Surface Acoustic Wave Devices Exploiting Palladium Layer Properties for Selective Detection of Hydrogen

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***Abstract*—For an increasing number of application (energy production, car industry, space, etc.), hydrogen represents a solution of the future as it is the most common body in the Universe (and therefore on Earth). However, due to its unstable properties, a particular care must be dedicated to control possible gaseous leaks close to tanks and facilities using this resource. In this paper, surface acoustic wave sensors are proposed for detecting gaseous hydrogen in standard environmental conditions (atmospheric pressure and room temperature). The proposed SAW sensors consists in two Rayleigh-wave delay lines built on Quartz, one equipped with a Palladium overlay and the other exhibiting a free path between the two interdigitated transducers. A specific gas test cell has been developed to test various sensor configurations submitted to hydrogen-composed atmospheres. A particular care was paid to avoid hydrogen leakage in the working environment and to perform the regeneration of the gas absorbing layer. The developed device allows for identifying different concentrations of hydrogen (in the 1-4% range) diluted in N_2 and is also able to detect H_2 in current atmosphere. SAW devices exploiting hydrogen absorption capabilities of palladium thin films have been here used to make the detection and the identification of hydrogen concentrations in the 1-4% range and the influence of outer parameters such as temperature and relative humidity variations on the sensor operation is also reported.**

***Index Terms*—gas sensors; hydrogen; Palladium; SAW device; Rayleigh waves.**

I. INTRODUCTION

The raising shortage of fossil energy resources added to the increasing concern towards environmental issues have led to consider hydrogen as one of the most promising energy resource. This odorless and colorless gas being highly explosive over 4% concentration in air, the availability of a fast and accurate detection system close to storing facilities and equipping hydrogen-operated machines is mandatory for obvious security reasons. Such a system must exhibit a significant selectivity as it must detect the presence of gaseous hydrogen in air with concentrations smaller than the above-mentioned critical limit at standard conditions (room temperature and atmospheric pressure) as well as in harsher environment (very low or significantly high temperature). Although some solutions have been proposed [1] [2] [3] [4] [5] [6] [7]. The current availability of such a detection system meeting modern specifications of hydrogen use and storage is still questionable. The mains improvements for such sensors are their sensitivity, their selectivity and their reliability together with sensor size, cost reduction, energetic needs and response time [8]. Many methods of detection of hydrogen and a comprehensive review can be found in the literature [9], providing a substantial material base to try and address the above challenges. Among the possibilities, SAW (Surface Acoustic Wave) sensors have been widely studied in the last decades because of their attractive capabilities. Indeed, SAW devices exhibit high sensitivity to surface perturbation since the quasi totality of the energy propagates in a region that thickness is a few times the wavelength of the propagating acoustic wave. It is also a mature technology, SAW device do exhibit limited size (less than 1 cm²) and they allow for wireless use [10]. Initial works were made by D'Amico et al. [11] using the properties of palladium layer to trap the targeted gas. Since this pioneer work, innovations concerning the selectivity and stability of sensitive layers versus external parameter have been proposed to improve hydrogen detection using SAW devices [12] [13] [14] [15] [16] [17] [18] [19]. In this paper, a SAW sensor is proposed for detecting gaseous hydrogen in standard environmental conditions (atmospheric pressure and room temperature). The proposed SAW sensor consists in two Rayleigh-wave delay lines built on Quartz, one equipped with a Palladium (Pd) overlay and the other exhibiting a free path between the two interdigitated transducers (IDTs) used to excite and detect the acoustic wave. These IDTs are built using aluminum electrodes, as this metal is known to be inert versus gaseous hydrogen. An innovative aspect of the proposed sensing system consist in the open-loop strategy for phase changes monitoring [20]. Moreover, delay lines are monitored in parallel using a synchronous detection approach that provides high frequency measurement resolution and that permits a systematic characterization of the device before operated. Along this approach, the impact of changes of intrinsic properties of the devices such as working frequency drift with aging can be minimized. These sensors

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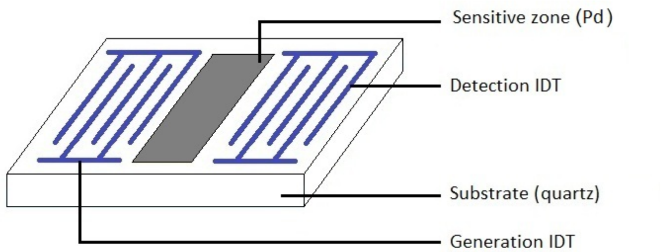

