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PANI/ZnO/Quartz structure for Love wave gas sensor

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Abstract. Everyone knows the importance of sensors in our society and the huge attempt to improve their properties in order to obtain better sensitivity and selectivity. In this paper, we are more particularly focused on gas sensors based on surface acoustic waves (SAW) device. In a previous work, we have developed and studied a structure composed of a 90° rotated ST quartz crystal covered with a ZnO layer. By developing inter-digital transducers (IDT) on this structure, we can generate different types of acoustic waves. Love waves which are confined near the surface are known to be very sensitive to fluids (liquids or gases). The aim of this work is to present the way we have developed this optimal structure and to test it with a specific polymer. This polymer is polyaniline (PANI). Its main advantage is that it should be deposited by cold pulsed plasma process.

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1 Introduction

Surface acoustic wave (SAW) devices are widely used for filtering applications in mobile telephony. Nowadays they are more and more used in the field of instrumentation and measurement because they are sensitive to many external parameters such as temperature, mechanical deformation, pressure, humidity or gases.

In this paper, we present the results of the development of a gas sensor based on a SAW structure. We first describe

the theoretical approach which identifies a priori the parameters (crystal cut, thickness, ...) in order to obtain the optimal structure. We then show experimental results obtained on the optimized ZnO/Quartz ST-90° Love wave structure. Finally, we test the developed sensor for the detection of nitrogen dioxide (NO_2) by adding a polyaniline sensitive layer (PANI).

2 Basic structure of the sensor: ZnO/Quartz

ST-90°

2.1 Theoretical approach of the Love wave

Love waves which are polarized transverse waves have been shown to present low radiation in fluids and a good sensitivity [1]. In order to obtain these guided waves, it is necessary to deposit a thin layer on a piezoelectric substrate. Moreover, the condition for the existence of Love wave mode is that shear velocity in the layer is smaller than the shear velocity in the substrate. In our device, the shear velocity of the ZnO layer ($V_C = 2650\text{m/s}$), used as the waveguide layer, is lower than that of the 90° rotated ST-cut quartz velocity ($V_S = 4996\text{m/s}$) [2]. Due to the relatively high velocity contrast between the guided layer and the substrate, it is possible to generate waves with a better confinement near the surface compared to classical structure obtained with *SiO₂/Quartz* or *PMMA/Quartz*. Furthermore, the ZnO film presents a relatively high electromechanical coupling coefficient (K^2) and a negative temperature coefficient of frequency (TCF) leading to a thermally compensated structure when combined with ST-cut quartz [3].

The numerical program was developed in the laboratory by using the Campbell and Jones method [4]. The equations describing the surface acoustic waves propagation in any medium have the following form:

$$c_{ijkl} \frac{\partial^2 u_l}{\partial x_j \partial x_k} + e_{kij} \frac{\partial^2 \Phi}{\partial x_j \partial x_k} = \rho \frac{\partial^2 u_l}{\partial t^2} \quad (1)$$

$$e_{jkl} \frac{\partial^2 u_l}{\partial x_j \partial x_k} - \epsilon_{jk} \frac{\partial^2 \Phi}{\partial x_j \partial x_k} = 0 \quad (2)$$

where c_{ijkl} , e_{kij} and ϵ_{jk} are respectively the elastic, piezoelectric and dielectric tensors. ρ is the mass density. The initial program is subsequently modified in order to take into account Love waves. The Christoffel matrix obtained from the first equations is divided into two sub-matrix for both quartz and zinc oxide [5]. Theoretical calculations were used to determine the dispersive curves of phase velocity (V), K^2 , TCF, and mass sensitivity as a function of ZnO normalized thickness ($kh_{ZnO} = 2\pi h/\lambda$). The electromechanical coupling coefficient reflects the ability of the material to convert the mechanical energy into electrical energy and vice versa. It is defined by the following equation:

$$K^2 = \frac{V_0^2 - V_m^2}{V_0^2} \quad (3)$$

where V_0 is the phase velocity on the open circuit (free surface) and V_m is the phase velocity of the short-circuit (metallized surface). The theoretical temperature coefficient of frequency was estimated by the equation :

$$TCF = \frac{1}{f} \frac{\Delta f}{\Delta T} = \frac{V(T) - V(T_0)}{V(T_0)} - \alpha_{ij} \quad (4)$$

with f the central frequency, Δf the frequency shift observed for a temperature variation ΔT . $V(T)$ and $V(T_0)$ are phase velocities at T and T_0 (reference temperature) respectively. α_{ij} is the thermal expansion coefficient of ZnO along the SAW propagation direction. The obtained simulations [6] have enabled us to extract the value of the normalized ZnO thickness, which provides temperature compensation and a better K^2 . We therefore get $kh_{ZnO} = 0.55$.

