SAW sensor exploiting palladium layer properties for selective detection of hydrogen.

Meddy Vanotti, Virginie Blondeau-Patissier, Jean-Yves Rauch, David Rabus, Benjamin Mazal
FEMTO-ST Institute, Besançon, France
Email: meddy.vanotti@femto-st.fr , virginie.blondeau@femto-st.fr, jyves.rauch@femto-st.fr, david.rabus@femto-st.fr, benjamin.mazal@femto-st.fr

Sylvain Ballandras
frec|n|sys
Besançon, France
Email: sylvain.ballandras@frecnsys.fr

***Abstract*—For an increasing number of application (energy production, car industry, space, etc.), Hydrogen (H_2) appears as 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 facilities using this resource. In this paper we propose surface acoustic wave sensors 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 (Pd) overlay (exploiting H_2 absorption capabilities of this material) and the other exhibits a free path between the two interdigitated transducers. A dedicated hermetical gas test cell has been developed to test the efficiency of the sensor when exposed 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 SAW devices have been manufactured using different Palladium thicknesses and used to detect Hydrogen and to measure its concentration in the 0.25-2% range diluted in nitrogen in current atmosphere. The influence of the palladium thickness on the gas detection as well as Yttrium doping of the palladium layer on the sensor behavior are reported.**

I. Introduction

The raising shortage of fossil energy resources added to the increasing concern towards environmental issues have led to consider H_2 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 H_2 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 H_2 use and storage is still questionable. The mains improvements for such detection purpose are their sensitivity, the sensor selectivity and their reliability together with their overall size, cost reduction, energetic needs and response delay [8]. A comprehensive review of H_2 detection can be found in the literature [9] describing several different methods developed in that purpose, providing a substantial material base to try and address the above challenges. Among the possibilities, Surface Acoustic Wave (SAW) 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 close-surface thickness a few times the wavelength of the propagating acoustic wave. SAW device do exhibit limited size (less than 1 cm²) and it is a mature technology allowing for wireless use [10]. Initial works were made by D'Amico et al. [11] using the properties of Palladium (Pd) 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 H_2 detection using SAW devices [12] [13] [14] [15] [16] [17] [18] [19]. In this paper, a SAW sensor is proposed for detecting gaseous H_2 in standard environmental conditions (H_2 diluted in nitrogen under atmospheric pressure at room temperature). The proposed SAW sensor consists in two Rayleigh-wave delay lines built on Quartz, one covered 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 to gaseous H_2. 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 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. The developed device allows for identifying different concentrations of H_2 diluted in N_2 and is also able to detect H_2 in current atmosphere. In the following section, SAW sensor as well as the exploited monitoring system will be first exposed. Experimental validation of H_2 detection then is reported, with a description of the chemical test bench and detection results for various Pd layer thicknesses. An analysis of the influence of both thickness variation and Yttrium doping on H_2 adsorption and their influences on SAW propagation is proposed to provide routes for the device optimization. Indeed,

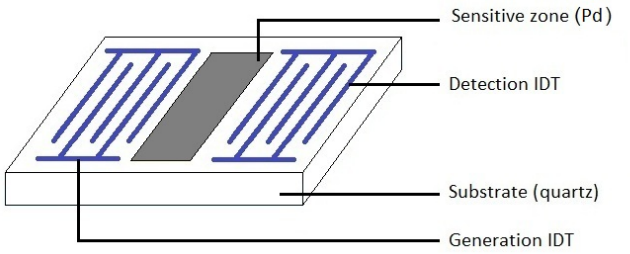

Fig. 1. Scheme of a Pd functionalized SAW delay line.

given that Yttrium atom has a larger radius than Palladium, the Yttrium doping of the Pd layer is expected to expand the Pd lattice promoting the diffusion of gaseous H_2 [21].

II. SAW SENSOR AND ASSOCIATED MONITORING SYSTEM

In this work, selective detection of H_2 at room temperature and standard pressure has been achieved using SAW delay lines exploiting temperature-compensated Rayleigh waves on AT-cut Quartz, trying to reduce as much as possible thermal contribution to the signal to detect. 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 and Y-Pd alloy films were deposited by thermal evaporation in a single run and shaped by a lift-off technique. The length of the film along the propagation path was 3mm and the corresponding thickness has been varied from 15 nm to 300 nm to test its influence on the detection conditions. The device configuration is shown in Fig. 1.