Fig. 1. Scheme of a SAW delay line using Rayleigh surface acoustic wave at 78MHz.

have been tested in a specific gas cell developed to experiment with various sensor configurations submitted to hydrogen-composed atmospheres. A particular care has been dedicated to avoid hydrogen leakage in the working environment and to promote the gas absorbing layer regeneration. The developed device allows for identifying different concentrations of hydrogen diluted in N_2 and is also able to detect H_2 in current atmosphere. The first section of the paper presents the SAW sensor as well as the exploited monitoring system. Experimental validation of H_2 detection then is reported, with a description of the chemical test bench and detection results for various H_2 concentrations. An analysis of the influence of H_2 adsorption on SAW propagation is proposed to provide routes for the proposed device optimization. In the same purpose, the last section of the article is devoted to characterizing the influence of external parameters such as temperature and relative humidity variations on the sensor operation, yielding conclusive discussions.

II. SAW SENSOR AND ASSOCIATED MONITORING SYSTEM

Selective detection of hydrogen at room temperature and pressure have been achieved using SAW delay lines exploiting Rayleigh waves on AT-cut Quartz, as the corresponding first order temperature coefficient of frequency (TCF) is close to zero, yielding frequency-temperature compensation for the above-mentioned operating conditions. The sensor structure correspond to a differential set-up in, which a sensitive track is achieved by depositing a Pd layer in between two IDTs whereas the reference track surface is left free to detect non-specific gas/surface interaction. Along this approach, one can significantly increase the sensitivity of the device and its robustness to correlated perturbations (temperature, vibration, non-specific adsorption). The configuration of both generation and detection IDTs used for the sensor consist in 50 fingers pairs with a grating period of 10 μm and a center-to-center spacing of 5mm (the reactive surface). The wavelength is 40μm, yielding a frequency operation in the vicinity of 78MHz as the wave velocity approaches 3100m.s^{-1}. The Pd film was deposited by thermal evaporation on a single run and shaped by a lift-off technique. Its length along the propagation path was 3mm and its thickness equal to 300nm. The device configuration is shown on Fig. 1.

Using a network analyzer, the transfer function of the device can be easily determine and hence the phase shift induced by

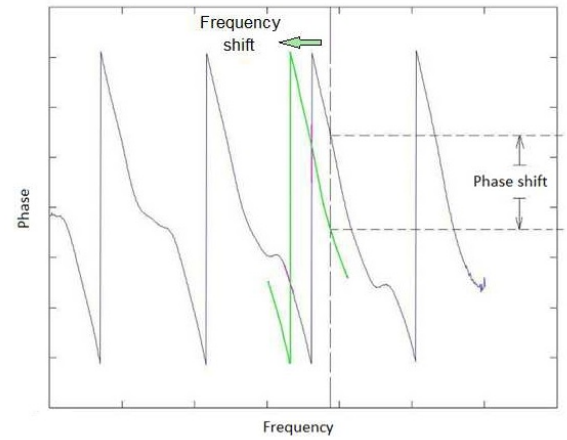

Fig. 2. Phase shift measurement principle using a dedicated instrumentation.

gas absorption has been first monitored that way. However, the use of a dedicated electronics has been experienced and delivers similar information [20]. This system actually operates as a network analyzer to detect the optimal operation condition (zero phase at maximum bandpass amplitude) and then tracks the phase shift in a phase-locked-loop protocol to keep the excitation frequency meeting the above condition. The sensitivity of the set-up allows for some tens mill-degrees resolution and is easily transportable. The response of the bare device and the functionalized one are respectively measured. This configuration has been used so as to make a systematic characterization of each new device used for H_2 detection.
Fig. 2 illustrates the way the phase shift measurement is achieved.

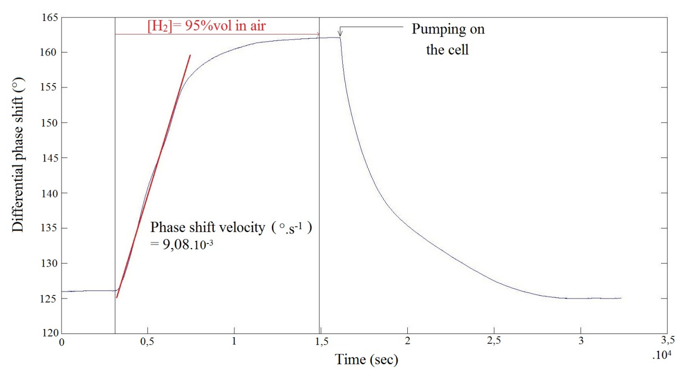

Fig. 3. Detection of hydrogen at high concentration in air.

