PdAu Based Resistive Hydrogen Sensor in Anaerobic Environment

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***Abstract*—Hydrogen is a promising gas for greenhouse gas emission reduction but also a reactive one. Thus, sensor for hydrogen detection in various atmospheres is mandatory. While leak sensors in air environments have been widely studied, only few researches have been done for hydrogen detection in anaerobic environments. In this work, the electrical resistance variation of a PdAu alloy as a sensitive film, is studied at various temperatures for hydrogen exposures in an anaerobic (N_2) environment. The $Pd_{0.8}Au_{0.2}$ alloy was deposited on a Si/SiO_2 substrate using magnetron sputtering followed by annealing at 200°C in N_2. The sensor was then tested at various temperatures for 0.3% H_2 exposure, the best operating temperature was found to be 50°C. Finally, sensor was able to detect at 50°C, concentrations from 0.3 to 3% H_2. These preliminary results are promising for further development of hydrogen sensors in anaerobic environment.**

Keywords-Hydrogen; PdAu; Resistive sensor; Anaerobic.

I. INTRODUCTION

The current context of climate change and the drive for sustainable development require the reduction of greenhouse gas emissions through the introduction of new technologies with minimal or no carbon emissions. Hydrogen gas has been identified as a very attractive energy carrier, since its combustion and its use to produce electricity generate only water as by-products [1]–[3]. As a result, a fast-growing hydrogen economy, based on the replacement of fossil fuels by hydrogen, will become a reality in several countries. Hydrogen is the lightest of chemical elements and the smallest molecule, having a great propensity to leak. Furthermore, hydrogen is a colourless, odourless, and tasteless gas, which has low auto ignition concentration in air (4 to 75%). Hence, high sensitivity hydrogen sensors, able to detect any leakage of hydrogen, are essentials wherever hydrogen is produced, transported and used. Gas pipelines are considered as a way to transport hydrogen (as a hydrogen/natural gas mixture) toward the end user, avoiding construction of new costly infrastructures and facilitate long term storage [4]–[6]. Gas impurities such as humidity and SO_2 are kept to a minimum limiting the corrosion and fragilization of pipelines [7] [8]. As a result, output gas can be considered as almost perfectly dry. While sensors for the detection of hydrogen leaks into the air have been widely studied for decades [9]–[11], no comprehensive study has yet been published on the measurement of high hydrogen concentrations in an oxygen-deprived atmosphere. To our knowledge, only two papers have focused on the anaerobic operation of hydrogen sensors [12] [13].

The main sensor technology able to measure selectively high hydrogen concentrations is Palladium (Pd) based thin film resistive sensors [10] [14]. Indeed, the Pd surface atoms decompose the adsorbed hydrogen molecules, and atomic hydrogen is easily absorbed into the Pd bulk to form Pd hydride. The absorbed hydrogen atoms cause changes in the crystal structure of the metal and an increase of electrical resistivity due to scattering of free electrons by the absorbed hydrogen atoms. However, the absorption of hydrogen causes an expansion of the Pd crystal lattice, leading to hysteresis in the sensor response and crack formation and delamination from the substrate.

One solution to avoid these serious drawbacks is to introduce, into Pd, metal atoms with an atomic radius larger than that of Pd atoms, e.g., Gold (Au) atoms. Hence, Au atoms, which occupy Pd lattice sites, slightly expand the Pd lattice, thereby reducing the strain induced energy barrier created upon hydrogen absorption, and thus hysteresis. As a result, hysteresis shrinks symmetrically and disappears about 20-25 % Au at room temperature [15] [16].

PdAu alloys were mainly used to realize optical sensors showing interesting performances [15], [17]–[19], but optical sensors are more complex and expensive than resistive sensors.

In this paper, we present preliminary results on the fabrication, characterisation and dry anaerobic sensing properties of a $Pd_{0.8}Au_{0.2}$ resistive hydrogen sensor. The paper is structured as follow: in section II we will describe the sensor fabrication and the experimental setup used for sensing characterization; then, in section III, the sensing results under various temperatures and hydrogen exposures will be discussed. Finally, in section IV, a conclusion is drawn with an insight of future work.

