TRENDS IN GAS SENSOR DEVELOPMENT FOR HYDROGEN SAFETY

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Abstract

Gas sensors are applied for facilitating the safe use of hydrogen in, for example, fuel cell and hydrogen fuelled vehicles. New sensor developments, aimed at meeting the increasingly stringent performance requirements in emerging applications are presented based on in-house technical developments and a literature study. The strategy of combining different detection principles, i.e. sensors based on electrochemical cells, semiconductors or field effects in combination with thermal conductivity sensor or catalytic combustion elements, in one new measuring system is reported. This extends the dynamic measuring range of the sensor while improving sensor reliability to achieve higher safety integrity through diverse redundancy. The application of new nanoscaled materials, nano wires, carbon tubes and graphene as well as the improvements in electronic components of field-effect, resistive-type and optical systems are evaluated in view of key operating parameters such as sensor response time, low energy consumption and low working temperature.

1.0 INTRODUCTION

Fuel cell systems, usually consisting of gas preparation and supply modules, pipes, connections, valves as well as a fuel cell stack, are susceptible to hydrogen leakages. Hence, there is a strong need to monitor and check the environment of the fuel cells for traces of leaked hydrogen. In addition, monitoring of the exhaust duct, especially the waste air duct is necessary. Membrane leakages as well as potentially explosive H_2-O_2 gas mixtures should be detected by the measurement of hydrogen in the waste air duct. In most existing applications monitoring of the single cell voltage is used to indicate possible membrane leakages. Sensors for temperature, pressure flow and humidity are used for control functions. In addition to system design measures e.g. redundant provision of shutoff and safety valves, hydrogen sensors can also contribute to the safety of the system. Different sensing technologies are employed to detect hydrogen. Classification of hydrogen sensors based on a range of technologies including catalytic combustion, thermal conductivity, work function based, mechanical effects and optical effects has been established and reviewed by Hübert [1]. A market analysis shows a wide selection of highly qualified commercially available hydrogen sensors [2]. However it has been shown that not all sensor performance requirements can be fulfilled for specific applications by any individual product. Therefore a lot of research is on-going to develop new sensing materials and to improve and optimise various elements of established hydrogen sensor types. We give an overview on new commercial available sensors and upcoming sensors under development using new materials or novel technologies. The presented results on scientific activities are based on a literature review performed using web of science in the time range from 2010 to 03/2013 which gave more than 500 publications.

2.0 REQUIREMENTS ON HYDROGEN SAFETY SENSORS

Hydrogen sensors are by no means 'new' devices as they have been used for decades in industrial environments under highly controlled and monitored conditions. As the use of hydrogen becomes increasingly commonplace in the emerging hydrogen economy, hydrogen safety sensors will become widespread in different applications under various working conditions. The US Department of Energy has set a number of target performance specifications for hydrogen safety sensors. Similarly end-users have specific requirements not only in terms of sensor analytical performance but also with respect to maintenance and calibration intervals, power consumption and lifetime. The various requirements can be summarised as follows [1, 3]:

- indication of hydrogen concentration in the range 0.01 - 10 %[1] (safety) or 1 - 100 % (fuel cells)
- safe performance, i.e. explosion proof sensor design and protective housing
- reliable response with sufficient accuracy and sensitivity (uncertainty 5 - 10 % of signal)
- stable signal with low noise
- robustness including low sensitivity to environmental parameters such as:
    - temperature (-30 to 80 °C (safety), -70 to 150 °C (fuel cells),
    - pressure (80 to 110 kPa)
    - relative humidity (10 to 98 %),
- gas flow rate independence,
- mechanical robustness
- fast response and recovery time (<1 s)
- low cross sensitivity (e.g. hydrocarbons, CO, H_2S)
- long life time (>5 years)
- low power consumption (<100 mW)
- low cost (<100 USD per system)
- small size
- simple operation and maintenance with long service interval
- validated and certifiable according to international standards.
- simple system integration and interface

Furthermore specific requirements on sensor performance and functional safety according to international standards have to be fulfilled to ensure a reliable and safe use [4-9].

3.0 NEW COMMERCIALLY AVAILABLE SENSORS

Several studies on commercial off the shelf (COTS) hydrogen sensors have demonstrated the inability of any one hydrogen sensing technology to meet all the performance requirements expected by customers in the wide variety of possible applications [2]. For this reason hydrogen sensor developers and manufacturers are pursing efforts to optimise their detection technology in addition to investigating novel ways to combine different sensing technologies in one detection device. In this section a number of commercial hydrogen sensors, which are new to the market, are reported highlighting innovative aspects of their design and performance data provided by the manufacturers.

