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ICHS
International Conference on Hydrogen Safety

BAM
Bundesanstalt für Materialforschung und -prüfung

TRENDS IN GAS SENSOR DEVELOPMENT FOR HYDROGEN SAFETY

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Outline

- Motivation & Objectives
- Requirements on hydrogen sensors
- New commercially available sensors
- Sensors under development
- Summary

Motivation & Objectives

National Aeronautics and Space Administration

SAFETY STANDARD FOR HYDROGEN AND HYDROGEN SYSTEMS

Guidelines for Hydrogen System Design, Materials Selection, Operations, Storage, and Transportation

"Hydrogen gas is colorless and odorless and normally not detectable by human senses. Means shall be provided for detecting the presence of hydrogen in all areas in which leaks, spills, or hazardous accumulations may occur."

- A short overview, not for sensor specialists
- State-of-the-art
- Inspire the use of sensors

Motivation & Objectives

Royal British Museum Victoria, B.C.

Requirements on hydrogen sensors

(1) indication range 0.01 - 10 % hydrogen (safety) or 1 - 100 % (fuel cells)
(2) safe performance, i.e. explosion proof sensor design and protective housing
(3) reliable response, sufficient accuracy, sensitivity (uncertainty 5 - 10 % of signal)
(4) stable signal with low noise
(5) robustness including low sensitivity to environmental parameters such as:

- (5a) temperature (-30 to 80 °C (safety), -70 to 150 °C (fuel cells),
- (5b) pressure (80 to 110 kPa)
- (5c) relative humidity (10 to 98 %, condensation),
- (5d) gas flow rate independence,
- (5f) mechanical robustness

(6) fast response and recovery time (< 1 s)
(7) low cross sensitivity (e.g. hydrocarbons, CO, H_2S)
(8) long life time (> 5 years)
(9) low power consumption (< 100 mW)
(10) low cost (<100 USD per system)
(11) small size
(12) simple operation and maintenance with long service interval
(13) validated and certifiable according to international standards
(14) simple system integration and interface

…. and ??

New commercially available sensors

Classification on hydrogen sensors

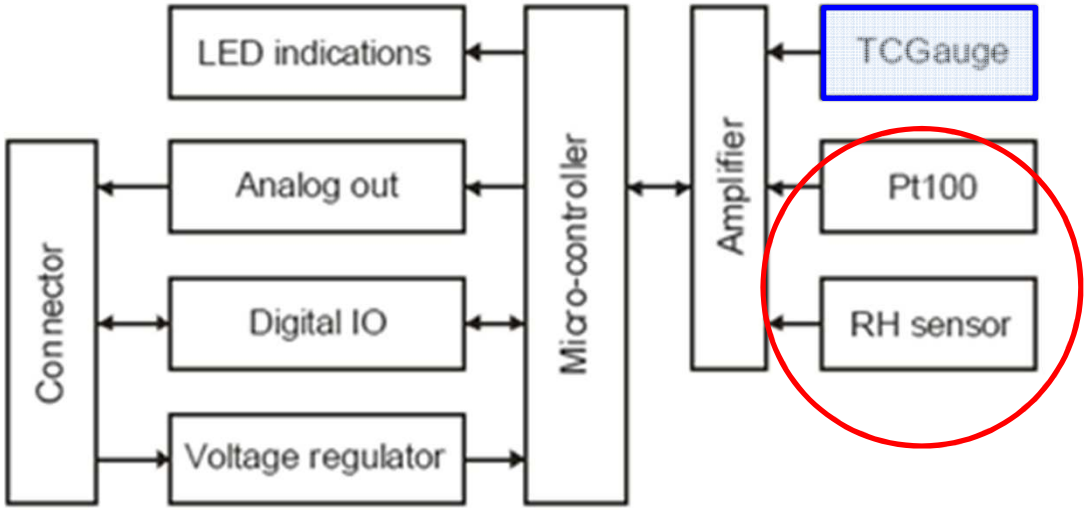
	sensor type	principle, device	Measurand
1	catalytic	heat of catalytic combustion	temperature, resistance, thermoelectric voltage
2	thermal	heat conduction	temperature, resistance, voltage
3	electrochemical	amperometric, potentiometric	current voltage
4	electrical	resistor capacitor diode transistor	impedance conductivity capacitance work function
5	acoustic	change of mass QMB SAW ultrasonic	wave velocity frequency shift time
6	optical	hydro-chromic optical fibre surface plasmon resonator	transmission, reflectance wave length, polarisation phase shift
7	mechanical	expansion due to hydrogen absorption	length