II. DESCRIPTION OF APPROACH AND TECHNIQUES

A. Sensor fabrication

PdAu deposition was made by radio frequency magnetron sputtering. Prior to the sensor fabrication, SiO_2/Si substrates were cleaned in an ultrasonic acetone bath followed by an alcohol and deionized water rinsing. Two cleaned substrates were placed in the sputtering chamber: one for structural characterization (sample A), the other for sensor realization (sample B). To allow rapid characterisation of hydrogen sensing, a simple basic sensor was made using a shadow mask consisting of a thin sheet of steel mechanically drilled. A picture of a typical fabricated sensor is shown in Fig. 1. The chamber was first pumped to a vacuum of 5×10^{-9} bar, then a thin titanium layer was deposited to promote adherence to the substrate as reported by several authors [20] [21]. The sputtering was performed on a Pd target partially covered by Au disks, at an argon pressure of 15×10^{-6} bar. Once deposition completed, the samples were annealed at 200°C in N_2 gas for several hours, since 200°C was found to be the best annealing temperature as described in [22]. Finally, a 120nm thick film was obtained, measurements were performed using a Dektak XT profilometer.

B. Experimental Setup for Sensor Characterization

The sensor was tested in a chamber of approximately 0.3 litre. Sensor was positioned on a heating plate with a Pt100

 ISBN: 978-1-61208-918-8

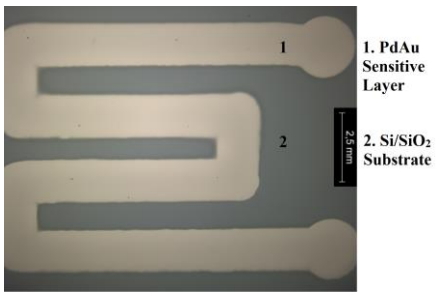

Figure 1. Optical microscope picture of a PdAu sensor made by sputtering.

(class B accuracy) temperature sensor attached next to it. The electrical resistance of the sensing film was measured by a Keithley Sourcemeter 2450 and recorded on a personal computer by a homemade software, every 0.5s. A programmable commercial gas mixing system was used for flow regulation. A continuous dry nitrogen (N_2) flow was used as baseline for every electrical measurement presented below. Hydrogen (H_2) concentrations were obtained by mixing a 3% H_2 in N_2 bottle with a pure N_2 bottle (used for baseline). Every H_2 exposure last 25 min. A 100sccm gas flow at atmospheric pressure was used on every experiment. As electrical resistance varies with temperature, only the sensor response (R_s) is calculated and presented in this work, using (1), were R_0 is the value of sensor stable base line resistance under constant temperature and pure nitrogen flow (value taken once, before any H_2 exposure), and R is the value of the sensor electrical resistance under H_2 exposure. The response and recovery time presented bellow are respectively defined as the time needed to reach 90% of the maximal R_s value for a given H_2 exposure (T_{90}) and as the time needed to return from stable R_s value to 10% of the stable baseline when hydrogen gas was stopped (T_{10}).

$$R_s\,(\%) = [(R - R_0)/R_0] \times 100 \qquad (1)$$

III. PHYSICOCHEMICAL AND ELECTRICAL CHARACTERIZATION

A. Chemical composition

Scanning Electron Microscopy (SEM) analysis was performed with a Zeiss Gemini SEM 500 ultra-high resolution Field Emission Scanning Electron Microscope (FESEM). For chemical analyses (Energy Dispersive X-ray Spectroscopy (EDS)), an Energy Dispersive Analysis of X-rays (EDAX) Octane Silicon Drift Detector (129 eV energy resolution for Manganese) was used at 15 kV, with a magnification of 10k on 3um x 3um area. Fig. 2 shows X-ray line spectra performed on sample A, with detected elements such as Palladium (Pd), Gold (Au), Silicon (Si) and Carbon (C). Four measurements were performed revealing an estimated alloy composition of 80% Pd and 20% Au.

Visual surface sample inspection is shown in Fig. 3, using SEM 100k magnification. No major variation is observed for surface morphology after annealing. Surface is composed of zones with small grains and zones of merged grains.