3.1 Certified hydrogen detector for H_2 refilling stations

The new gas detector series, **SMART S-SS,** is designed by Sensitron S.r.l. to meet with the toughest industrial requirements, allowing monitoring of hydrogen also in harsh environments. The detector is equipped with a single sensor technology (catalytic combustion or electrochemical cell) and has a single 4-20 mA 3-wires output or 3 relay outputs, and RS485 serial communication Modbus. Optional HART communication interface with 2 relay output can be offered. It offers an 8 digits back-lit display and 5 mode status LED‘s for the gas concentration reading and feature non-intrusive

[1] The content of gases is always given as a volume fraction in per cent.

calibration for an accurate and easy adjustment either via Hall-effect switches or IrDA interface and keypad, without opening the instrument and declassifying the area (see Fig. 1).

Figure 1. Certified detector (SMART S), dual sensor module (Cyber Genius)
and ATEX/IEC Ex certified head transmitter

The **Cyber Genius** is a sensor module that combines the two technologies of electrochemical cell and pellistors in one single device exploiting the advantages of both technologies in terms of response time and measuring ranges with an added benefit of a detection backup for advanced security and reliability. This sensor module can be used in SMART S-IR and in other detector solutions such as compact transmitter in certified ATEX/IEC Ex heads. Two types of sensor heads are available, the NET2X with the sensor and electronics sealed inside or the NET3X where the sensor and electronics are replaceable.
In a continuous endeavour to increase the security and reliability of their gas sensing systems, Sensitron have put great efforts into developing products that meet high functional safety requirements according to the standards EN 50402 and IEC 61508 part 1 to 7. This includes the correct operation of the device in response to the inputs and safe management of problems that can occur due to operator errors, hardware failures and environmental changes in order to minimise risks to the operator's health. The devices mentioned above have been developed in order to meet the requirements for SIL 2 regarding the hardware and SIL3 for the software. Further, as first Italian manufacturer of gas detection systems, Sensitron S.r.l. obtained for the SMART S detector the ATEX II2G performance certification according to the IEC/EN60079-29-1 with specific approval for hydrogen gas and TŰV improvement. This is a legal expression for the high precision, reliability and robustness of the detector.

3.2 Selective hydrogen sensor with a low response time for fuel cell systems

One approach for the reliable measurement or rather detection of hydrogen in the wide target range from a few ppm up to several % is the combination of two suitable sensing principles including a sophisticated data evaluation within one sensing system. The sensor elements of the **H_2-Semicon®**-Detector of UST Umweltsensortechnik GmbH comprise a semiconductor gas sensor based on SnO_2 and a thermal conductivity sensor that, in an innovative combination, complement each other in a diverse redundancy gas detection device. The signals of both sensors are evaluated in a conjoint unit and combined via a weighting function. Safety-related functions like the recognition and signalling of failure states and error handling procedures even during the measurement are integrated in the module. A schematic of the sensor system is given in Fig. 2. The H_2-Semicon® sensor system offers highly selective measurement of hydrogen concentrations in a continuous range from 0…4 % (optional up to 100 %) (see Figure 3); response time <1 s (t_{60} at 5.000 ppm H_2); high zero-point stability (avoidance of false alarms); humidity resistant from dry air up to condensation and a wide operating temperature range (-20°C to +80°C). Continuous temperature measurement and corresponding sensor calibration ensures almost no temperature dependency of the measurement signal. The system delivers an analogue interface (0.5 V to 5 V, linear) and digital interface (RS232/CAN-Bus) for data logging and external calibration; miniaturized and modular housing concept that is adaptable to application-specific needs supporting a gas feed by pipe integration (tee connector) or diffusion.

