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PdAu Based Resistive Hydrogen Sensor in Anaerobic Environment

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Clément Occelli received his engineering degree in Materials from the Polytech'Marseille engineering school, Marseille, in 2016. During this period, he was at the IM2NP institute at the Aix-Marseille University in France for 3 months, working on WO_3 sensor for ozone detection. He was in industry from 2017 until 2019 where his work was focused on materials and products testing. He is currently a 2nd year Ph.D. student back to the IM2NP Institute, developing hydrogen sensors for anaerobic environment.

Outline

I. Context, technology and detection principle
  a) Environmental context
  b) Palladium gold alloy for hydrogen detection
  c) Introduction to resistive sensor
  d) Detection and characterization principle

II. Thin film deposition and crystalline structure
  a) PdAu thin film deposition
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III. Sensor electrical characterization
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  b) Sensor performance at different temperatures
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IV. Conclusion and perspective

I. Context, technology and detection principle

Environmental context

Current climate change drives for greenhouse gas emission reduction

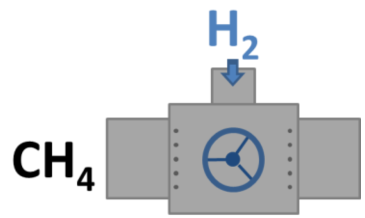
<u>Hydrogen is a promising energy carrier :</u>

- ✓ Low environmental footprint

- ✓ Complementary use with renewable energy

Energy conversion

- ✓ Use of current gas pipeline



Pipeline Injection

Injection of Hydrogen in pipeline must **<u>not exceed 20%</u>**

Various **<u>hydrogen sensors exist</u>** for leak detection **<u>in air</u>** only few have been reported operating in anaerobic environment

Palladium gold alloy for hydrogen detection

Pd is a promising candidate for H_2 detection but cannot be used alone

Advantage
- ✓ Selectivity to hydrogen
- ✓ Operate without oxygen and low T°
- ✓ Sensitivity to ppm

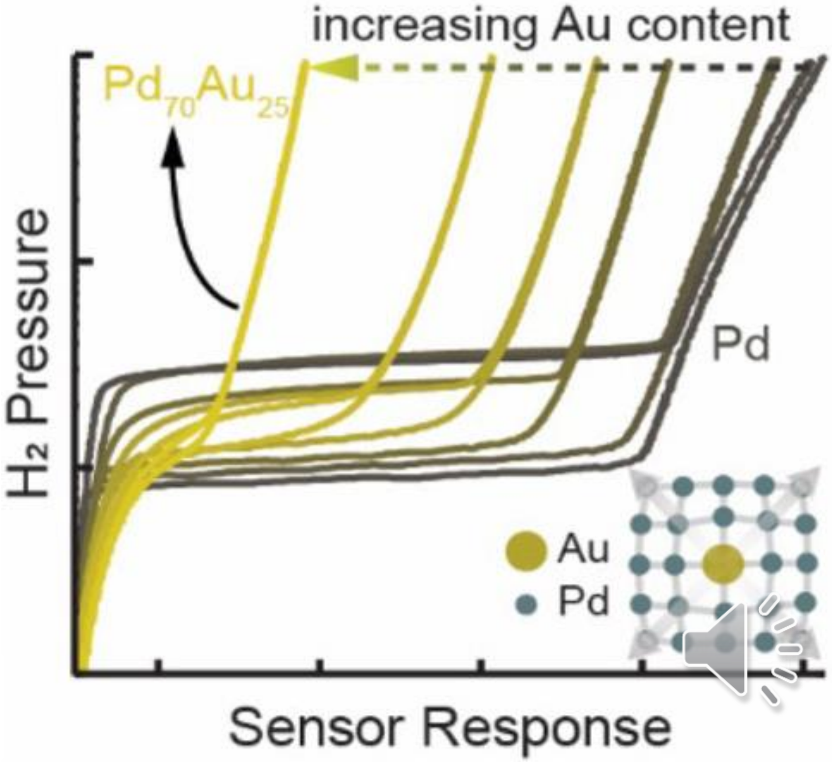
Drawback
- × Measurement hysteresis
- × Ageing of material in H_2
- × Slow detection (min)

Solution by addition of another element → Fabrication of an alloy

Addition of Gold :
- **Suppression of hysteresis**
- **Protect layer from delamination**
- **Fasten detection**