Using a network analyzer, the transfer function of the device can be easily determine and hence the phase shift induced by gas absorption has been first monitored along that way. However, the use of a dedicated electronics shown in Fig. 2 [20] has been implemented and delivers similar information. This system includes two separated phase measurement schemes: a rough characterization stage using the AD8302 phase and magnitude detector, and a high sensitivity phase measurement using dedicated phase detectors and variable gain, low noise amplifiers as presented in [20].

The sensitivity of the set-up allows for some tens milli-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. 3 illustrates the way the phase shift measurement is achieved.

III. SIMULATION RESULTS

A crucial part of the development of such a sensor consists in the improvement of its sensitivity and its response time. Simulation results are expected to provide informations on the way the sensing layer has to be designed to optimize its

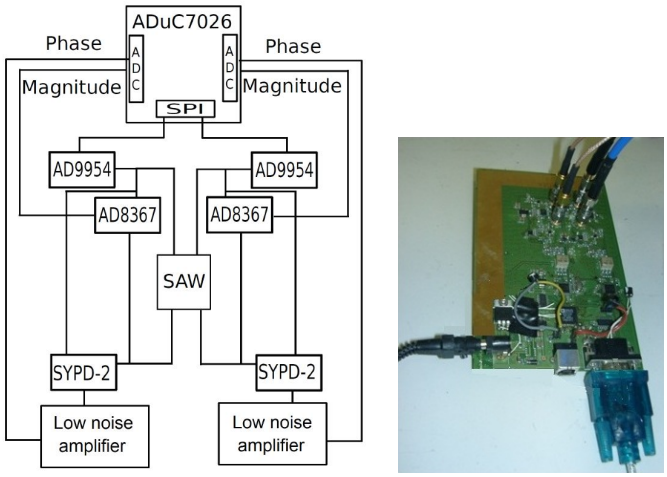

Fig. 2. Scheme and photograph of the SAW device probing card.

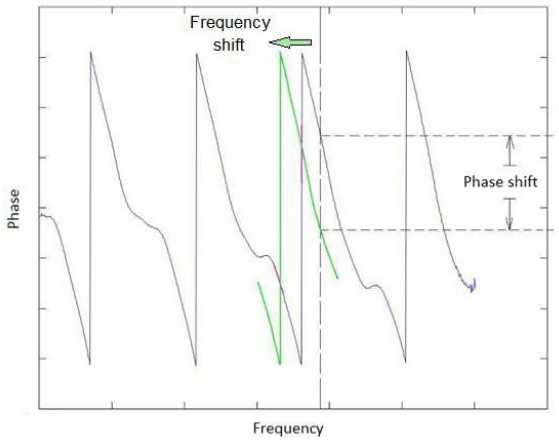

Fig. 3. Phase shift measurement principle using our dedicated instrumentation (Fig. 2).

efficiency. In that purpose, a theoretical study of the influence of the palladium layer thickness on the sensor response during the hydrogenation is reported here.

Accurate calculations have been achieved, based on a set of programs dedicated to the analysis of stratified structures used as elastic wave guides. Described in [22] [23], the calculation principle is based on the derivation of a surface or interface effective permittivity yielding numerous information about the wave propagation characteristics such as the wave velocity, the mode coupling and possible propagation losses. The model accounts for all the known linear properties of the materials composing the layered structure. These properties directly condition the accuracy of the results as no assumption is made on the device operation (provided flat interfaces). Moreover, since only devices composed of Quartz substrates have been used here, changes in electrodes conductivity are not consider as a possible origin of the observed phase velocity drift and therefore were not taken in account in the proposed analysis. Electromechanical coupling of Rayleigh waves on Quartz

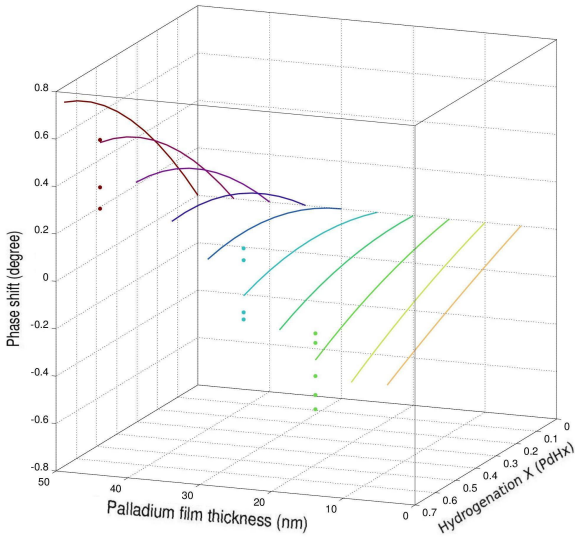

Fig. 4. Simulated phase shift of the Rayleigh wave that propagates under Pd films of different thicknesses during its hydrogenation.