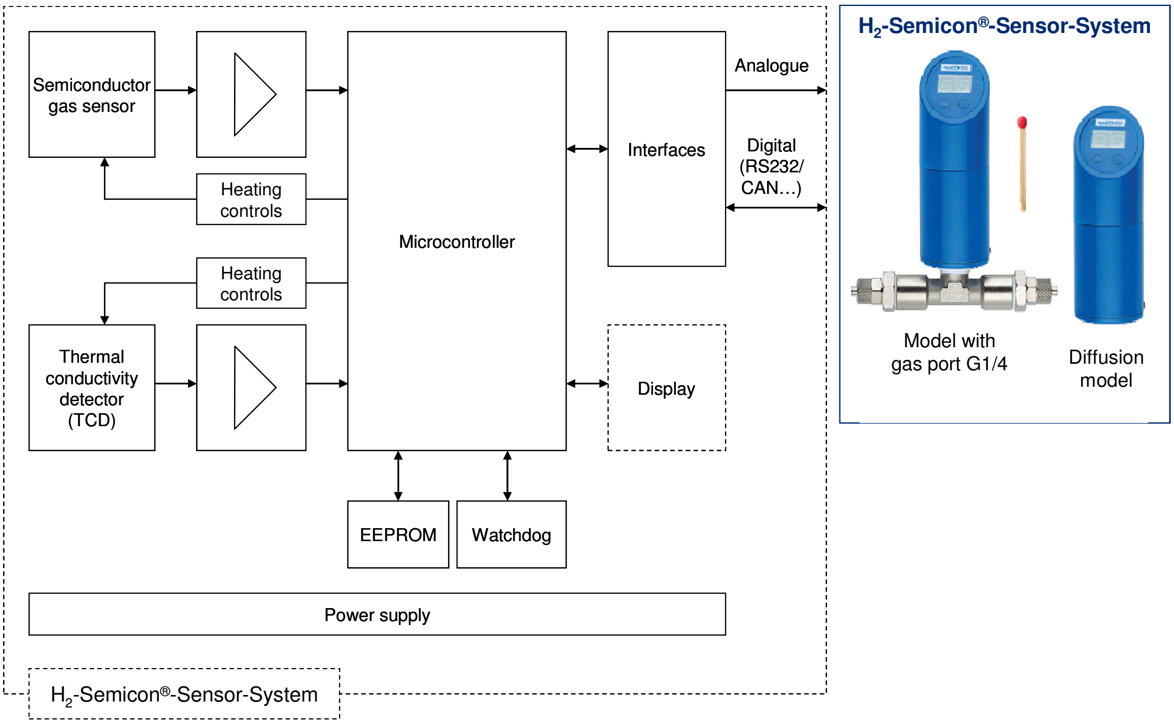

Figure 2. Schema of H_2-Semicon®-Sensor System

Due to the implemented diverse redundancy in combination with high sensitivity, selectivity and stability as well as the safety-related functions, the H_2-Semicon® sensor system is particularly suitable for applications with high safety-related requirements and can be certified in dependence of SIL IEC 61508 and according to EN50194 (see Fig. 3 and 4). The sensor may be used for leakage monitoring in fuel cell systems, monitoring of chemical processes and equipment in the industrial or facility sector as well as the mobile and stationary gas leakage detection. The H_2-Semicon® sensor system was successfully tested and evaluated under operating condition of fuel cell systems.

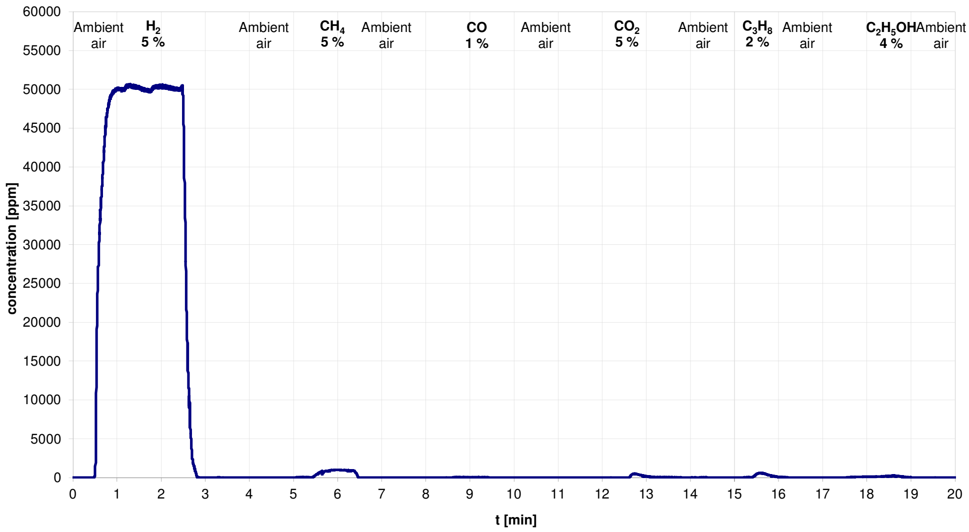

Figure 3. Low cross sensitivity of H_2-Semicon®-Sensor System to various gaseous species