A. Detection of hydrogen at room temperature and atmospheric pressure.

Hydrogen detection in the percent order have been achieved at room conditions. Figs. 3 and 4 present experimental results when using either nitrogen or air as carrier gas. As it can be observed in Fig. 4, the detection of about 95%vol of hydrogen in air at 35% RH and 20°C can be achieved with a response delay of about 20 seconds considering that the determination

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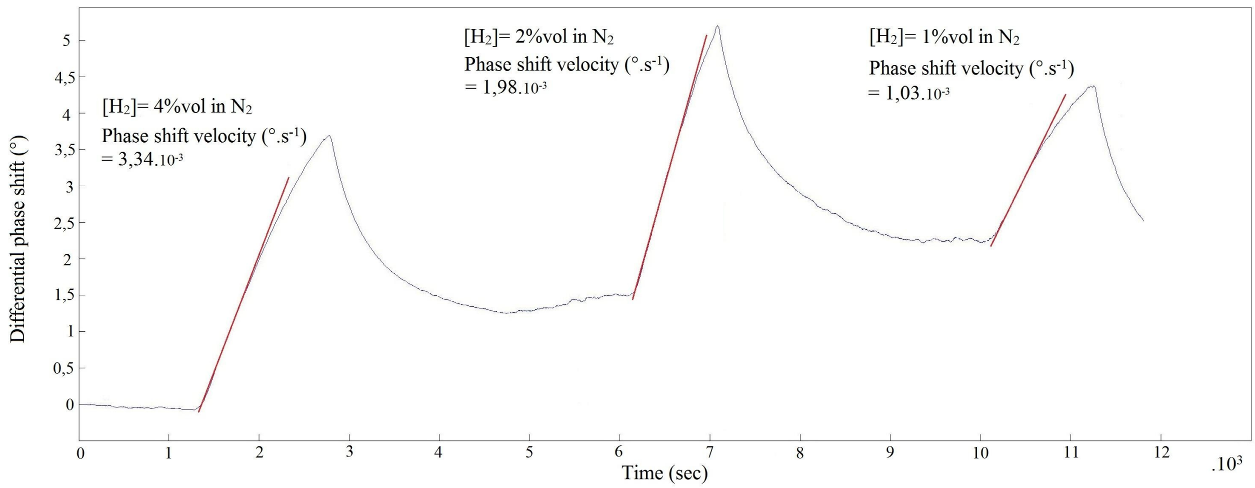

Fig. 4. Detection of hydrogen in the range 4% to 1%vol in N_2.

of the H_2 concentration in the melting gas is derived from the phase shift velocity during the exposure and not from the steady state. It is notable that this value depends on a large part on the performance of the hydrogen generation setup. Therefore, the intrinsic response delay of the device is expected to be shorter. Fig. 3 shows that the device allows for identifying different concentrations of hydrogen diluted in a nitrogen flow of 100sccm.

III. Analysis of hydrogen absorption on Pd films and its influence on SAW propagation.

Absorption of hydrogen into Pd layer induce modifications on the SAW propagation conditions. The effective physical characteristics of the wave then varies with the amount of absorbed H_2 (especially its phase velocity). It has been shown [21] that the two main parameters that influence the phase velocity change of elastic waves are mass- and elastic-loading as it can be seen on the equation bellow [21]. Since only devices using quartz substrates have been used here, changes in electrodes conductivity is not consider as possible origin of the observed phase velocity drift and therefore will not be taken in account. Electromechanical coupling of Rayleigh waves on Quartz substrates is actually smaller enough to consider conductivity changes negligible.

$$\frac{\Delta\nu}{\nu} = \left(\frac{\pi h}{2\lambda}\right)\Bigg[-\frac{\Delta\hat{\rho}}{\hat{\rho}}\{(A_x^2+A_y^2+A_z^2)\hat{\rho}\nu_0^2\}\ \text{mass-loading term}$$
$$+\frac{\Delta\hat{C}_{44}}{\hat{C}_{44}}\{(4A_z^2+A_x^2)\hat{C}_{44}\}\text{elastic-loading term}$$
$$+\left\{\frac{\left(1-\frac{\Delta\hat{C}_{44}}{\hat{C}_{44}}\right)^2}{\left(1-\frac{\Delta\hat{C}_{11}}{\hat{C}_{11}}\right)}-1\right\}\left(4A_z^2\frac{\hat{C}_{44}^2}{\hat{C}_{11}}\right)\Bigg]\ \text{elastic-loading term}$$