To determine the sensitivity to the mass effect, we take into account the work of Mc Hale [7]. His theoretical method takes into account the theory of disturbances developed by Auld [8]. In the case of a **three** layer system consisting of a sensitive layer and the ZnO/Quartz structure, the mass sensitivity should be given by the following formula:

$$S_m = \frac{1}{\rho_l} \left[\frac{1 - V_p^2/V_0^2}{1 - V_l^2/V_0^2} \right] \frac{f_0}{V_l} \left(\frac{d \ln(V)}{dz} \right)_{z=z_0} \quad (5)$$

where V_p and V_l are respectively the velocity in the sensitive layer and in the guiding layer. z_0 is the guiding layer thickness ($z_0 = d/\lambda$) at the operating point. Due to the very small thickness of the sensitive layer (less than 1% of the wavelength) and the choice of the Love wave (confinement of the wave in the ZnO layer), it is possible to determine the mass effect sensitivity without considering the sensitive layer. We therefore modify the previous equation by substituting V_p with V_l .

Figure 1 presents the theoretical result where the maximum mass sensitivity is obtained for $kh_{ZnO} = 0.25$. The value of $kh_{ZnO} = 0.55$ will give us a sensitivity of 0.4 which is 30% less than the maximum. Nevertheless for that value, we will also have a temperature compensation and a better K^2 .

2.2 Experimental results obtained on the developed structure.

Figure 2 shows the frequency response observed with the structure based on the theoretical approach. We note that, as expected, it appears a response corresponding to the

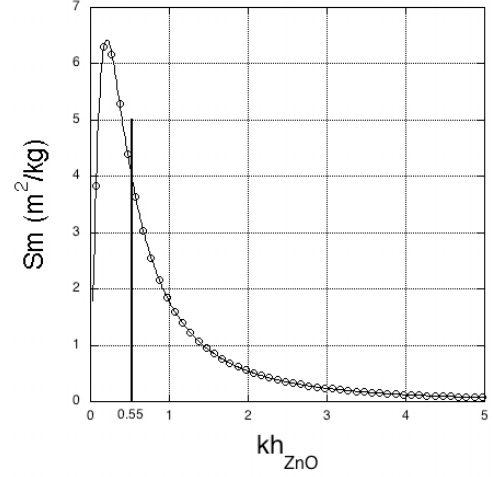


Fig. 1. Theoretical mass sensitivity determination versus normalized ZnO thickness.

Rayleigh wave at $475MHz$. This peak should be associated to the pure Rayleigh wave generated by the ZnO layer. Two peaks ($507MHz$, $823MHz$) are due to the Love wave generated by the pure shear wave of the quartz ST- 90° and the guiding layer. Although the mode 1 of the Love wave presents fewer losses than the mode 0, we better use **the mode 0** because it is less sensitive to temperature variation.

To study the temperature coefficient of the frequency, we develop series of ZnO/Quartz ST- 90° structures with different wavelengths. We then test each of them as a function of the temperature. Figure 3 shows the obtained responses. We note that the theory is in good agreement with experimental. Moreover for a kh_{ZnO} of around 0.55, we have a temperature compensation as it was predicted.

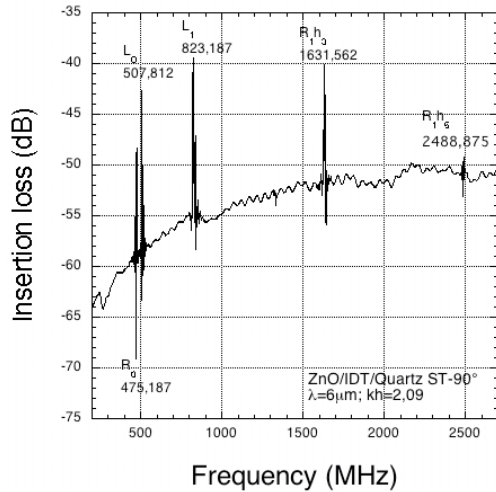


Fig. 2. Frequency response of the ZnO/Quartz ST-90° structure with a IDT periodicity of $6\mu\text{m}$

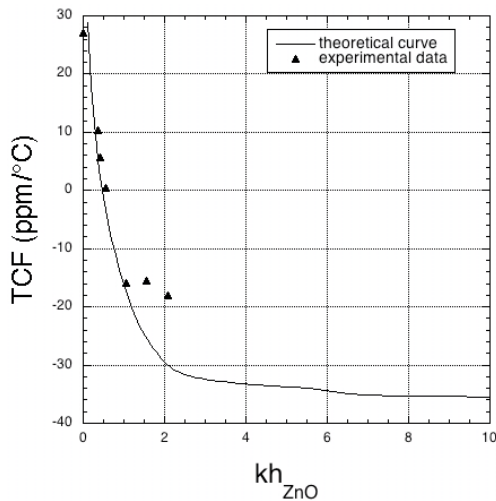


Fig. 3. Temperature coefficient of frequency versus ZnO normalized thickness. Experimental and theoretical results.

