Pd based MEMS Hydrogen Sensors

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Abstract

Pd-based thin film hydrogen sensors are available on the market since several years. They run due to different physically switching mechanisms, such as optical switching, changing resistance or capacity of thin film structures. This article describes the capabilities of a new sensor based on a micro-electromechanical system (MEMS). These sensors utilise the volume change of Pd due to hydrogenation, thus they switch mechanically. Pd and Pd-alloy ultrathin films have been deposited on the membrane of Si-MEMS chips by magnetron sputtering. Our investigations revealed a reversible switching of MEMS-Pd-sensors without any drift. The sensor shows a fast response for hydrogen concentrations at and below the lower explosion limits up to 100%vol. hydrogen. Thus, the Pd-MEMS gas sensor fulfil the requirements of ISO 26142 for control and explosion protection of stationary facilities. For hydrogen concentrations between 1% vol. and 100% vol, the t_{90} response time is about 5 s. Besides this, Pd based sensors show low cross sensitivities and particularly no cross sensitivity to methane (CH_4) since the switching mechanism is a physical one. This type of MEMS sensor has low power consumption, is miniaturised and can be produced in a mass production at low costs by silicon technology.

Keywords: Hydrogen sensor, MEMS, palladium, response time, cross sensitivity

1 Introduction

For more than 100 years, since hydrogen has been used technically, there has been a need to detect and reliably measure hydrogen concentrations. The risk of a hazardous event involving hydrogen can be mitigated through the use of reliable, robust and accurate hydrogen safety sensors which detect hydrogen before concentrations rise to hazardous levels [1]. Hydrogen sensors have meanwhile become established in many branches of industry, e.g. in the chemical industry, in metallurgy, in mining, and for monitoring nuclear power plants. The physico-chemical principles on which these sensors are based have been well researched for many decades [2]. Because it features reversible absorption of H_2, palladium (Pd) is often used as active material in H_2 solid-state sensors [3]. Recently, researches focused on Pd-coated cantilever [4] and Pd-based MEMS resonant devices with increased sensitivity and low response time, together with high selectivity [5, 6]. When it is mixed with air, hydrogen gas is highly flammable, thus made the importance of robust and fast hydrogen safety sensors for leak detection highly apparent and by such a high demand for highly sensitive and cost-efficient H_2 gas sensors.

2 Motivation

A large number of H_2 sensors available on the market are based on a few measuring principles, including mainly electro-chemical sensors, catalytic pellistors, metal-oxide sensors, thermal conductivity sensors, and metal-oxide-semiconductor sensors. These sensors are mainly used for monitoring and explosion protection of stationary systems and meet the relevant standards. Gas sensors should fulfil requirements described in general in ISO/DIS 26142, [7], these are the following requirements:

- Measuring range up to 4% in air min,
- survivability up to 100%vol,
- detection limit 100 ppm,
- response time (t_{90}): 30s,
- recovery time (t_{10}): 60s,
- ambient temperature: -20 to +50°C,
- ambient pressure: 80-110 kPa,
- humidity: 20-80% relative humidity,
- Measurement accuracy: ±25 or 50% depending on the H_2 concentration.

Specific requirements arise for process control applications and in particular for new fields of application in the field of renewable energies [7], e.g. for monitoring fuel cells, in the automotive sector, when feeding regeneratively produced hydrogen into natural gas pipelines, as well as in medical technology for measuring H_2 -proportions in the breathing gas, eg to detect lactose intolerance [8]. These new requirements relate primarily to an extended measuring range for monitoring mobile fuel cells e.g. up to hydrogen concentrations of 100%vol, faster response times, in the automotive sector e.g. less than 1s and in the medical technology sector significantly lower detection limits of well below 100 ppm. A disadvantage of the above-mentioned commercially available H_2 sensors, especially for the new areas of application mentioned, is that all of them, with the exception of thermal conductiv (TCD) sensors, have more or less strong cross-sensitivities to other combustible gases [9]. H_2 sensors that are based on the physical switching of Pd or Pd alloys and are therefore free of cross-