substrates is actually small enough to consider conductivity changes negligible. As shown by Anisimkin and al in [24] the two main phenomena that influence the phase velocity change of elastic waves on Quartz are mass- and elastic-loading. This theoretical study takes into account the contribution of both phenomena provided some parametric adjustement. Indeed, even if Palladium is known to expands when exposed to H_2, this expansion seems to depend on the thickness of the Pd layer. Here we consider an expansion of the very thin layer close to zero because of the influence of the substrate. This assumption permits to explain the density increase during H_2 absorption that induces mass-loading observed for very thin films. It is actually shown here that the thinner the sensitive layer is the more mass-loading effects dominates. Otherwise, the damping of the transfert function in magnitude of the delay line evidences mass-loading. On an other hand, the Rayleigh wave is more affected by elasticity modification of the Pd layer than mass-loading when the Pd film thickness overcomes 25μm. One can see on Fig. 4 the theoretical phase shift during hydrogenation for different film thicknesses. These calculation are in adequacy with experimental results symbolized by the points. One can notice a difference between the shape of simulation results and the experimental ones exposed in the next section. Actually, calculations do not take into account the absorption dynamics of the hydrogen through the palladium layer. The comparison with experimental data is performed considering a total hydrogenation of the Pd layer that corresponds to an hydrogenation coefficient $X = 0.66$ on Fig. 4.

IV. Experimental results

Detection of H_2 using SAW delay lines exhibiting different Pd overlay thicknesses as functionalizing films have been achieved at room conditions. Figures. 5 and 7 present experimental results when using nitrogen as carrier gas. The

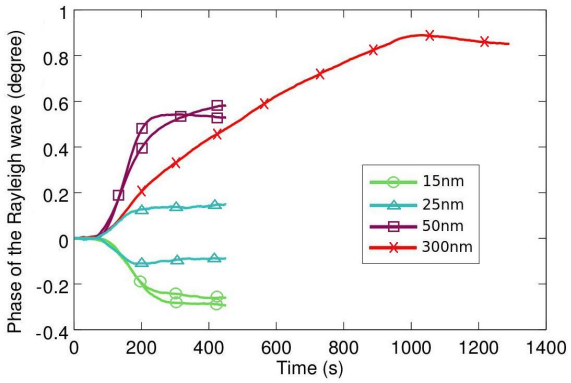

Fig. 5. Experimental Rayleigh wave phase shift induced within palladium layers of different thicknesses during hydrogenation under 2%vol H_2.

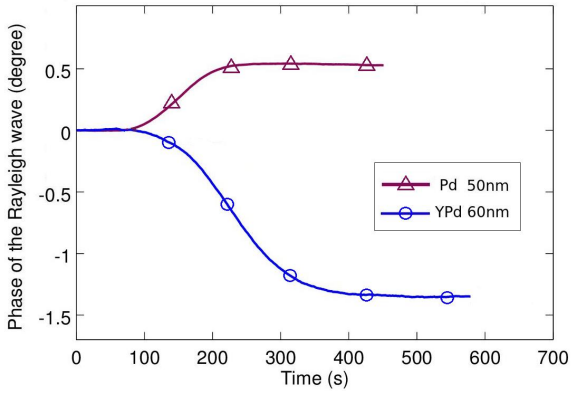

Fig. 6. Experimental Rayleigh wave phase shift induced within Pd and Y-Pd alloy sensitive layers during hydrogenation under 2%vol H_2.

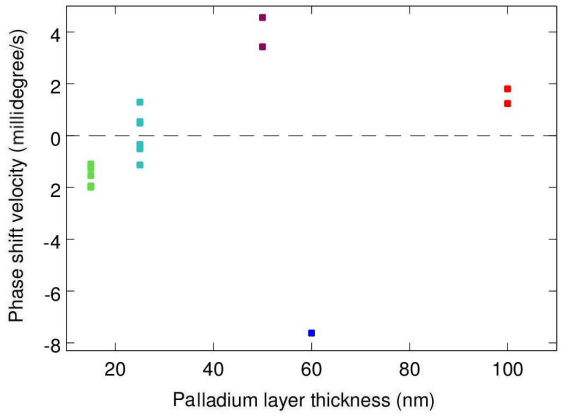

Fig. 7. Experimental delay line phase shift velocity observed for different Pd and Y-Pd film thicknesses under 2%vol. H_2 exposition

detection of about 2%vol of H_2 in N_2 at 35% RH and 20°C can be achieved with a minimum response delay of 10 seconds considering that the determination of the H_2 concentration in the melting gas is derived from the velocity of the phase shift during the exposure and not from the total phase shift at the steady state. As shown in Fig. 7, the Pd film thickness appears as a way of improving the reactivity of our sensor.