But
- **Lower sensitivity**

Best compromise about 20-25% in literature



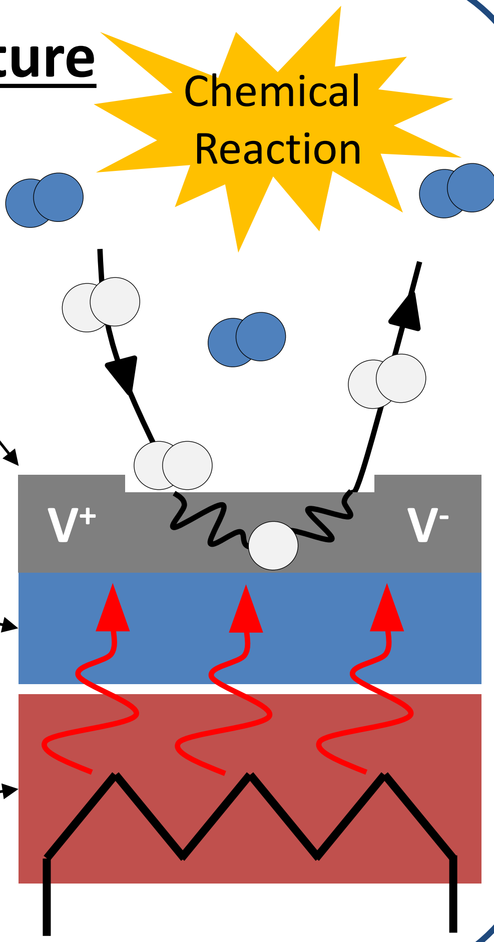
10.1021/acssensors.0c02019 →

Resistive sensor structure

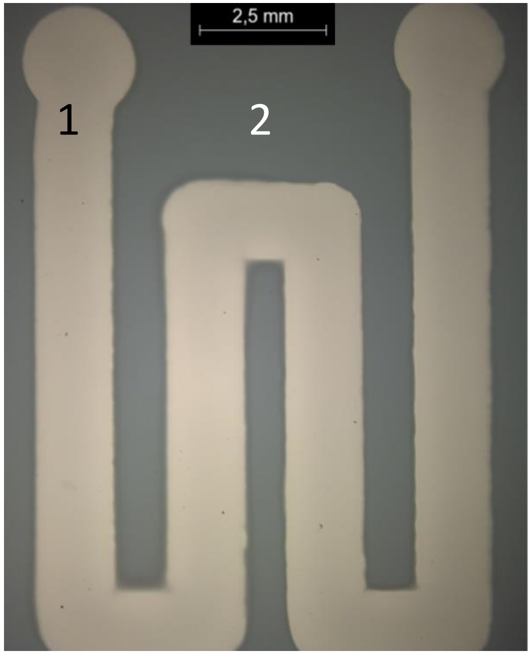
1) Sensitive film / Measuring electrode
Gas interaction / Information reading

2) Substrate (Si/SiO_2)
Electrical insulation

3) Heating device
Reaction control



Sensor Design



1 . PdAu sensitive layer
2 . Si/SiO_2 substrate

Detection principle :

Pd and PdAu crystallize in a FCC structure

Absorbed hydrogen occupy octaedral interstitial site

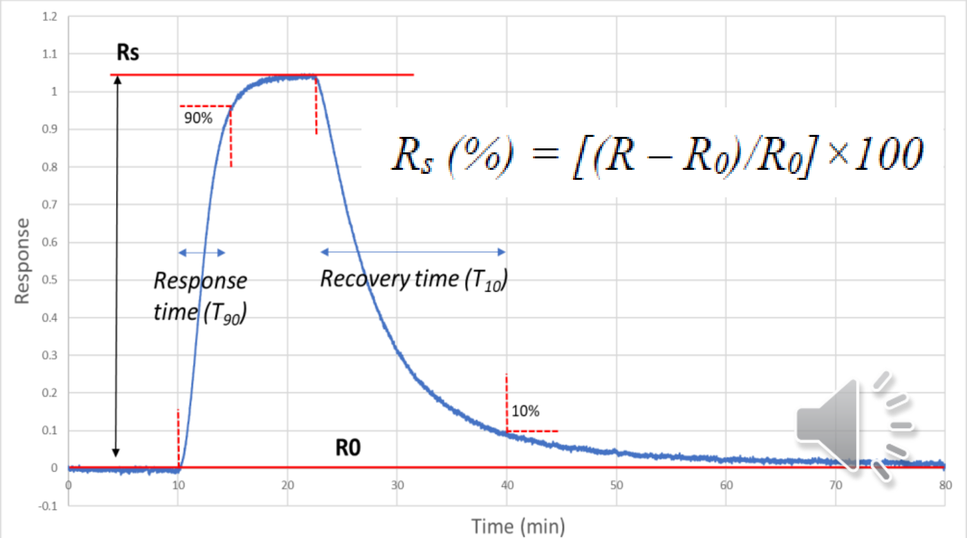
Hydrogen site occupation induces electron scattering which increases material resistivity
➔ **Sensing principle**