In case of H_2 adsorption on Pd layer that thickness is h traversed by a SAW that wavelength is λ, the mass density $\hat{\rho}$ and the elastic constants $\hat{C}_{11}$ are both decrease, whereas the $\hat{C}_{44}$ constant increases. The values of normalized mechanical displacement A_i for palladium are reported in [22] and [23]. Numerical calculations of hydrogen absorption in Pd layers [21] predict an increase of $\hat{C}_{44}$ elastic constant, yielding an increase of the phase velocity of the Rayleigh wave propagating under such an overlay. These calculations are in agreement with the experimental observations presented here.

IV. The influence of humidity and temperature on hydrogen detection.

As SAW devices are known to suffer from interference due to humidity and temperature, the influence of these parameters on the sensor operation have been investigated and are exposed here. The observations reported in this section are expected to provide information allowing for the improvement of the differential acquisition setup. One can see in Fig. 5 that an increase of the relative humidity (RH) of the injected gas causes a mass-loading effect that results in a decrease of the measured phase of the delay line. Indeed, the adsorption of condensated water onto the surface of the device leads to a raise of the mass at the surface of the device (mass loading) leading to the decrease of the phase velocity experimentally observed. Fig. 6 evidences the impact of temperature variations on the capability of the SAW sensor to detect hydrogen at atmospheric pressure. Temperature changes lead to a shift down of the delay line synchronicity frequency characterized by a sensitivity of -219.10^{-3}°.°C^{-1}. That phase decrease totally compensates the phase shift toward the high frequency observed when detecting hydrogen in absence of any temperature changes. It appears that the delay line used as a reference do not undergoes any phase shift when exposed to heated gas since the device is temperature compensated. However, the TCF of the Pd detection channel notably changes as the Pd overlay tends to lower the 1st order TCF. This behavior currently represents an obstacle

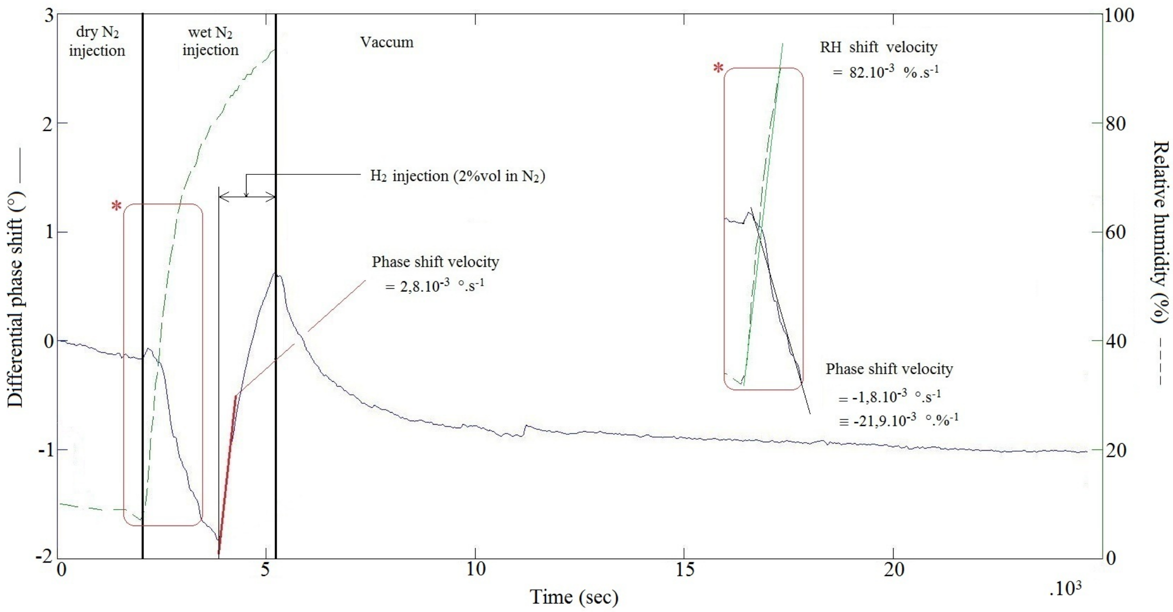

Fig. 5. Influence of humidity on the detection of hydrogen at constant room temperature (19.3±0.1°C).