Indeed, an effective maximum phase shift velocity of 4±0.7 degree.s^{-1} has been observed for the 50nm Pd functionalized device. Contrary to the others for which the phase shift velocity doesn't exceed 2 degree.s^{-1}. One will note that the parameter to improve is the absolute value of the phase shift velocity. Actually, depending on either mass- or elastic-loading is the dominant effect occurring during the hydrogenation, a decrease or an increase of the phase will be observed. The aim of this work is to maximize the phase shift velocity irrespectively of the direction of change.

As the sensitivity and the reactivity of our device depends on the capability of the functionalizing layer to trap the surrounding Hydrogen, a chemical doping of this layer has been considered to investigate its influence on the sensor operation. Preliminary result concerning Yttrium doping is reported in Fig. 6 and 7. It shows that the Yttrium doping allows for increasing the phase shift velocity during the hydrogenation. Indeed, this velocity is -7.62 mili-degree.s^{-1} for an exposition to 2%vol H_2 in N_2 that is about twice the largest value reached with non-doped Pd Layer. In this case, mass-loading is the dominant effect that impacts the behavior of the wave. We note that this is an encouraging preliminary result that needs to be validated in terms of repeatability and reversibility.

V. Conclusion and further works

In this paper, the capability of our H_2 sensor to operate in the 0.25-2% range diluted in nitrogen has been demonstrated. The influence of thickness of the Pd film together with an Yttrium doping of the sensing layer have been studied. It finally appears that the use of a certain sensing layer thickness allows for exploiting either mass- or elastic-loading that both occure during the hydrogenation. It has been observed that the use of Pd layer that thinner than 300nm allows for minimizing the dependence of the response delay of the device on the adsorption dynamics of H_2 through Pd.

Further works will consist in correlate the delay line response and the absorption dynamics of H_2 through Pd and Y-Pd films regarding the influence of the film thickness and the Y/Pd ratio. Then we will carry on investigating how to promote a faster absorption to enhance the sensitivity and reactivity of our sensor. Physical analysis of sensitive layers during hydrogenation will be made in order to explain and improve the parametric adjustment used to simulate the behavior of our devices. The use of different thicknesses of Y-doped Pd films will also be studied in order to reinforce our knowledge concerning this promising way of trapping hydrogen.

Acknowledgment

This work was partly supported by the french RENATECH network and its FEMTO-ST technological facility.

References

[1] V. Katti, A. Debnath, S. Gadkari, S. Gupta, and V. Sahni, "Passivated thick lm catalytic type h2 sensor operating at low temperature," *Sens. Actuators B: Chem.*, vol. 84, pp. 219 – 225, 2002.

[2] C. Ramesh, N. Murugesan, M. Krishnaiah, V. Ganesan, and G. Periaswami, "Improved naon-based amperometric sensor for hydrogen in argon," *J. Solid State Electrochem.*, vol. 12, pp. 1109 – 1116, 2008.

[3] I. Simon and M. Arndt, "Thermal and gas-sensing properties of a micromachined thermal conductivity sensor for the detection of hydrogen in automotive applications," *Sens. Actuators B: Chem.*, no. 9798, pp. 104 – 108, 2002.

[4] T. Anderson, H. Wang, B. Kang, F. Ren, S. Pearton, A. Osinsky, A. Dabiran, and P. Chow, "Effect of bias voltage polarity on hydrogen sensing with algan/gan schottky diodes," *Appl. Surf. Sci.*, vol. 255, pp. 2524 – 2526, 2008.

[5] F. D. et al., "Mems-based hydrogen gas sensors," *Sens. Actuators B: Chem.*, vol. 117, pp. 10 – 16, 2006.

[6] T. Kiefer, A. Salette, L. Villanueva, and J. Brugger, "Large arrays of chemo-mechanical nanoswitches for ultralow-power hydrogen sensing," *J. Micromechn. Microeng.*, vol. 20, 2010.

[7] Z. Zhao, M. Carpenter, H. Xia, and D. Welch, "All-optical hydrogen sensor based on a high alloy content palladium thin lm," *Sens. Actuators B: Chem.*, vol. 113, pp. 532 – 538, 2006.

