), based on interdigital transducers (IDT) of aluminium with a thickness of 200 nm were used. The configuration for each IDT consisting of four strips per period is called double-electrode-type or split-electrode-type. The period formed by four fingers (λ) is 28 μm, the centre-to-centre separation between both IDTs (Lcc) is 150λ and the acoustic aperture (W) is 75λ that is the length of the strips (Fig. 1).

2.2. Theoretical background

A coordinate reference system is represented by x_1 the wave propagation direction that is perpendicular to the x crystallographic axis, x_2 parallel to shear polarization direction, and x_3 the normal direction to the structure, as shown in Fig. 2. Substrate is supposed semi-infinite in $x_3 < 0$. Every layer is supposed infinite along the plane. The top layer composed of ITO nanoparticles, has a thickness, h_1 (m), mass density, ρ_1 (kg/m^3), shear stiffness module, μ_1 (N/m^2), and electric permittivity, ε_1 (F/m). SiO_2 layer ε_2 has a thickness, h_2, mass density, ρ_2, shear stiffness module, μ_2, and elastic permittivity, Elastic, c (N/m^2), permittivity, ε, and piezoelectric, e (C/m^2), matrix constants define the substrate properties [31]. The relation between shear stiffness module and density in the n isolated layer results in $V_n = \sqrt{\mu_n/\rho_n}$ velocity of shear acoustic wave as dispersion equation for a bilayer structure is described by Eq. (1) from the general N multilayered equation. Eq. (1) must be solved numerically in order to obtain the surface that describes the relation between the phase velocity v (m/s) and layers thickness h_n (m).

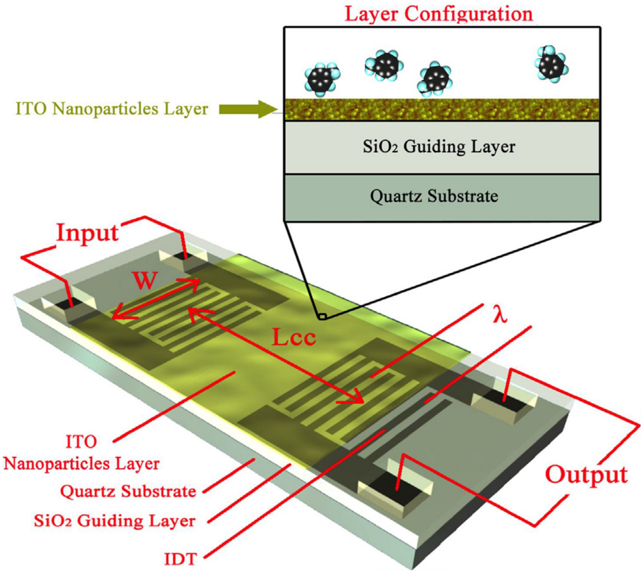

Fig. 1. 3D scheme representing Love-wave sensor. Multi-guiding layers system is compound by ITO nanoparticles layer and SiO_2 layer over a ST-Quartz substrate. Also, ITO nanoparticles as sensitive layer is used for gas detection. Acoustic waves are excited and received by IDTs.

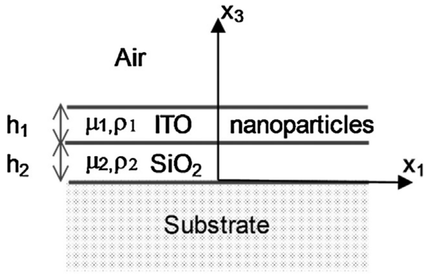

Fig. 2. Schematic of the bilayer waveguide for Love waves.

$$\mu_2\beta_2 \frac{\mu_2\beta_2 \tan\left(k\beta_2 h_2\right) + \mu_1\beta_1 \tan\left(k\beta_1 h_1\right)}{\mu_2\beta_2 - \mu_1\beta_1 \tan\left(k\beta_1 h_1\right) \tan\left(k\beta_2 h_2\right)} = \frac{(D_1 - \bar{\varepsilon}_{L2})T_2 - (D_2 - \bar{\varepsilon}_{L2})T_1}{(D_1 - \bar{\varepsilon}_{L2})A_2 - (D_2 - \bar{\varepsilon}_{L2})A_1} \qquad (1)$$

where D_1 and D_2 correspond to normal electric displacement of electric field at the substrate surface (F/m), A_1 and A_2 (m/V) are the ratios of magnitude displacement to that of the electrical potential, T_1 and T_2 are the components of normal stress acting on the surface particle of the substrate (C/m^2), $\bar{\varepsilon}_{L2}$ is the equivalent permittivity of the layered waveguide that describes the electric field and $\beta_n = \sqrt{v^2/V_n^2 - 1}$ is the transverse propagation constant in the n^{th} layer. These parameters are obtained from applying mechanical and electric boundary conditions.

The dispersion equation is an important tool for Love-wave sensor analysis and for obtaining parameters such as mass sensitivity, elastic sensitivity and electromechanical coupling.

Mass velocity sensitivity S_m^v (m^2/kg) can be defined as a relative variation in the propagation velocity due to load of mass distributed over the surface of the guiding layer as shown in Eq. (2).

$$S_m^v = \frac{1}{v}\left(\frac{\Delta v}{\Delta m}\right)_{\Delta m \to 0} = \frac{v}{\mu_1 \beta_1^2} \frac{dv}{dh_1} \qquad (2)$$

where Δv is a small change in the velocity phase due to a small mass Δm (kg/m^2) applied uniformly over the top surface and