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sensitivities have recently been on the market. These include optical, resistive and metal-oxide (MOS) sensors with Pd-based thin films [10]. Other new challenges relate to acceptance in the above-mentioned fields of application, since the measuring systems are used decentrally, close to the end consumer, for example in regenerative energy generation, for mobile devices and in the automotive sector and especially in medical technology. In this context, there are new requirements in terms of safety, energy consumption, miniaturization and price. Pd-based thin-film sensors also have potential in this regard, since they can be mass-produced using silicon technology. The purpose of this work is to investigate and describe the capabilities of a new sensor based on a micro-electromechanical system (MEMS). These sensors utilise the volume change of Pd due to hydrogenation, thus they switch mechanically. Pd and Pd-alloy ultrathin films have been deposited on the membrane of Si-MEMS chips by magnetron sputtering.

3 Materials and Methods

3.1 Physical properties of the Pd-H systems

The switchable physical properties are based on the effect of the atomic storage of hydrogen at interstitial sites in the metal lattice. Depending on its concentration, the hydrogen is first adsorbed when it hits the metal, dissociated and then dissolved in the metal lattice by diffusion. The α-phase, a solid solution, is formed. If a certain metal-specific hydrogen concentration is exceeded, the hydride phase (α -phase or often referred to as β -phase) is formed. This process takes place at room temperature and is reversible. In Pd, the α-phase exists at room temperatures up to a hydrogen concentration of 1.68%. In the concentration range from 1.68 to 37.6% the material system is two-phase and consists of the α and the β phase. From 37.6% is only β-phase [11]. The solubility of hydrogen in palladium decreases with increasing temperature and increases with increasing H_2 partial pressure. The α-phase is metallically conductive and opaque. The resistance increases with increasing concentration of H in the metal lattice due to electron scattering due to intercalation. The β-phase is semiconducting and transparent [12]. A change in volume occurs during the storage of hydrogen and in particular during the phase change. The lattice constant for pure Pd is 3.887 Å, up to a hydrogen content of approx. 2% it increases to 3.895 Å and for the β-phase with approx. 37.6% hydrogen the lattice constant is 0.402 Å [13]. This is associated with a volume expansion of 3.5% [11] According to the formula:

$$\Delta V/V=\Delta v/\omega\ C_H \quad (1)$$
$$\Delta a/a=1/3\ \Delta v/\omega\ CH \quad (2)$$
$$\Delta a/a=\alpha_H C_H \quad (3)$$

ΔV - Change in volume of the metal when n hydrogen atoms are dissolved
V - initial volume of the metal
Δv - characteristic change in volume per hydrogen atom, Δv is directly related to the molar volume ($V_M = \Delta vL$, L - Avogadro constant)
ω - atomic volume of a metal atom
C_H - ratio n/N, ratio of the number of hydrogen atoms to the number of metal atoms (at 50% is C_H =1)
a - lattice constant
α_H - expansion coefficient with regard to H intercalation is 0.063 for Pd
This volume change of Pd is the cause of poor adhesion of Pd thin films. Strategies to improve this consist of alloying the Pd or applying adhesion-promoting layers, are described by Fedtke et al. [14]. The hydrogen concentration in the a-phase is a function that is strictly dependent on the partial pressure. The storage of hydrogen in the metal is proportional to the square root of the hydrogen partial pressure (Sievert's law).

$$C_H = p(H_2)^{1/2}/K \quad (4)$$

$p(H_2)$ - hydrogen partial pressure
K - temperature-dependent Sieverts constant, for Pd = 0.12 at 300K.