[8] L. Boon-Brett, J. Bousek, G. Black, P. Moretto, P. Castello, T. Hubert, and U. Banach, "Identifying performance gaps in hydrogen safety sensor technology for automotive and stationary applications," *International Journal of Hydrogen Energy*, vol. 35, no. 1, pp. 373 – 384, 2010.

[9] T. Hubert, L. Boon-Brett, G. Black, and U. Banach, "Hydrogen sensors a review," *Sensors and Actuators B: Chemical*, vol. 157, no. 2, pp. 329 – 352, 2011.

[10] T. Rétornaz, N. Chrétien, J.-M. Friedt, G. Martin, and S. Ballandras, "Time reversal: a flexible approach for identifying and measuring surface acoustic wave delay lines acting as wireless, passive sensors," *IFCS Proceeding*, 2012.

[11] A. D´Amico, A. Palma, and E. Verona, "Palladiumsurface acoustic wave interaction for hydrogen detection," *Appl. Phys. Lett.*, vol. 41, p. 300, 1982.

[12] W. P. Jakubik, M. W. Urbaczyk, S. Kochowski, and J. Bodzenta, "Bilayer structure for hydrogen detection in a surface acoustic wave sensor system," *Sensors and Actuators B: Chemical*, vol. 82, no. 23, pp. 265 – 271, 2002.

[13] W. P. Jakubik, "Hydrogen gas-sensing with bilayer structures of wo3 and pd in saw and electric systems," *Thin Solid Films*, vol. 517, no. 22, pp. 6188 – 6191, 2009.

[14] D. Phan and G. Chung, "Identifying performance gaps in hydrogen safety sensor technology for automotive and stationary applications," *Sensors and Actuators B: Chemical*, vol. 161, no. 1, pp. 341 – 348, 2012.

[15] S. Ippolito, S. Kandasamy, K. Kalantar-Zadeh, and W. Wlodarski, "Layered saw hydrogen sensor with modified tungsten trioxide selective layer," *Sensors and Actuators B: Chemical*, vol. 108, no. 12, pp. 553 – 557, 2005.

[16] A. Sadek, W. Wlodarski, K. Shin, R. Kaner, and K. Kalantar-zadeh, "A polyaniline/wo3 nanofiber composite-based zno/64 yx linbo3 saw hydrogen gas sensor," *Synthetic Metals*, vol. 158, no. 12, pp. 29 – 32, 2008.

[17] D.-T. Phan and G.-S. Chung, "Surface acoustic wave hydrogen sensors based on zno nanoparticles incorporated with a pt catalyst," *Sensors and Actuators B: Chemical*, vol. 161, no. 1, pp. 341 – 348, 2012.

[18] N. Dewan, S. Singh, K. Sreenivas, and V. Gupta, "Influence of temperature stability on the sensing properties of saw nox sensor," *Sensors and Actuators B: Chemical*, vol. 124, no. 2, pp. 329 – 335, 2007.

[19] S. Fardindoost, A. Zad, F. Rahimi, and R. Ghasempour, "Pd doped wo3 films prepared by solgel process for hydrogen sensing," *International Journal of Hydrogen Energy*, vol. 35, no. 2, pp. 854 – 860, 2010.

[20] D. Rabus, J. Friedt, S. Ballandras, G. Martin, E. Carry, and V. Blondeau-Patissier, "A high sensitivity open loop electronics for gravimetric acousticwave-based sensors," *EFTF Proceeding*, 2010.

[21] L. Yi, C. You-ping, S. Han, and Z. Gang, "Hydrogen gas sensor based on palladium and yttrium alloy ultrathin film," *American Institute of Physics*, vol. 83, 2012.

[22] A. Reinhardt, T. Pastureaud, V. Laude, and S. Ballandras, "Scattering matrix method for acoustic waves in piezoelectric, fluid, and metallic multilayers," *J. Appl. Phys.*, vol. 94, pp. 6923 – 6931, 2003.

[23] T. Pastureaud, V. Laude, and S. Ballandras, "Stable scattering-matrix method for acoustic waves in piezoelectric multilayers," *Appl. Phys. Lett.*, vol. 80, pp. 2544 – 2546, 2002.

[24] V. Anisimkin, I. Kotelyanskii, P. Verardi, and E. Verona, "Elastic properties of thin-film palladium for surface acoustic wave (saw) sensors," *Sensors and Actuators B: Chemical*, vol. 23, no. 23, pp. 203 – 208, 1995.