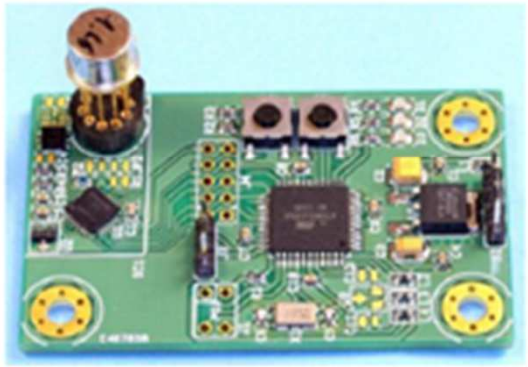
"an altruistic selection"

New commercially available sensors

1. Advanced sensor electronic

Thermal conductivity sensor





XEN-5310

2. Further sensors

New commercially available sensors

3. Dual gas sensor technology

3.1 catalytic combustion or/and electrochemical cell

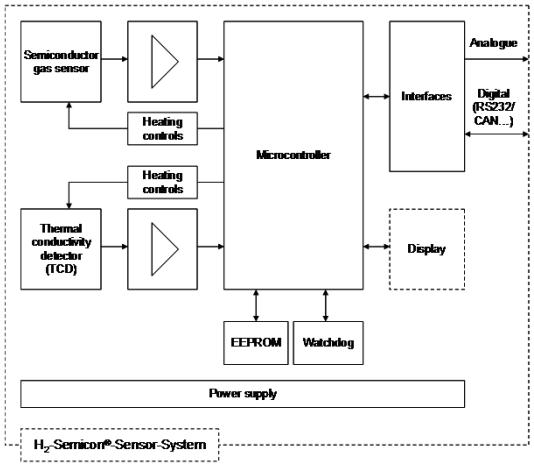
- 4-20 mA 3-wires output or 3 relay outputs,
- RS485 serial communication Modbus.
- Optional HART communication interface
- ATEX/IEC Ex certified