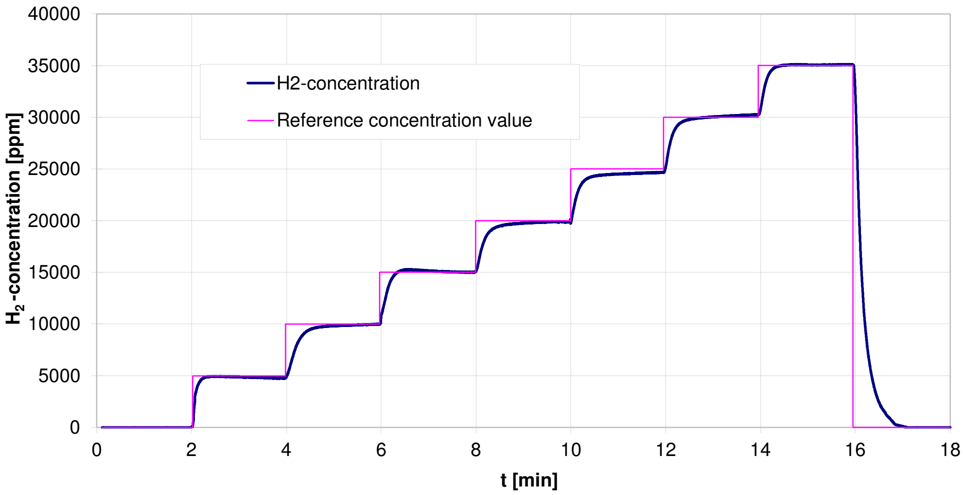

Figure 4. Indication of H2-Semicon®-Sensor System and gradual increasing reference concentration

3.3 Field effect sensor technology for hydrogen

A field effect transistor, operating in a diode-coupled mode, is employed by AppliedSensor GmbH in their hydrogen detection device. Absorption of hydrogen at the catalytic metal gate effects a change in voltage. Combination with a temperature sensor, a heater and a thermal conductivity sensor element improves sensor performance and widens the measuring range. The silicon technology offers a low cost sensor component with superior sensor properties. Thus two new sensors designed for ATEX 100a, Zone 2, **HLS-440P**, for harsh environment such as fuel cell exhausts to measure hydrogen in the range of 0 to 10 % and **HPS-100** for the measuring range to 100 % with an uncertainty of 0.5 % H_2 and 2 % are available. The response time, t_{90}, and the recovery time, t_{10}, are below 5 s. The sensors can operate in the temperature range -50 °C to 95 °C and in relative humidities up to 100 v% including condensation. The sensors have a CAN bus interface and MQS connectors and were developed in accordance to IEC 61508 (SIL2) [10].

3.4 Intelligent gas sensor for hydrogen detection

The new XEN-5310 sensor from Xensor Integration BV is a thermal conductivity type sensor which can be used for the detection and measurement of hydrogen gas in concentration ranges from 0 – 1 %, 0 – 4 % and 0 – 100 %. Temperature is measured independently allowing for compensation of any influences changes in the ambient temperature may have on the sensor response. The device is also equipped with a relative humidity sensor for compensation of humidity changes which could otherwise have a significant influence on the measurement particularly at higher temperatures and high humidities. Temperature and humidity compensation are made by means of an integrated micro-controller with the result that a reference measurement, typical of many thermal conductivity sensors, is not required. Figure 5 shows a schematic of the sensor components.
The sensor can be operated in a temperature range -20 to + 55 °C, a relative humidity range 1 to 100 % and a pressure range 0.8 to 1.2 bar. The micro-machined thermal conductivity device has a power consumption of 100 mW and a response (t_{90}) and recovery time (t_{10}) of around 1s. The device boasts a low drift of some hundreds ppm per year. Typically calibration is only required when the response deviation is between 1000 – 2000 ppm. Nevertheless periodic monitoring of the correct functioning of the sensor is advised.

Xensor's detection technology has been applied for around a decade for O_2 measurement in medical applications. Recognizing the suitability of their technology for leak detection in emerging hydrogen applications Xensor are pursuing certification of this product according to ISO 26142:2010. This standard defines the performance requirements (including accuracy, response time, stability, measuring range, selectivity and poisoning) and test methods of hydrogen sensors used to measure and monitor hydrogen concentrations in stationary applications.