Tools for performance characterization:

Sensor response (Rs) : Comparasion of resistance under gas (R) to reference value (R0)

Response time (T_{90}) : Time to reach 90% of Rs value

Recovery time (T_{10}) : Time to return to 10% of Rs



II. Thin film deposition and crystalline structure

PdAu thin film deposition

- **Film Deposition**

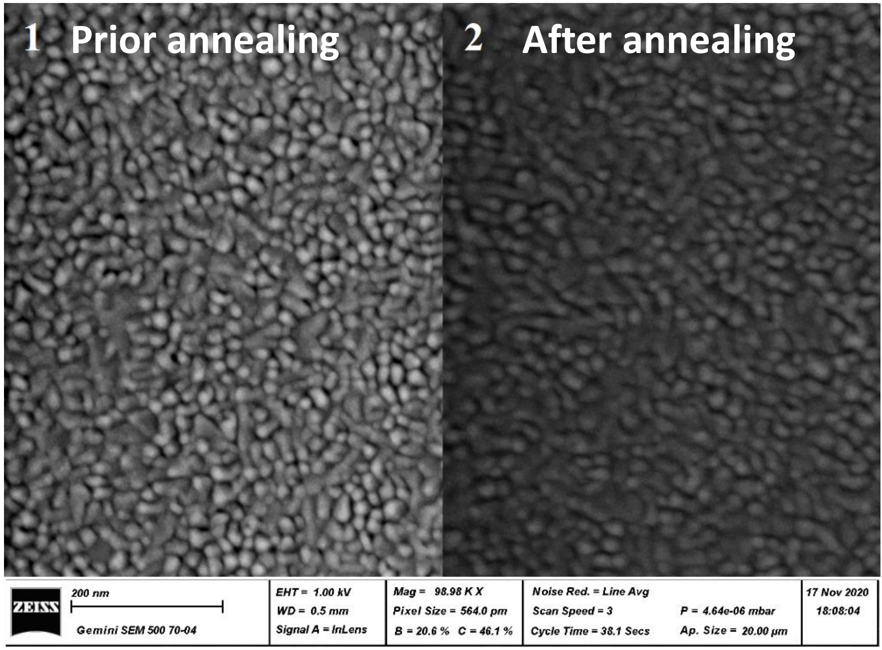
RF magnetron sputtering
Ti adhesion layer
PdAu Layer thickness : 120nm