3.2 Sensitivity and selectivity of Pd-based hydrogen sensors

Pd-based hydrogen sensors are available on the market today and are offered with different measuring principles. Resistive Pd-based sensors use the resistance of the thin films, which increases by up to 80% during the transition from the α- to β- phase as a measure of the hydrogen concentration. These sensors can measure hydrogen concentrations of up to 100%. These sensors can detect small hydrogen concentrations, they are based on the fact that the metallic α-phase changes its resistance with increasing hydrogen storage. **Table 1** shows an overview of the principles and measuring ranges of commercially available Pd-based hydrogen sensors.

Table 1 Overview of Pd-based hydrogen sensors available on the market [10]

Manufacturer	Measuring principle	Measuring range
H_2 scan	resistive	0,5-100%
H_2 scan	capacitive	15 ppm-1%
Makel Engineering	resistive	0,1-100%
Applied Nanotech	resonance	100ppm-5%

Information on the sensitivity and response time of Pd-based sensor systems in peer-reviewed specialist journals, report that the response times of less than 3s are not achieved. Response time is inversely proportional to hydrogen concentration, the smaller the concentration, the slower the sensor. For small concentrations between 10 and 100 ppm, Lim [15] reports between 2min to 30s response time. Self-supporting nanoscale Pd/C nanowires produced using microsystems technology were investigated here.

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The sensitivity of hydrogen sensors is a very important parameter and specification of the minimum hydrogen concentration detectible, or the lower detection limit, is a convenient indication of a sensor's ability to detect low concentrations [1]. With regard to the lower detection limit, it is consistently reported that nanoscale layer thicknesses and crystallite sizes as well as nanoscale structured carrier materials lead to higher sensitivity: Su et al. [16] report on resistive measurements on CNT-supported nanoscale Pd structures and reach 200 ppm as the lower detection limit. Structures supported by graphene are reported by Panday et al. [17] and also show a minimum detection concentration of 200 ppm in resistive measurements. The response times in both reports are several minutes. A systematic study of nanoscale Pd structures is shown by Noh et al. [18]. 2-D palladium thin films, 1-D (nanowire) sensor structures and nanoparticles (0-D) are examined in resistive measurements. It is shown that the more nanoscale the structures, the shorter the response time. Minimum detection limits of 100 ppm and response times between 10 and 30s are achieved. Investigations of the selectivity of Pd-based sensors in international trade journals unanimously show that Pd-based H_2 sensor structures, regardless of the measuring principle, do not exhibit any cross-sensitivities to other gases relevant to the above-mentioned applications. Comparative studies of commercially available hydrogen sensors are e.g. by Palmisano et al. [9] has been carried out. Accordingly, Pd thin-film sensors do not show any cross-sensitivity to 1%vol. CH_4, CO_2 and 50 ppm CO. Panday et al. [17] show resistive measurements on graphene-supported Pd nano thin films that there is no cross-sensitivity to CO, ethanol and toluene.

3.3 MEMS based hydrogen sensors

Micro-electromechanical sensor structures for detecting hydrogen physically use the volume change of Pd or Pd alloys when hydrogen is stored. The measurement technique for detecting the change in volume can vary. Baselt et al. [19] report on a micro-cantilever which, like a bimetallic strip, is coated with Pd on one side and deforms under the influence of H_2. This deformation is measured capacitively and allows the detection of 1000 ppm to 100%vol. hydrogen. a response time of 90s is specified for 1%vol. by volume of hydrogen. Gurusamy et al. [20] also describe a microcantilever. 50 ppm H_2 can be reliably detected by optical reading of the deformation of the cantilever. Lee et.al [21] describe design proposals for so-called nanogap-based sensors. They are based on resistive brasses on Pb nanostructures, which percolate when they expand in volume and thus become more conductive. For a simple on-off arrangement, it was shown that 100 ppm H_2 can be reliably detected.