B. X Ray diffraction

The sample A microstructure was examined by X-ray diffraction, prior and after annealing was performed. The diagrams have been carried out with a theta-theta configuration and CuKα radiation (λ=0.154 nm) using an Empyrean diffractometer, equipped with a rapid detector,

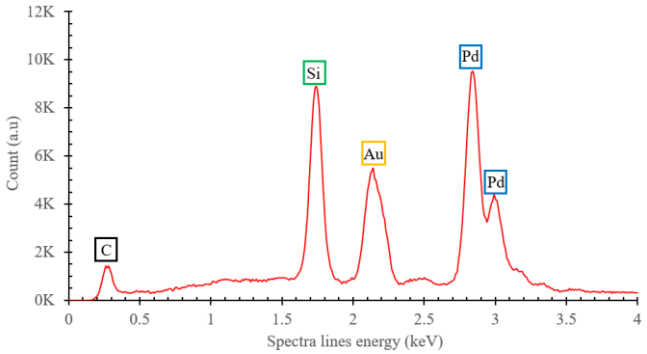

Figure 2. EDX analysis performed on sample A, for ease of reading, Au peak at 9.72 keV is not displayed.

using a 2° offset to avoid to be aligned with Si substrate. The average crystallite grain size (G_s) was estimated using the Scherrer formula (2).

$$G_s = [0.89 \times \lambda]/[\,\beta \times \cos\theta] \qquad (2)$$

Where λ is the X-ray wavelength, β the FWHM of (111) peak and θ the diffraction angle. Fig. 4 evidences that, for our sputtering parameters and film thickness, the film crystallizes mainly with a (111) preferred orientation and this trend is kept even after annealing. Small diffraction peaks are detected for the (311) and (222) planes; * symbol refers to SiO_2/Si substrate diffraction peak. Heat treatment has a noticeable impact on the microstructure with an increase of the crystallinity as (111) peak intensity grows from 13700 to almost 19400 counts. But, as suggested by Fig. 3, the grain size estimated from the Scherrer formula seems to be stable about 20 ±1 nm. Otherwise, the 2θ angle shift of the diffraction peaks is suggesting stress relaxation during the heat treatment.

C. Temperature influence on sensor response to hydrogen

Temperature of measurement is of crucial importance as it both affects sensor performance in term of response/recovery time and sensitivity. Furthermore, for practical applications, high operating temperatures are power consuming and hazardous for explosive environment [23]. Response/recovery time is usually reported to decrease with increasing temperature of measurement. Regarding sensor response to H_2 exposure, data vary. Some authors see their response dropping [24] [25], others increasing [20] [25] [26].

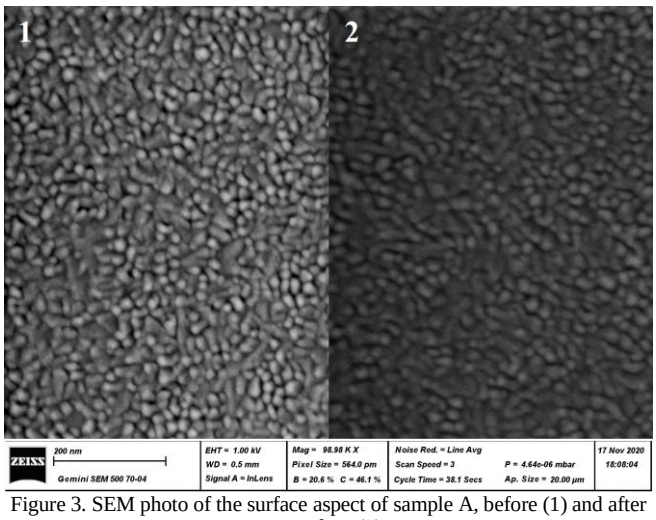

Figure 3. SEM photo of the surface aspect of sample A, before (1) and after annealing (2).

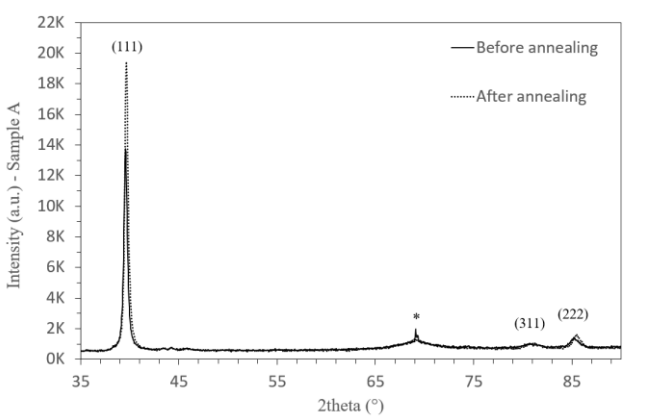

Figure 4. XRD diagram of sample A before and after annealing (λ=0.154 nm). The star indicates the trace of the Si substrate diffraction peak.