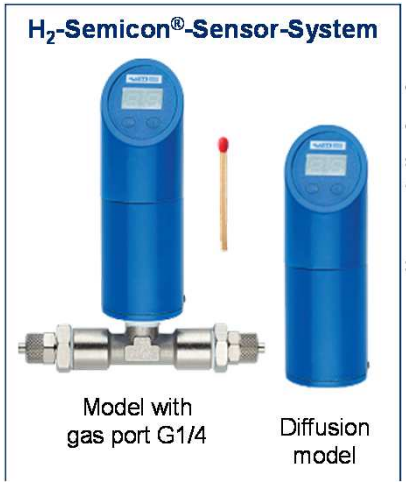
SMART S-SS

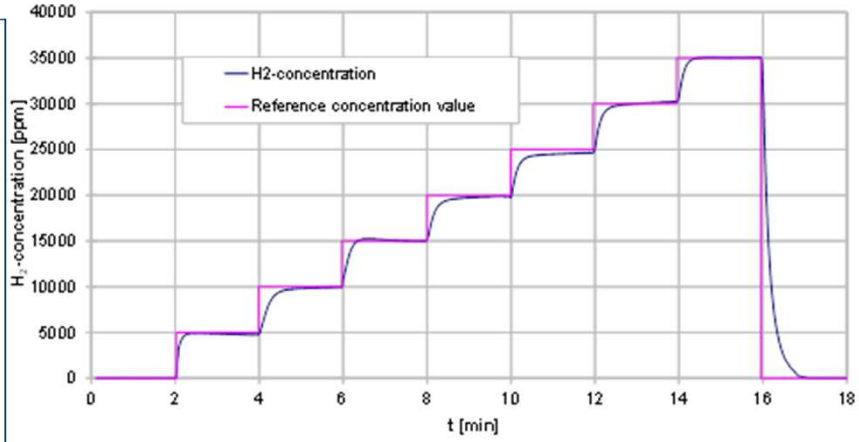
Cyber Genius

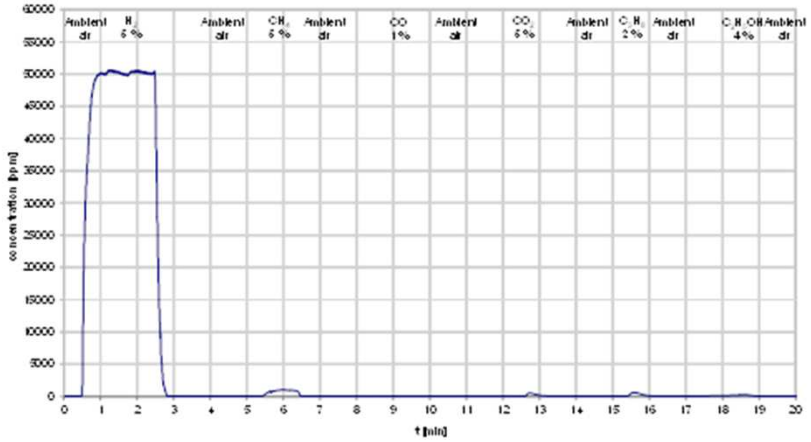
New commercially available sensors

3.2 Semiconductor or/and thermal conduction





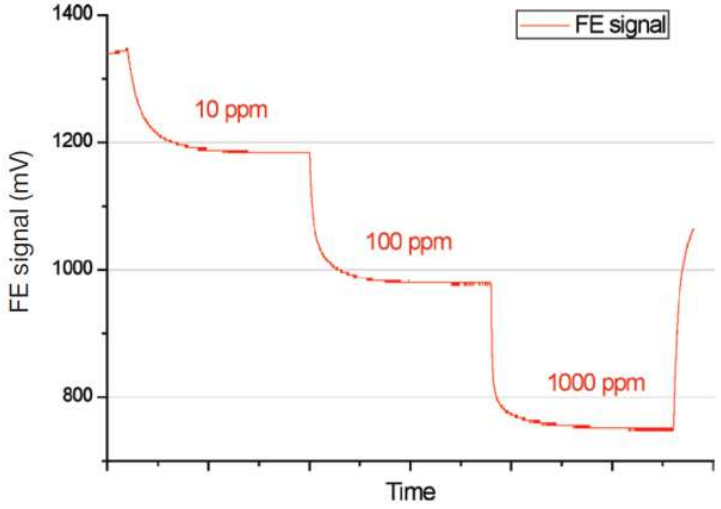




- hydrogen concentrations in a continuous range from 0…4 % (optional up to 100 %)
- response time <1 s (t60 at 5.000 ppm H2);
- high zero-point stability (avoidance of false alarms);
- humidity resistant from dry air up to condensation
- wide operating temperature range (-20°C to +80°C).
- analogue interface (0.5 V to 5 V, linear) and digital interface (RS232/CAN-Bus) for data logging and external calibration