In this work commercially available MEMS pressure sensors were coated with Pd/Au thin films (100 nm, magnetron sputtering with patchwork target). **Figure 1** shows a schematic diagram. The MEMS pressure sensors are based on the piezoresistive properties of silicon. Resistance structures in the form of a Wheatstone bridge are detuned when the Si membrane deforms.

MEMS pressure sensors are mass-produced using silicon technology. The output signal of the MEMS sensor is used in the following figures as a measure of the hydrogen concentration.

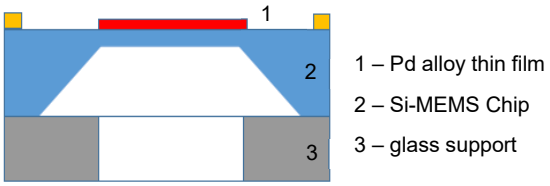

Figure 1 Sensor principle of a Pd modified MEMS sensor

3.4 Methodology for Sensor preparation

The device has been fabricated following a lithographic microfabrication process. Pd and Pd-alloy ultrathin films have been deposited on the membrane of Si-MEMS chips by magnetron sputtering. Before coating the sensors are mounted in the Mask frame to hold for coating and pressure equalization. The Argon gas flow was 50 sccm/min and the pressure was 4.7 x 10^{-3} mbar. The variation of the layer thickness was realized by different power and sputtering times.The deposition parameters were 40 W for the sputtering for 10 min coating process and for 40W for 5 min for a buffer layer. The thickness and material of this buffer layer determine the stiffness of the MEMS membrane. The Pd coated MEMS chips have been bonded on widely used sensor sockets.

3.5 Measurements setup

The measurement setup (see **Figure 2**) consists of a gas flow-controller that to generate a variation of the gas flow. It consists of a control unit and two valves with 100 sccm/min for H_2 and 100 sccm/min for Air, then the gas mixture is sent through a flow cell measuring chamber where the Pb MEMS are placed in such a way as the entire socket is also inside the chamber. Supply Voltage of 5V is applied. Resistance structures in the form of a Wheatstone bridge are detuned when the Si membrane deforms. All the data are processed with the coupled PC.

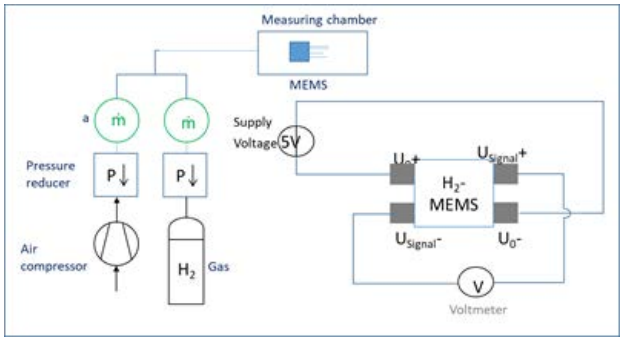

Figure 2 The measurement: - a gas flow-controller; - facility to generate a variation of the gas flow for H_2 and Air; - an example of a thin film sensor; - Supply Voltage of 5V; - Wheatstone bridge; - Voltmeter which is connected with a IEEE connector to the PC with LabView

4 Results

4.1 Sensitivity of Pd based MEMS Hydrogen Sensors

Experimental results are presented in the **Figure 3** as sensitivity versus time graph for Pd based MEMS sensors exposed to increase in H_2 concentration from 0 to 100% vol. in air.

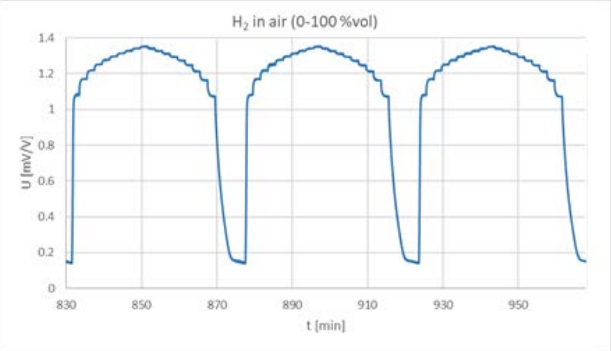

Figure 3 Supply voltage: 5V, flow rate: 100 sccm, increase in hydrogen concentration in air from 0 to 100% vol in 10% vol steps

The calibration curve for the measurements in **Figure 3** is shown in **Figure 4**. In this graph the normalized relative transmission is given over the logarithmic scale of the hydrogen concentration. It can be seen that the curve has linear behaviour.