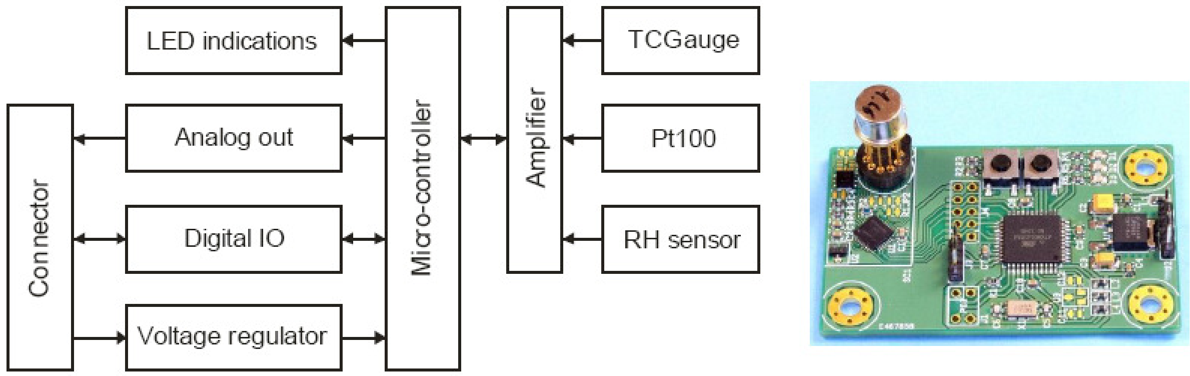

Figure 5. Thermal conductivity hydrogen sensor with temperature and relative humidity compensation

3.5 Low power consuming Schottky diode

A titania based Schottky-diode as a sensor element for hydrogen detection in the range of 0 to 4.4 % is offered by ODB-Tec&Co. KG, Germany. The sensor has a very short response time t_{90} below 2 s for a jump to 5 % H2 and also a recovery time t_{10} in the same order. The power consumption is in the range of 20 nA @100 mV [11].

3.6 Optical Hydrogen sensor system

The optical sensor detects the changes in thin films of transition metals due to hydrogen absorption and is delivered by Materion GmbH in two specifications for the measuring range of 0.1 to 4 % (**MOHS 2.2**) and an uncertainty of 10 % and for the range of 0.1 to 100 % (MOHS 3 Z) and an uncertainty of 10 to 30 %. The response time t_{90} is < 60 s. The operation temperature is -15°C to 50 °C at relative humidity of 0 % to 70 %. The sensor signal will not be interfered by saturated hydrocarbon, N_2, O_2 and inert gases.

3.7 Hydrogen leak detector

A low-cost leak detection based on a colour changing pigment (tungsten oxide) which can be precipitated as paint, spray or as a thin film, called **DeteCoat®H**, is offered. Also indicator polymer foils can be wrapped around a hydrogen gas carrying component. Using an optical readout, a wireless data transmission (RFID) is possible [12].

4.0 SENSORS UNDER DEVELOPMENT

Hydrogen sensor research is evolving and expanding rapidly. A review of the scientific literature revealed that development is progressing along four main lines, namely:

- preparation and evaluation of new hydrogen sensitive materials
- development of different types of hydrogen sensing technologies
- sensor designed for room temperature operation
- application of new techniques for mass fabrication of micro hydrogen sensors.

The most common and noteworthy research and findings are briefly reviewed in this section. The review is based on a Scopus literature search performed over the last 30 years which yielded a total of nearly 1400 publications on hydrogen sensors. Figure 6 shows the number of publications each year over the last 30 years.