New commercially available sensors

3.3 Field effect transistor (and thermal conduction)



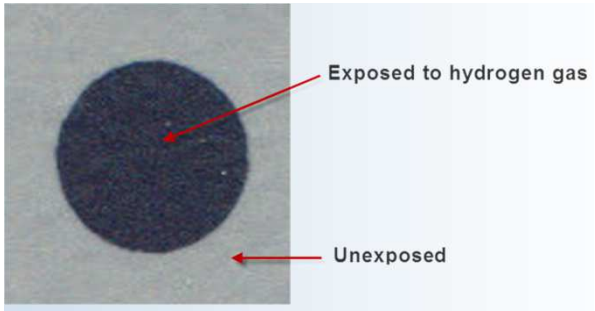
- hydrogen measuring range 0 to 4.4 %, 10 % or up to 100 %
- uncertainty of 0.5 % H2 to 2 %
- response time (t90) <2 s, recovery time (t10) < 10
- temperature range -40 °C to 110 °C
- no cross sensitivity to many other gases
- no influence of relative humidities up to 100 % including condensation
- CAN bus interface and MQS connectors, in accordance to IEC 61508 (SIL2)
- for harsh environment
- ATEX 100a, Zone 2

HLS-440, HLS 440P, HPS-100

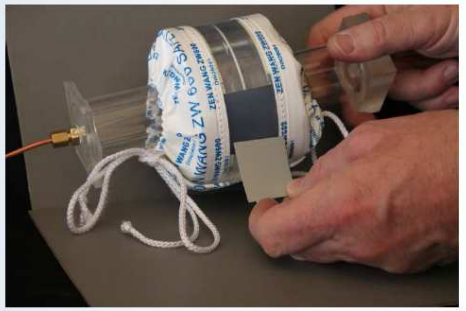
New commercially available sensors

4. “Dialectic” : Hydrogen leak indicator

- based on a colour changing pigment (tungsten oxide)
- precipitated as paint, spray or as a thin film
- indicator polymer foils can be wrapped around a hydrogen gas carrying component
- optical readout
- wireless data transmission (RFID) possible



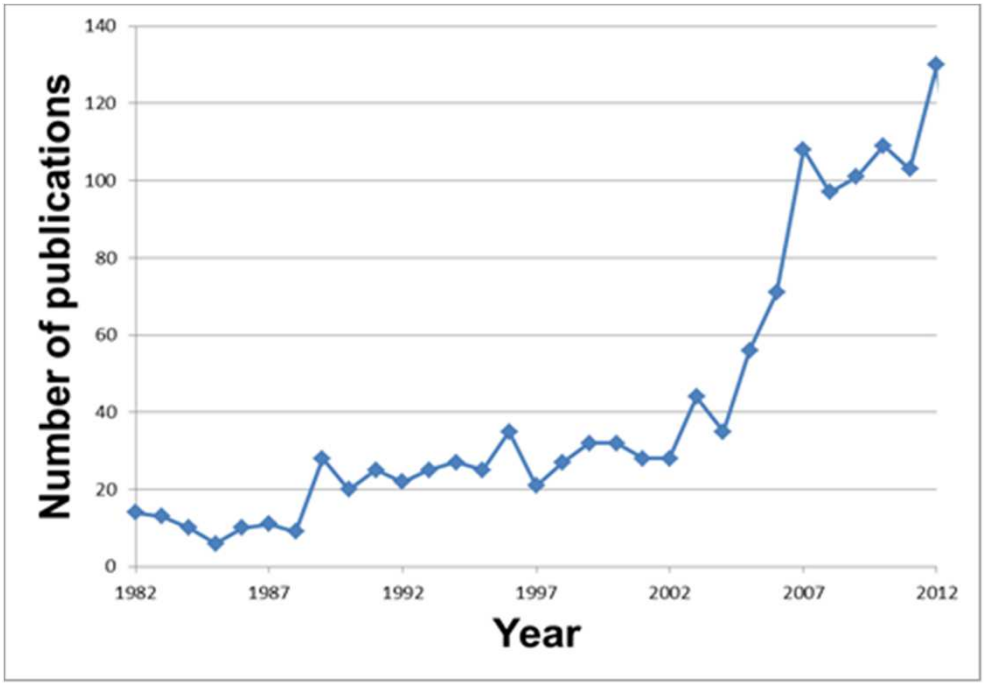
Time = 0 (start)



Time = 20 (end)