Fig. 5 shows the sensor response to 0.3% H_2 in N_2 exposure, at various temperatures. Response and recovery time as well as response amplitude are decreasing with increasing temperature. The response (T_{90}) and recovery time (T_{10}) are respectively 6min50s and 68min at 25°C, 5min40s and 17min30s at 100°C. Those results are in line with previous literature. Regarding sensor amplitude, it can be seen that upon heating, the maximal response value to 0.3% H_2 exposure diminishes and signal tends to become noisy, thus sensor will be less sensitive to H_2 variations. Yet, sensor was found to be operative for hydrogen detection in an anaerobic environment at all temperatures, 1.9% being the maximal response, obtained at 25°C and 0.5% being the lowest response, obtained at 100°C. Best operative temperature was found to be 50°C as it combines sufficient short response and recovery time (6min20s and 21min40s respectively), good sensitivity with 1.3% response toward 0.3% H_2 and a clear signal. Response and recovery time as well as sensor response are plotted for all temperatures in Fig. 6 and Fig. 7 respectively.

The sensor response dropping with increasing temperature can be explained as follows. The hydrogen absorption capacity of Pd and its alloys is linked to their Fermi level and the number of free d-states at this level [27] [28]. When increasing temperature, the number of low energy free d-sites tends to diminish as Fermi level rises, thus, more and more energy is needed for octahedral site occupation. For a given H_2 concentration, less site occupation will occur at elevated temperature, resulting in a lower response amplitude.

Finally, sensor sensitivity to others H_2 concentrations was investigated with a 1.5% and 3% H_2 exposure, results are

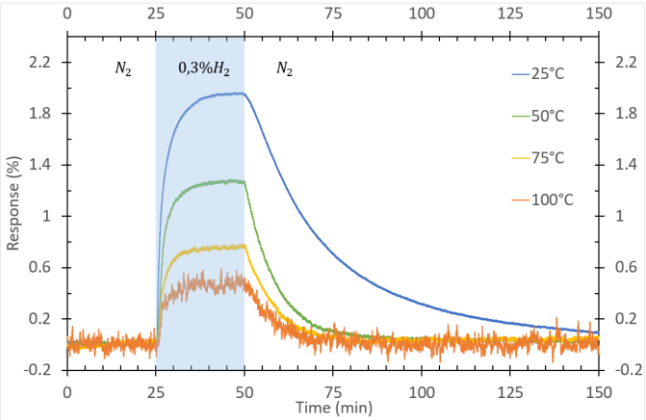

Figure 5. Sensor responses to 0.3% H_2 in N_2 at various temperatures

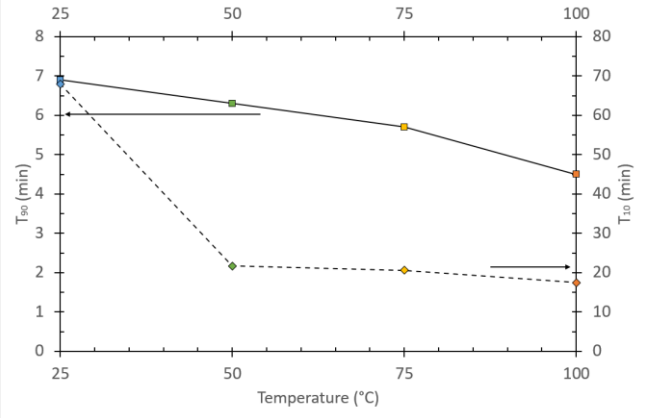

Figure 6. Plot of response (T_{90}) and recovery (T_{10}) time of sensor for 0.3% H_2 in N_2 at various temperatures.

presented in Fig. 8. Response amplitude is 2.6% for 1.5% H_2 and 3.4% for 3% H_2. Response and recovery time are respectively 6min20s and 20min20s for 1.5% H_2, 6min and 20min40s for 3% H_2. Those data show that our sensor was able to detect hydrogen from low to high concentration with a stable baseline.