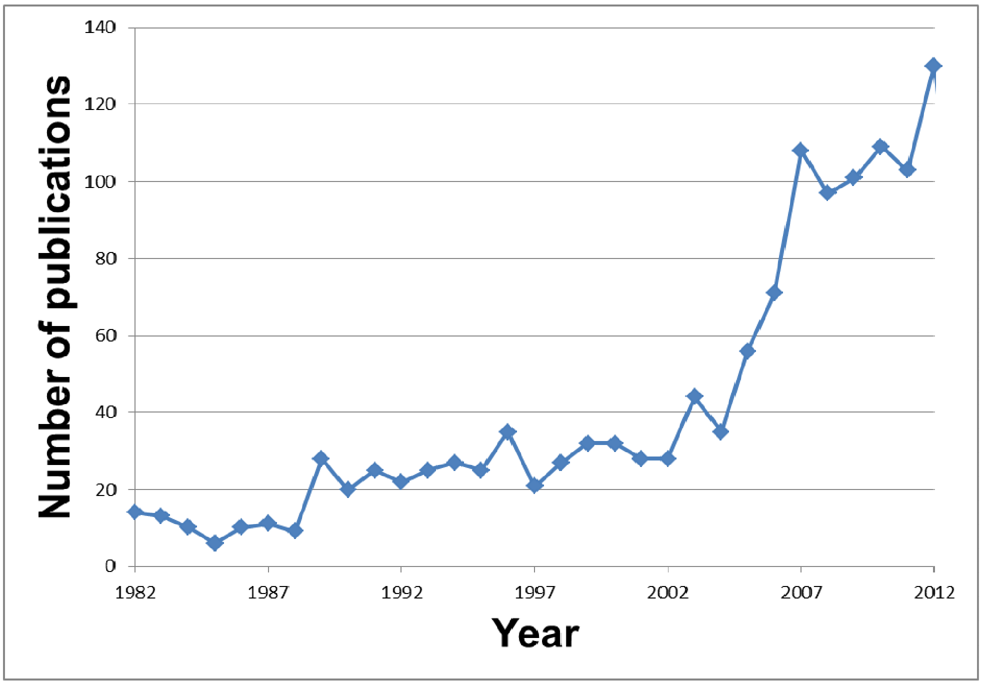

Figure 6. Number of publications on hydrogen sensors according web of science

4.1 New hydrogen sensitive materials

4.1.1 *Nano particles and nano wires*
Nanomaterials are of interest for sensor development because of their high surface area, possible increased reactivity due to the small particle size and compatibility with miniaturization of sensor elements and sensor electronics. While nanomaterials may offer possibilities to operate at room temperature, issues with slow response and long recovery times and further requirements have to be overcome.

Nano scaled carbon materials including single and multiwall carbon nano tubes (CNT), as well as two-dimensional graphene sheets - have outstanding properties due to their high aspect ratio, large surface area with respect to volume, superior chemical and thermal stability, high electrical conductivity, good heat conductance and excellent mechanical strength. It is expected that gas sensors based on CNT or graphene networked films can provide high sensitivity, fast response, good reversibility, higher resolution, selectivity by functionalization, simplified and stand-alone operation, low power consumption and low running costs. Graphitic layers, carbon nano tubes and two dimensional graphene sheets were tested alone or in combination with other substances including palladium, for hydrogen sensing mostly in resistive mode [13], [14], [15], [16].

Other new nano materials are used in resistive and work function-based sensor elements. Palladium interaction with hydrogen is the basis for hydrogen detection in platforms using palladium nanowires whose properties may overcome limitations experienced with palladium thin films [17]. Tin oxide nano rods are grown by gas phase methods (CVD, thermal evaporation) or liquid phase processes (sol-gel, hydrothermal). In a recently reported tin oxide nano rod sensor a change of resistance was already detected at room temperature at a hydrogen concentration of just 100 ppm; however a better sensitivity is obtained at 250 °C [18]. Zinc oxide nano rods and wires are also reported and were fabricated using anodized aluminium oxide nano template or were deposited by molecular beam epitaxy (MBE). ZnO nano rod arrays exhibit a high sensitivity for hydrogen in a wide concentration range from 5 to 500 ppm, as do Pd- or Pt-coated GaN and InN nano wires [19], [20]. Titania nanotubes are also used for hydrogen sensing and have been produced by anodic oxidation of titanium in hydrofluoric acid with subsequent annealing at about 500 °C resulting in pores with a diameter of 70 nm. This material can sense hydrogen in the range of 10 to 100 ppm at temperatures between 200 and 300 °C [21], [22],

[23]. Doped silicon wires or Ag-doped molybdenum oxide nanowires can be used for hydrogen detection [24] [25], [26].
Whereas most palladium-based resistive hydrogen sensors reduce conductivity when hydrogen is absorbed due to electron scattering, nano gap sensors and reversible on-off switches show an opposite behaviour. In these systems hydrogen absorption, causing palladium volume expansion, close nano gaps in the material resulting in an increase of conductivity [27].

4.1.2 *Sensor elements using porous materials*
Porous silicon is a promising material for gas sensing mainly due to the high surface to volume ratio and strong adsorption for gases. It is easy to fabricate by electrochemical anodization using a mixture of HF and ethanol in different ratios as the electrolyte solutions. Through the variation of the formation parameters, the surface morphology can be advantageously controlled. Porous silicon layers have large internal surface areas of up to 200 to 500 $m^2 \cdot cm^{-3}$, and high activities in surface reactions. Porous silicon is compatible with silicon technology and modification with catalytic palladium makes it suitable for hydrogen detection. However the distribution of Pd over the porous silicon can have a strong influence on the hydrogen sensing parameters [28]. In addition to silicon porous GaN and SiC can be prepared by an electrochemical etching process and used for hydrogen detection [29], [30].