3 Gas sensor development

3.1 Polyaniline sensitive layer

To detect gaseous compounds, it is necessary to add a sensitive layer on the wave path in order to measure perturbations. The layer must present the best affinity with the compound to detect. Polymers are nowadays increasingly

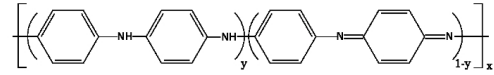


Fig. 4. General structure of polyaniline

used because they offer a wide variety of properties and a significant adaptability by chemical treatment. Conducting polyaniline (PANI) exhibits extraordinary electronic properties, such as low ionization potential and high electron affinity. As a result, it can be easily reduced or oxidized. PANI has wide variety of applications in batteries, electromagnetic devices, biosensors, gas-separating membranes, electromagnetic shielding, and antistatic materials. That is why we choose to use the polyaniline (Fig. 4). Besides, it was shown that post-treatment can improve sensitivity to certain species [9]. PANI is mostly synthesized by aniline oxidation either with a chemical oxidant (chemical route) or through electrochemistry. The method used here is a plasma polymerization [10]. Films are deposited in a pulsed plasma RF reactor with a time of discharge of tenth of a millisecond. The power generator is set at $80W$ and the vacuum pressure is of $3.10^{-6}Torr$. The aniline monomer liquid is contained in a glass jar at room temperature and sprayed into the vacuum chamber during deposition. The pressure in the reactor is maintained at $0.02Torr$ during curing. In order not to perturb the wave propagation and the basic structure, we have limited the thickness of the deposited film to a hundredth of the wavelength. Thus PANI films have a thickness of $265nm \pm 7nm$, thickness obtained within 30 minutes. Figure 5 shows the final structure. In Figure 6, we present the

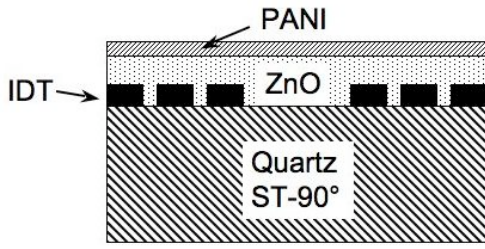


Fig. 5. Complete SAW structure: PANI(265nm)/ZnO(2.1 μ m)/Quartz ST-90°.

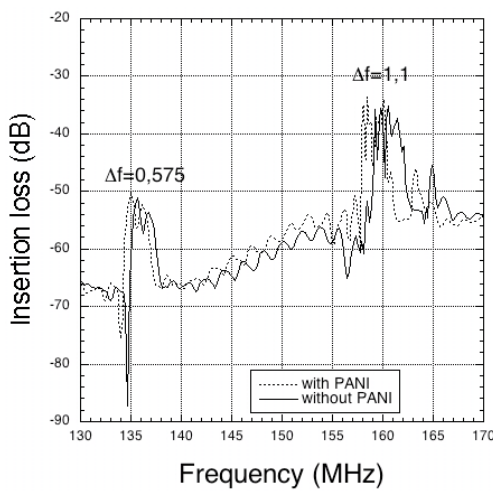


Fig. 6. Frequency response of the ZnO/Quartz ST-90° SAW device with and without PANI.

frequency response of the ZnO/Quartz ST-90° SAW device substrate with and without a polyaniline film 265nm. The wavelength is fixed to 24 μ m, covered with a ZnO layer of 2.1 μ m. We first find that the experimental velocities correspond to theoretical velocities, 3250m/s for the Rayleigh wave and 3826m/s for the Love wave against 3335m/s and 3926m/s, respectively, for the theoretical values. These divergences should be due to the mass effect caused by the PANI layer. We note that the PANI layer perturbs slightly the frequency response. Indeed, the insertion losses are quite similar.