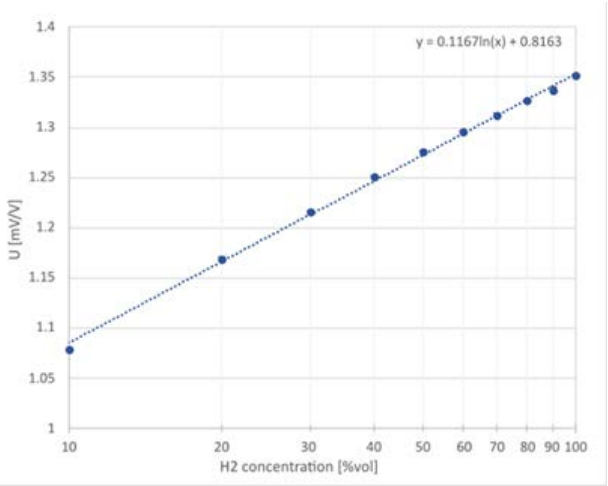

Figure 4 Logarithmic representation of the step test in **Figure 3**, interpolation points determined as the mean of 3 individual values, error bars are negligibly small

4.2 Selectivity of Pd based MEMS Hydrogen Sensors

Cross-sensitivity here refers to how sensitive a sensor is toward unwanted stimulus by another species and thus related to selectivity. Initial investigations into cross-sensitivity were carried out with the sensor structure described by exposing the sensor to CH_4-air mixtures and hydrogen air. A corresponding measurement with CH_4 concentrations in steps from 0 to 40%vol. is shown in **Figure 5**. It is clear that Pd based MEMS sensors do not exhibit any cross sensitivity to methane (CH_4). Full reset possible within a few minutes if the flow is increased.

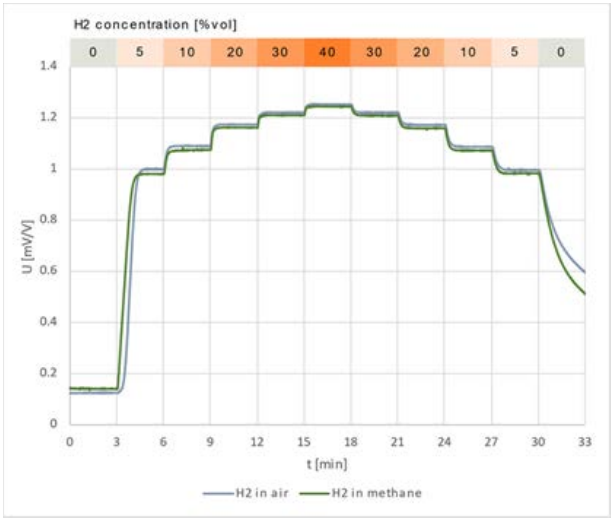

Figure 5 Supply voltage: 5V, flow: 80 sccm: increase in hydrogen concentration in air and methan from 0 to 40% vol% hydrogen

Graphic in **Figure 6** present the Pd based MEMS sensors during a time frame of 45min for a methane concentration in air up to 100% vol. First step is formed at 0,3 mV/V for 20% CH_4 concentration. A stable signal course with a constant signal level can be seen., as proving that the Methan concentration do not have any influence to the Pd based MEMS sensors reaction.