Regarding response time, literature usually shows response/recovery time in the order of a few tens of seconds for the same material. An explanation for such difference with our minutes order response time could be due to : (1) thickness and width of our sensor design, simulation [29] show that expanding sensor volume largely increases reaction time; (2) low gas flow compare to cell volume. Fick's second law is usually used to ascribe the hydrogen diffusion dependence to H_2 partial pressure [29]. Thus, a long filling time results in a non-maximal kinetic of diffusion in the sensing layer. Recent work put in evidence long filling time of our cross chamber [30], validating above hypothesis.

IV. CONCLUSION AND FURTHER WORK

In summary, we have fabricated a resistive hydrogen sensor, using $Pd_{0.8}Au_{0.2}$ alloy as sensitive film, by magnetron sputtering and tested it in an anaerobic environment at different temperatures. DRX analysis shows the preferential growth along the (111) plane. Thermal treatment increased the film crystallinity, while grain size remains at 20 ±1 nm. The best operating temperature was found to be at 50°C as it combines a relative fast response and recovery time, a sufficient response amplitude to 0.3% H_2 in N_2 and a clear and exploitable signal. Sensor was also able to detect hydrogen from low (0.3%) to high concentration (3%). After this preliminary work showing PdAu alloy ability to measure hydrogen in an anaerobic atmosphere, the next steps of the study will concern :

- Characterisation of the sensitivity and selectivity
- Improving response and recovery times
- Testing the effect of different Au contents in the alloy under anaerobic atmospheres containing up to 3%H_2.

 ISBN: 978-1-61208-918-8

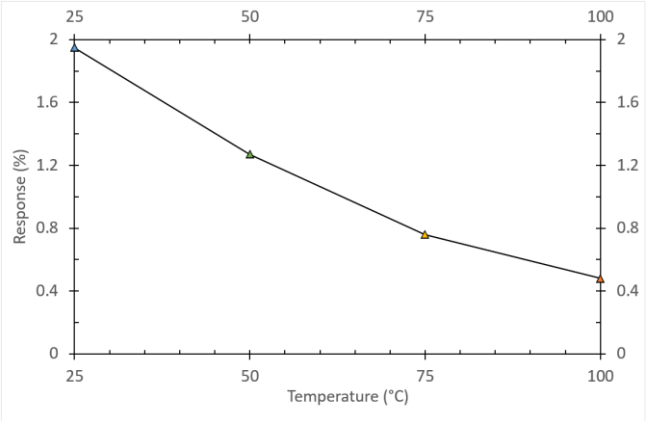

Figure 7. Plot of sensor response for 0.3% H_2 in N_2 at various temperatures.

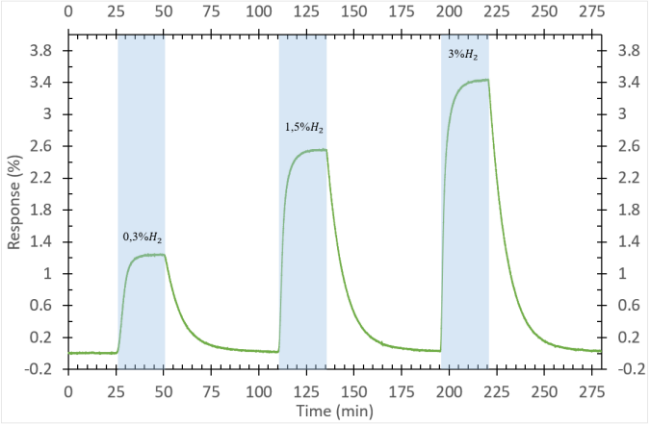

Figure 8. Sensor responses to 0.3%, 1.5% and 3% H_2 in N_2 at 50°C.

ACKNOWLEDGMENT

The authors thank Soilihi Moindjie, Jean-Jacques Furter, CP2M laboratory for their technical support and Khaoula El Ouazzani for performing XRD.
Clément Occelli would like to thank Région Sud of France and CMR Group for financial support.

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 ISBN: 978-1-61208-918-8