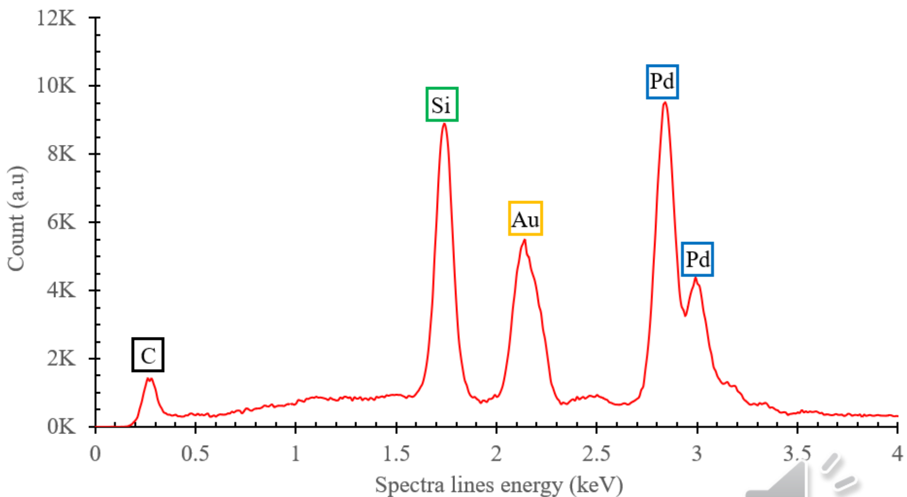
- **Annealing**

200°C in N_2 for several hours

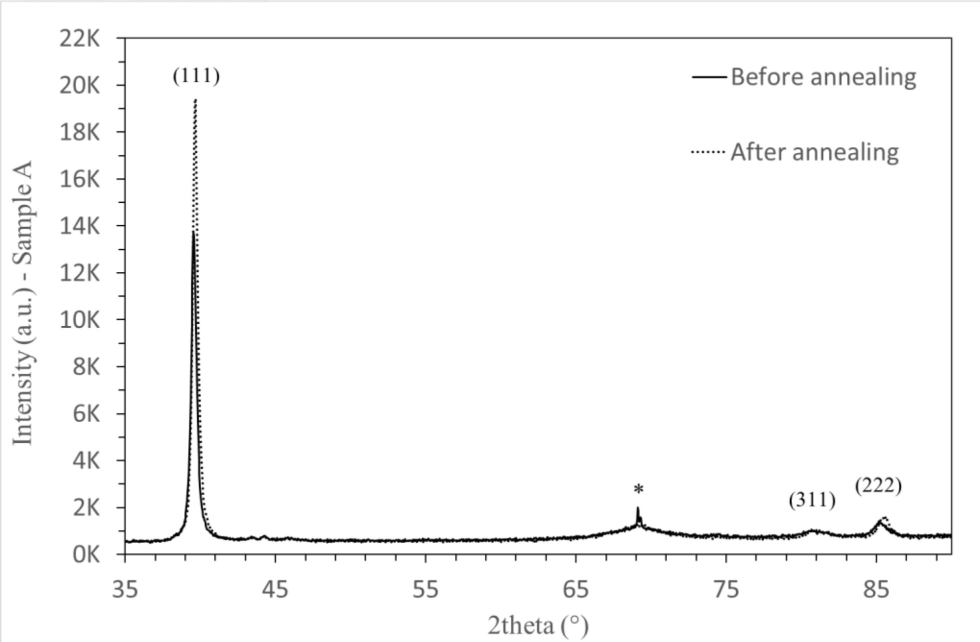
- **EDXS measurements** (after annealing)

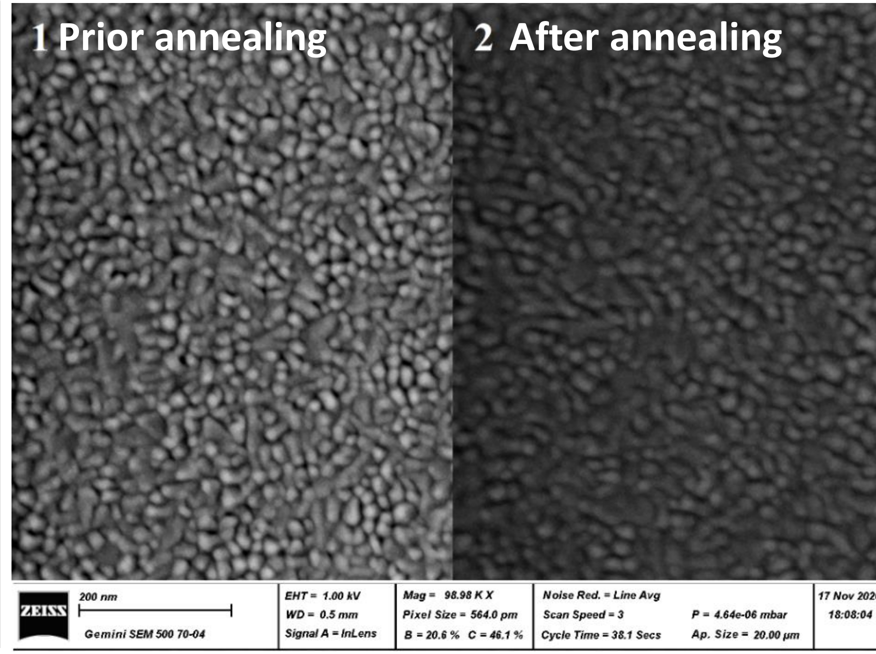
Estimated composition of 80%Pd and 20%Au