4.2 Hydrogen sensing technologies development

4.2.1 *Sensors based on work function*
Work function based hydrogen sensors have been described and reviewed previously [1]. While not a new technology the number of sensors reported in the literature employing this technology continues to escalate. Detection is based on the change of the work function of a catalytic metal following absorption of hydrogen. Devices which can measure this change in work function, including diodes, capacitors and transistors, can be used to transform the signal into a hydrogen concentration measurement. Figure 7 illustrate the typical structure of the different types of work-function sensors being developed. Research on these sensors is focused on improvements of the hydrogen sensitive material used, sensor design optimization and elucidation of the hydrogen sensing mechanism.

Schottky diodes are the most common type of work function hydrogen sensor reported due to their simple structure and ease of fabrication [31]. They can be prepared via vapour deposition techniques requiring high vacuum and energetic electron beams. Semi conductive materials employed in diodes include Si, GaN, SiC or ZnO. Diodes based on GaN exhibit higher chemical stability and can operate at higher temperatures compared to Si-based Schottky diodes. GaN also has a wide band gap (3.4 eV) making it a promising candidate for high-power and high-frequency electronic devices including sensing diodes [32], [33]. Similarly SiC, another wide band gap semiconductor, is also suitable for high power and high frequency applications. In addition it has far superior thermal stability making it suitable for hydrogen detection in harsh environments [34], [35] however further improvements are needed concerning the availability of SiC substrates and processing technology. Nevertheless SiC is also used for hydrogen sensing in a p-n-junction diode, MOS capacitor and in field effect transistor arrangement [34].

While Pd is typically used as the catalytic metal in work function sensors a PdNi alloy has been reported in a Schottky barriers diode. The Pd ensures selectivity towards hydrogen while the Ni suppresses the irreversible phase change at higher hydrogen concentrations which occurs when pure palladium is used [36].

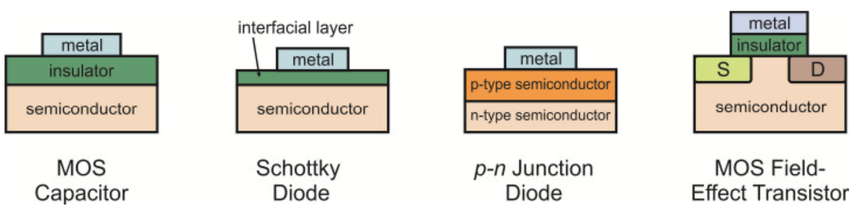

Figure 7. Schema for different field effect sensor arrangements

4.2.2 *Optical sensors systems*

Up to 20 % of all publications on hydrogen sensors describe optical sensors which detect hydrogen through a change in the optical properties of the hydrogen active material. In contrast to electrical sensors, optical fibre sensors are electrically isolated which makes them interesting candidates for operating in explosive atmosphere. There will be no risk of gas ignition since the optical detector has no electrical contacts and so cannot generate sparks. Types of optical sensors include Fibre Bragg grating [37], interferometric [38], micro mirror [39], evanescent optical fibre [40], surface plasmon resonance [41] and colorimetric technology [42]. Reviews on the widespread use of palladium in optical hydrogen sensors are given by Silva [43] and Perotton [44].

Sensors using **Bragg-grating** were prepared using different material combinations based on palladium, like Pd-Ni, Pd-Ag, Pd-Y. The alloying of palladium results in better long term stability of the thin coatings. Figure 1 in [37] shows a typical sensing arrangement for Fibre Bragg Grating.

A new fast optical fibre sensor system based on an $Ag/SiO_2/Pd$ multilayer stack for **surface plasmon resonance** is reported. The sensor employs wavelength modulation and has a response time of less than 15 s [44].

Numerous optical fibre hydrogen sensors have been developed, but most of them do not meet many of the performance specifications recommended by industries or governmental agencies. In particular, their response times are often too slow and they need to be calibrated to compensate for drift and aging effects. Nevertheless research is continuing to improve these performance aspects of optical hydrogen sensors [45].