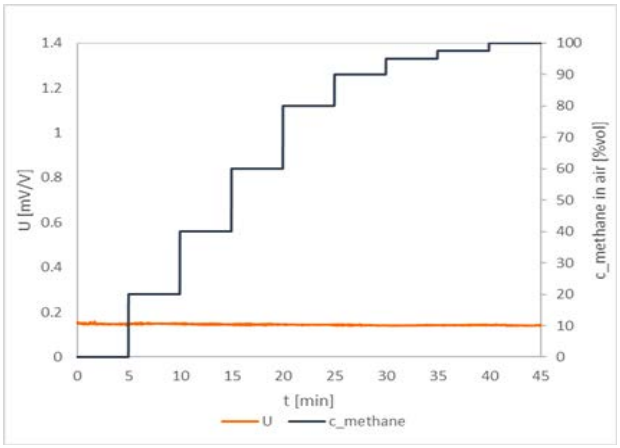

Figure 6 Supply voltage: 5V, flow rate 80 sccm : increase in methan concentration in air from 0 to 100% vol%

4.3 Response time of Pd based MEMS Hydrogen Sensors

One of the most challenging targets to meet is the sensor response time, but also one of the most obvious ones to rationalize why it is important from a safety perspective. Sensors property to respond to the presence of hydrogen it is imperative, as the sensors must respond and alert quickly to the presence of hydrogen in air. Response time (t_{90}) is expressed as the time interval between the instantaneous variation from clean air to a hydrogen gas mixture and the

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time when the sensor response reaches 90% of the final (maximum) indication [1].
The Pd based MEMS sensor shows a fast response for hydrogen concentrations at and below the lower explosion limits up to 100% hydrogen. For hydrogen concentrations between 1% and 100%, the t_{90} response time is about 5s. The response time for small concentrations below 5000 ppm is larger than 30s, it is about some minutes for concentrations in the 100 ppm range. The recovery time (t_{10}) is expressed as the time interval between the instantaneous variation from hydrogen gas mixture to clean air and the time when the sensor response reaches 10% of the initial (maximum) indication [1].
Figure 7 shows several measurement cycles with changing H_2 concentrations between 1 and 10 vol% in air, measured with the Pd-modified MEMS sensor structure. Measurements were conducted with test gas 10% H_2 in N_2, no absolute response times was observed as it depends on the flow rate, volume of the measuring chamber, mixing of the gases. The response time t_{90} is a few seconds in each case, when jumping from 1 to 10 vol% hydrogen in air the t_{90} time is 5s.

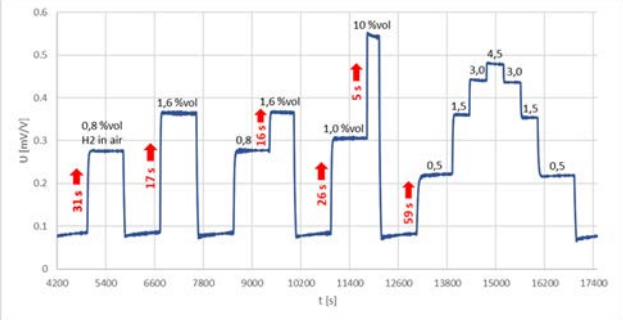

Figure 7 Supply voltage 5V, flow rate 100 sccm, measurements with test gas 10% H_2 in N_2.

Figure 8 shows a measurement cycle over 4 hours with a change in the H_2 concentration from 0 to 1000 ppm, flow rate 100 sccm, test gas 1000ppm H_2 in N_2. The measurements were carried out at 20°C and 45°C.