Effect of annealing on film microstructure



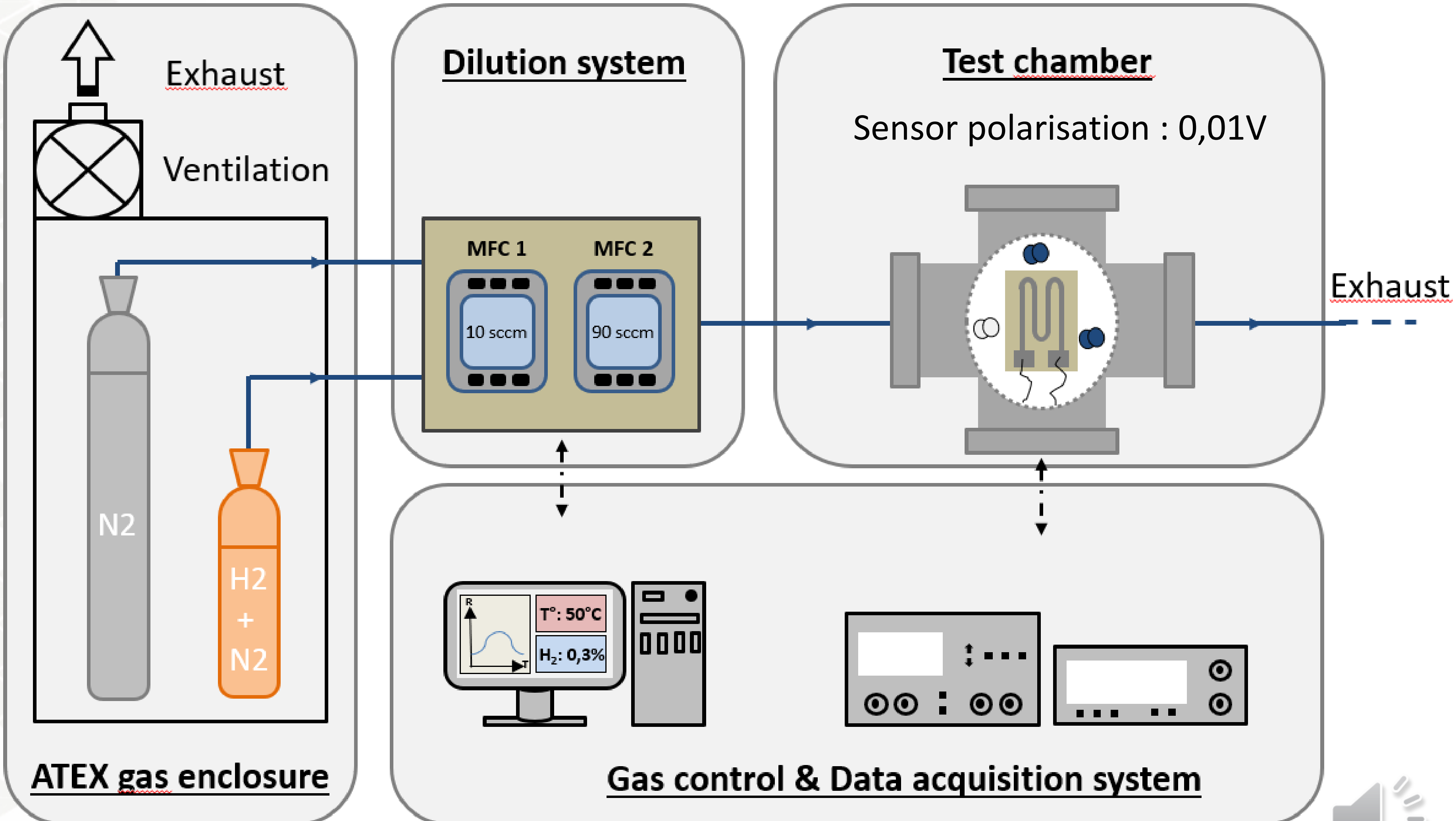


- Film crystallizes mainly with a (111) preferred orientation
- Small diffraction peak for (311) and (222) planes
- Heat treatment increases the crystallinity 13700 → 19400 counts
- Scherrer formula give a stable grain size of 20 +/-1 nm