DeteCoat®H

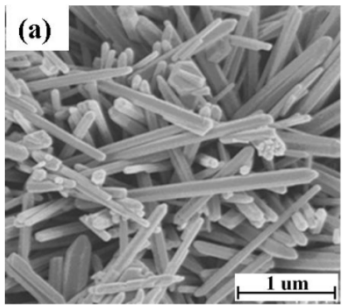
Sensors under development



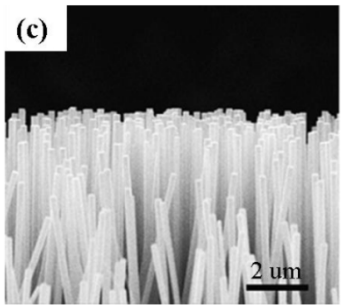
“publish or perrish”

Sensors under development

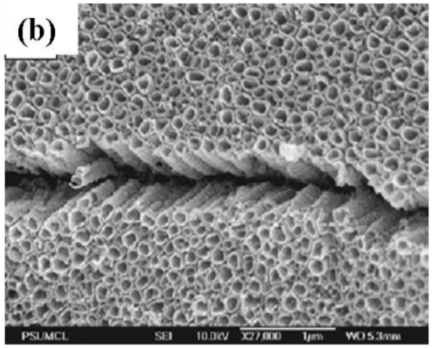
New hydrogen sensitive materials
nano particles and nano wires



ZnO

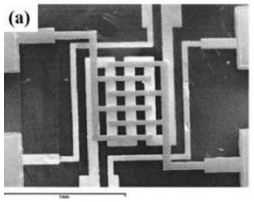


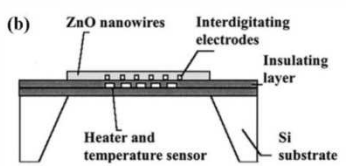
porous materials



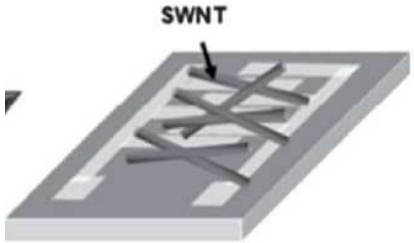
TiO_2

Sensor element





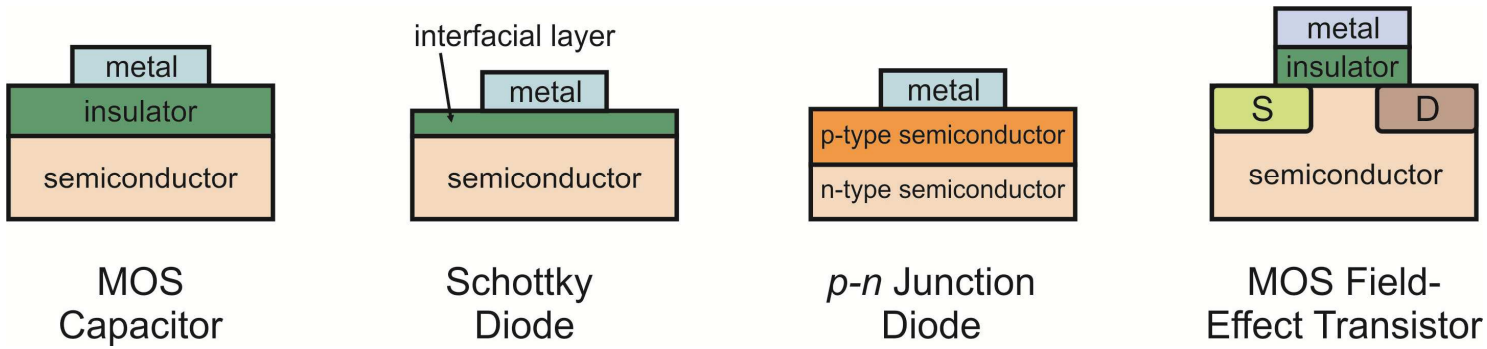
Schematic illustration of a tube-type 1-D nanostructured gas sensor



Sensors under development

Sensors based on work function

Detection is based on the change of the work function of a catalytic metal following absorption of hydrogen.