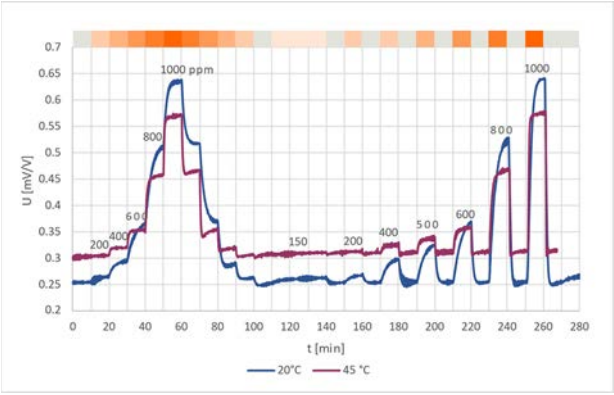

Figure 8 Supply voltage 5V, flow rate 100 sccm, test gas 1000 sccm H_2 in air, temperature 20°C and 45°C

The Blue line corresponds to measurements at 25 ^{0}C and it can be observed that it is more sensitive to lower and higher values, from 0 to 1000ppm, while the red line has a faster response.

5 Discussion

The developed sensor shows a fast response time (5s), a high selectivity to hydrogen, and a high sensitivity up to the Lower Explosive Limit (LEL). Experimental findings emphasise that, Pd based MEMS Hydrogen Sensors switch mechanically, because they utilise the volume change of Pd due to hydrogenation. Magnetron sputtering technique was used to deposit Pd and Pd-alloy ultrathin films on the membrane of Si-MEMS chips. The measurement results presented show that the sensory properties of Pd can be explained very well by physical properties of the Pd-H system. Under Hydrogen exposure, the deformation of the Si-Membrane occur and cause a resistance change in a Wheatstone bridge structure in the piezoelectric Si-MEMS. The absorption of hydrogen by Pd is reversible, it follows the external partial pressure in the sample gas (Sievert's law). The hydrogen initially adsorbed on the surface diffuses into the metal lattice. The driving force is the concentration gradient; an equilibrium concentration of H atoms in the metal lattice is established, which corresponds to the phase equilibrium. Experimental investigations revealed a reversible switching of MEMS-Pd-sensors without any drift. The sensor shows a fast response for hydrogen concentrations at and below the lower explosion limits up to 100% vol. hydrogen. Thus, the Pd-MEMS gas sensor fulfil the requirements of ISO/DIS 26142 [7] for control and explosion protection of stationary facilities. For hydrogen concentrations between 1%vol. and 100%vol, the t_{90} response time is about 5s. The response time for small concentrations below 5000 ppm is larger than 30s, it is about some minutes for concentrations in the 100 ppm range; however, this is in agreement with data from literature, which reveal, that the response time increases for low hydrogen concentrations due to the diffusion driven process. Besides this, Pd based sensors show low cross sensitivities and particularly no cross sensitivity to methane (CH_4) since the switching mechanism is a physical one.

6 Conclusion

The purpose of this work has been to demonstrate that the Pd-based MEMS sensors can reliably measure hydrogen concentrations from 0.1 to 100% vol. and have potential for new fields of application, since they are based on the physical switching of Pd at room temperature. Results show new potentials for hydrogen sensor applications like new application fields for insitu control of hydrogen concentrations. Pd-based MEMS systems have short response times of a few seconds in the concentration range 1-100%vol, this fact make them suitable for applications in high hydrogen concentrations as well as in case of low hydrogen concentrations. Applications for processes working in high hydrogen concentrations of up to 100%vol, such as in metallurgy, for fuel cells, or chemical process engineering. Applications for process control at low hydrogen concentrations, widely below the explosive limit, the new sensor concept particularly show potentials because of their low cross sensitivity. The relatively long response times

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described would be acceptable in application fields, where hydrogen concentrations are fare below the explosion limits, and however could be improved by further development, particularly by nano strategies.
The most interesting application potential field for the MEMS hydrogen sensor is the injection of regenerative produced hydrogen into the natural gas system. It was demonstrated that the sensors have no cross sensitivity to methane and this type of Pd based MEMS Hydrogen Sensors has low power consumption, is miniaturised and can be produced in a mass production at low costs by silicon technology.

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