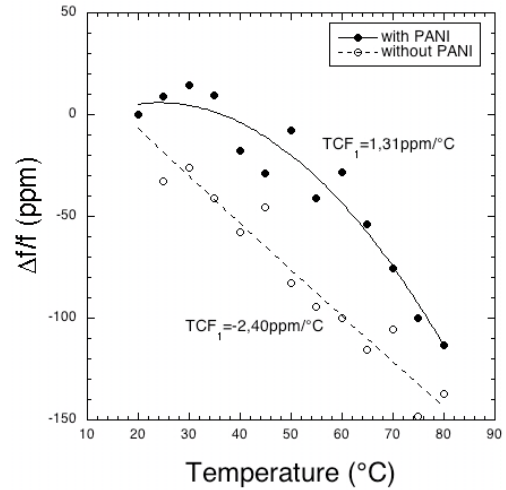


Fig. 7. Frequency shift versus temperature of the developed structure with and without PANI.

With regard to the temperature stability (Fig. 7), there are some variations between theoretical and experimental data. For both structures, this should be related to the technological dispersion of the ZnO characteristics and to constant values used for the theoretical determination. Moreover, the addition of the PANI layer improves the temperature compensation of 45% ($TCF_{without\ PANI} = 2.4\text{ppm}/^\circ\text{C}$; $TCF_{with\ PANI} = 1.31\text{ppm}/^\circ\text{C}$).

3.2 First gas test results

Nitrogen dioxide (NO_2) was chosen to be tested. It is part of NO_x family which is harmful to the environment as well as sulphur dioxide (SO_2). SO_2 may also appear and alter microsystem process. Experimental set-up is based on a permeameter for low concentration generation and mass flowmeters to control the flow and further dilute the gas test. Figure 8 and 9 represent the frequency shift of the PANI/ZnO/Quartz ST-90° after many gas introduc-

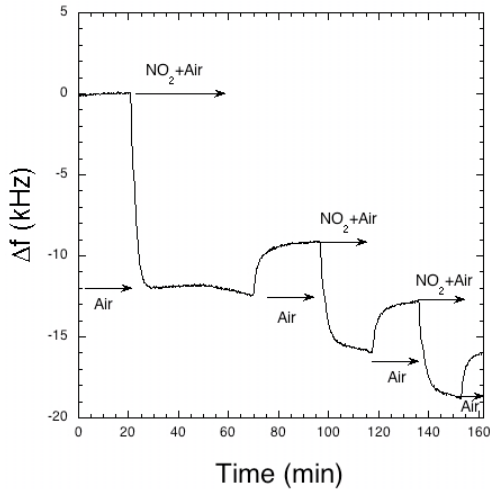


Fig. 8. Frequency shift versus time after NO_2 introduction (54ppm).

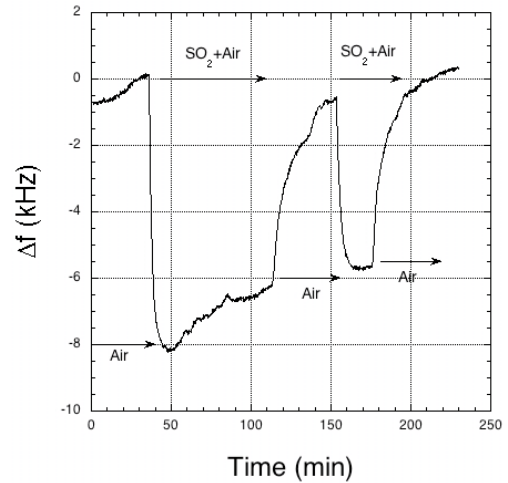


Fig. 9. Frequency shift versus time after SO_2 introduction (34ppm).

tion cycles (NO_2 /Dry Air and SO_2 /Dry Air). For each of the two tested gases, we observe a frequency variation corresponding to the variation of the Love wave velocity due to the mass effect. The frequency variation is about 6kHz for a NO_2 concentration of 54ppm. This variation is ten times higher than that obtained without the layer of PANI for the same concentration. This sensitivity should be enhanced by functionalizing the polymer. This polymer presents a lack of selectivity because it reacts also to other gases like SO_2 (Fig. 9). We note also on the two curves a short term drift of the baseline, opposited for NO_2 and SO_2 . This should be attributed to the airflow circulation on the device generating a higher gas concentration

4 Conclusion and outlook

We have developed a surface acoustic wave device with good characteristics in terms of K^2 , TCF and mass sensitivity. The use of this structure for the detection of gas

requires a sensitive layer. The choice of polyaniline polymer offers an opportunity because this may be functionalized thereafter. It will then be possible to create, from the same initial structure, a set of different sensors. We should then produce a gas sensor array. Moreover the plasma deposition process also offers the advantage of simultaneously deposit ZnO and PANI without contamination of the guiding layer.

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