Research focus on

- modified and new materials: PdNi alloys , Si, GaN, SiC or ZnO
- sensor design optimization and
- elucidation of the hydrogen sensing mechanism

- High resistivity
- Fast response
- Reproducibility of properties
- Mass production

Sensors under development

Optical sensors systems

up to 20 % of all publications on hydrogen sensors !

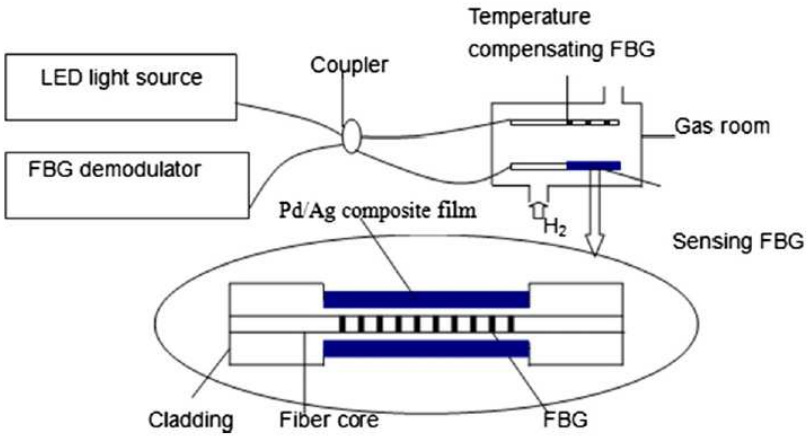


Fig. 1. Configuration of optical fiber hydrogen sensor characterization.

- Potential for explosive atmosphere
- extended experimental set up
- Expensive device
- to long response time

interferometric
micro mirror
evanescent optical fiber
surface plasmon resonance ($Ag/SiO_2/Pd$ multilayer stack)
colorimetric technology .

Bragg-grating material combinations based on palladium, like Pd-Ni, Pd-Ag, Pd-Y.

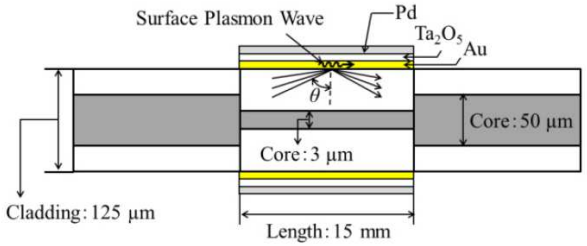


Fig. 1. Structure of SPR hydrogen sensor based on hetero-core optical fiber.

Sensors under development

Sensors working at or near room temperature

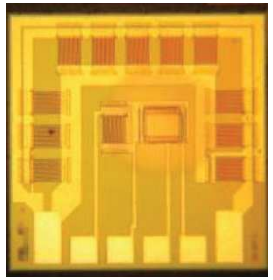
- Electrochemical (amperometric)
- Work function based sensors (field effect)
- Surface acoustic wave (SAW) sensors
- Speed of sound measurement
- Resistive nano crystalline palladium, nano wires
- Resistive polymers (polyaniline)
- Thermal conductivity

- Low Energy consumption
- Flexible substrates
- Lower response
- Thermal reactivation

Summary

TRENDS IN GAS SENSOR DEVELOPMENT FOR HYDROGEN SAFETY

- New sensors on the market
  - advanced sensor electronics
  - additional environmental sensors
  - dual gas sensor technology
  - miniaturised size
  - colometric hydrogen indicator
- Sensors under development
  - optical sensor
  - nano materials (fibres, rods, graphene)
  - nano technology: MEMS
- Room temperature operation



- increased performance
- system comparability
- internal safety (ATEX) approved

Further R&D for:

- reduced response time
- higher accuracy
- lower costs
- integration into hydrogen devices

Acknowledgements

FCH JU financial support Contract No. 325326

- Reduce the gap between sensor academics – manufacturer - user

Thank you for your attention !