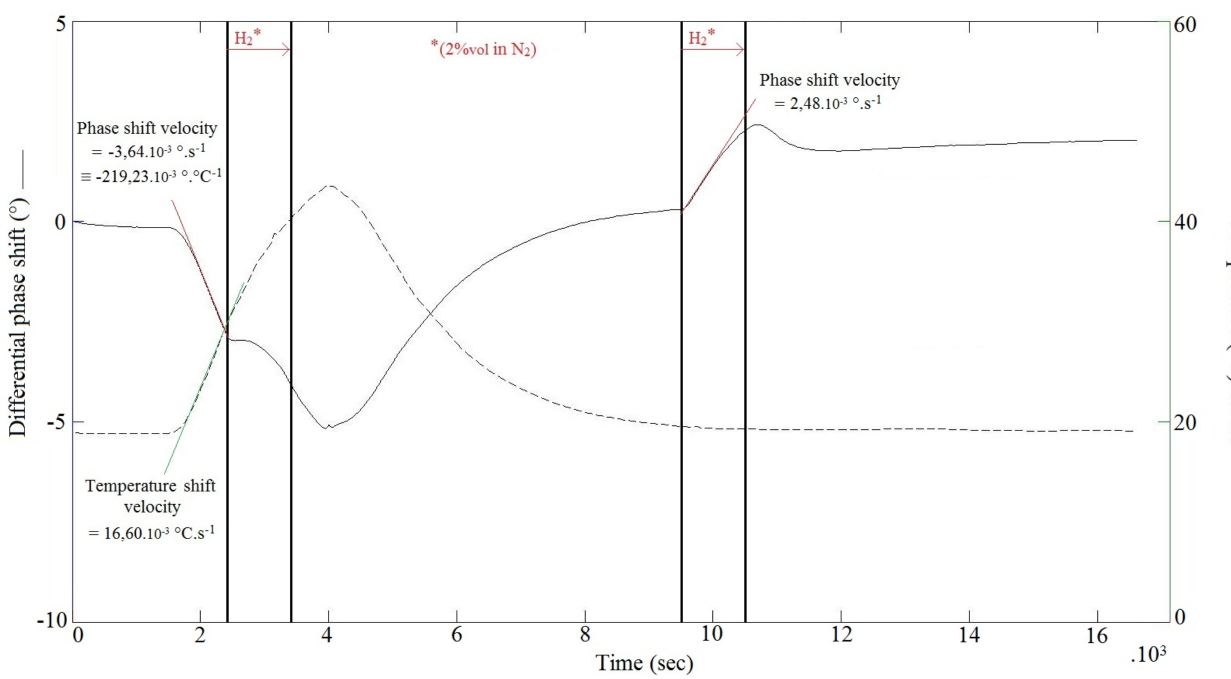

Fig. 6. Influence of temperature on the detection of hydrogen (RH in the 3-8% range).

to accurate hydrogen detection but can be avoided by the use of an appropriate reference (covered by a layer inert to hydrogen which induces the same TCF change as experienced here for the detection channel). Simulations are engaged to provide the information needed for the development of such a device. As one can see on the second part of the graph, the detection of H_2 at 2%vol in N_2 is still clearly possible considering a stable operation temperature at room conditions.

V. Conclusion and future work

In this paper, a differential SAW sensor based on Rayleigh wave on quartz has been developed and successfully tested. The sensor consist of two adjacent delay lines, one being used as a reference and the second one being functionalized with a Pd overlay, a metal known to be affected by gaseous hydrogen. The observation of specific phase shifts on the sensitive track compared to reference in presence of gaseous hydrogen using different gas carrier did assess the operation of the sensor. The use of the Pd overlay actually allows to segregate the nature of the gas inserted in the reaction cell and provides quantitative information about its composition. The impact of temperature and humidity on the sensor operation also were analyzed. Although the differential nature of the sensor is expected to reject such interferences, it appears necessary to control this parameters at very minimum. Concerning the analysis of the sensor operation itself, some work still has to be carried out even if strong convictions arise from the experiment that the main change is related to the elastic properties of the Pd film due to hydrogen absorption. The crystalline structure of the film having an effective influence on the way hydrogen interact with the metallic film, it still has to be determined in order to improve simulation accuracy of the leverage of hydrogen absorption on the SAW device response. In this optic, further work will consist in the elaboration and characterization of palladium layers with different crystalline structures. Simulation of SAW device exhibiting different sensing layers will also be carried out in order to validate the experimental observations and to predict the structure of the delay-line to use in order to improve the differential acquisition setup. These investigations are expected to enhance the performance of our sensor in terms of sensitivity and selectivity toward outer parameters such as temperature and humidity.

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