4.3 Sensors working near room temperature

The requirement for low power consumption can be met, to a certain degree, by sensors operating at room temperature. Room temperature operation is also an important aspect to achieve intrinsically safe performance in potentially hazardous situations. Room temperature operations can be realized in different ways depending on the type of sensor and sensing material [46]. Some sensor types working at room temperature are already known for long time; new achievements are in the area of resistive and field effect-based sensors:

a) Amperometric hydrogen sensors possessing a liquid or solid electrolyte (e.g. KOH, H_2SO_4, NAFION) and a polymer membrane (Teflon, PTFE) are working near room temperature [47]. However electrochemical sensors have a limited life time depending on converted hydrogen and need a relative electrical circuit and power supply.
b) In most cases optical sensors are operating at room temperatures. They can operate without oxygen and in explosive atmosphere and are hardly influenced by electromagnetic field. Sensor element can be separated from the electrical readout. Current developments are reviewed in chapter 4.2.2 [43].
c) Surface acoustic wave (SAW) sensors are operating with mostly with interdigital structures on a piezo electric substrate near room temperature. The sensor system needs a high effort for signal generation and output. Also temperature and cross sensitivity effects have to be depressed. A low cost variant is not available [48].
d) Since the speed of sound in hydrogen is much faster than in other atmospheric gases, via a measurement of the speed of sound at room temperature an absolute value of hydrogen concentration in the air or in other gases can be determined [49].
e) Also resistance based sensors can operate at room temperature [50]. New materials are nano crystalline palladium, nano wires or polymers like polyaniline (see chapter 4.1.1) [51], [52].
f) Work function based sensors are working at room temperature; however from time to time need short time heat impulse for refreshment [53], [11], [54].

Sensors exploring the high thermal conductivity of hydrogen are operating at ambient temperatures. However the operation principle is based on the measured heat loss from a hot body to the surrounding gas. It is obvious that a certain electric power is consumed.

Sensors based on catalytic combustion or thermoelectric effects are less suitable for ambient temperature operation.

If it is possible to overcome disadvantages of low response and recovery time or saturation effects in room temperature operating sensors, then this concept has a promising perspective. However, not only the sensor element is responsible for low energy consumption, also electronic part for data transmission, processing and data output has to be considered.

4.4 Fabrication of micro hydrogen sensors

Micro hydrogen sensors are typically fabricated from silicon and have dimensions on the micrometer scale. The ability to fabricate hydrogen sensors at this scale offer advantages in terms of performance and cost. Silicon micro-fabrication offers the potential for mass production of these devices which can drive down their manufacturing costs. Performance parameters such as response time, lower detection limit and low power consumption are significantly improved when compared with conventional hydrogen sensors [55].

Micro-hydrogen sensors have been reported for various detection technologies. Many traditional technologies are conducive to miniaturisation including thermal conductivity sensors [56], metal-oxide sensors [57] and catalytic pellistors [58]. A new micro-machined thermoelectric catalytic sensor, whose working principle is based on the Seebeck effect, reports promising results particularly in terms of lower detection limit [59]. This sensor is capable of detecting hydrogen down to a concentration of just 50 ppm with a measuring range up to a few %. Other micro-machined hydrogen sensor types include those based on a thin metal film whose resistance changes in the presence of hydrogen [60, 61]. These resistive-type sensors employ a micro-hotplate or heater to heat the metal film at low power ratings to increase hydrogen sensitivity and lower the response time to hydrogen. True micro-electromechanical system (MEMS) hydrogen sensors have also been proposed. MEMS sensors are devices which, in addition to being fabricated on a micrometer scale, involve some mechanical motion or vibration in their detection mechanism. Micro-machined MEMS cantilevers are an example of such devices [62].

Mechanical robustness remains a concern with micro-hydrogen sensors where sensor performance degradation and premature failure due to lack of physical robustness has been observed [63]. On-going analysis in this area suggests that some detection platforms, particularly thermal conductivity sensors, are more suitable for miniaturization than others [55].

5.0 SUMMARY

New COTS hydrogen sensors with superior performance metrics are presented which promise to fulfil many of the performance requirements demanded by end-users in existing and emerging hydrogen applications. The pursuance of product certification by some of the sensor manufacturers indicates the improved reliability and accuracy of these products. Use in the field will confirm their true performance under the ambient conditions of an application.

Research on new hydrogen sensing materials, development of novel sensing technologies and miniaturisation of sensor platforms which yield devices with improved performance at a lower cost is also presented. Many sensing platforms use palladium or platinum for hydrogen detection and these platforms are prone to aging effects and signal drift. Reducing the use of noble metals in sensors through miniaturization can remarkably reduce the costs of sensor elements.

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