III. Sensor electrical characterization

Sensor test bench

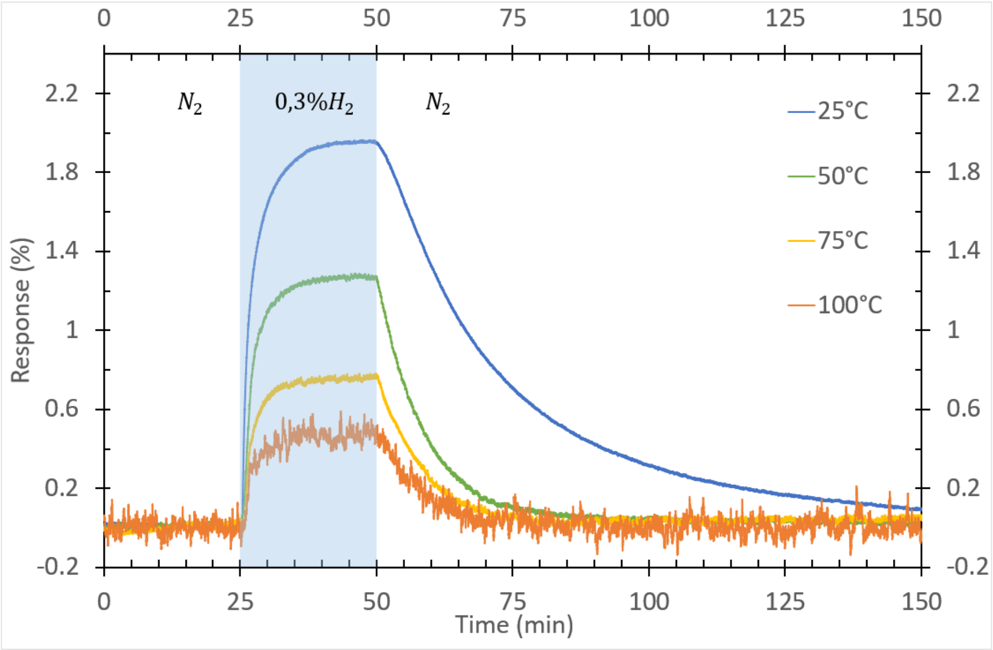
Flow rate : 100 sccm ; H_2 : 0 – 3% ; Exposure time : 25min; Operating temperature : 25°C – 100°C



Operating temperature affects sensor performances ➔ Determine the best condition

Sensor tested at four temperatures : **25**, **50**, **75** & **100**°C under 0.3%H_2 in N_2

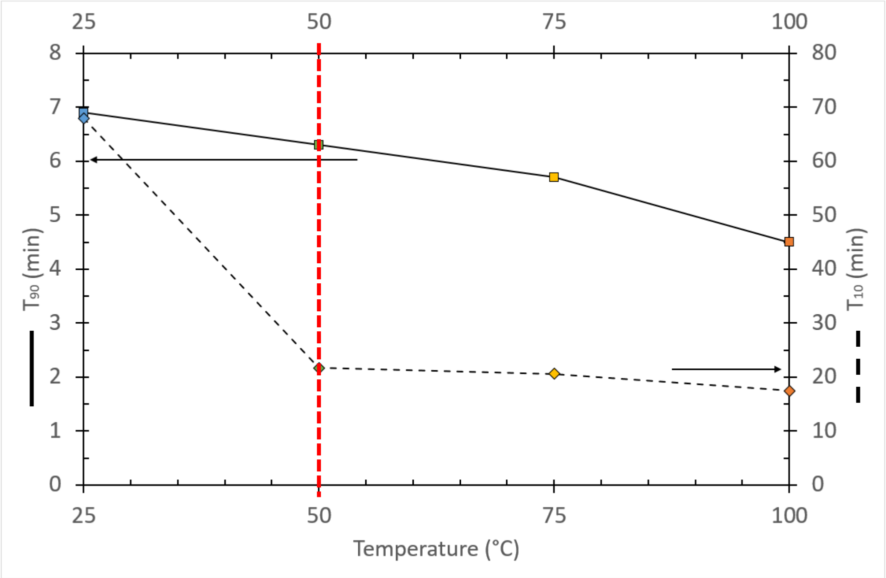
Sensor response for 0.3% H_2 at various temperatures



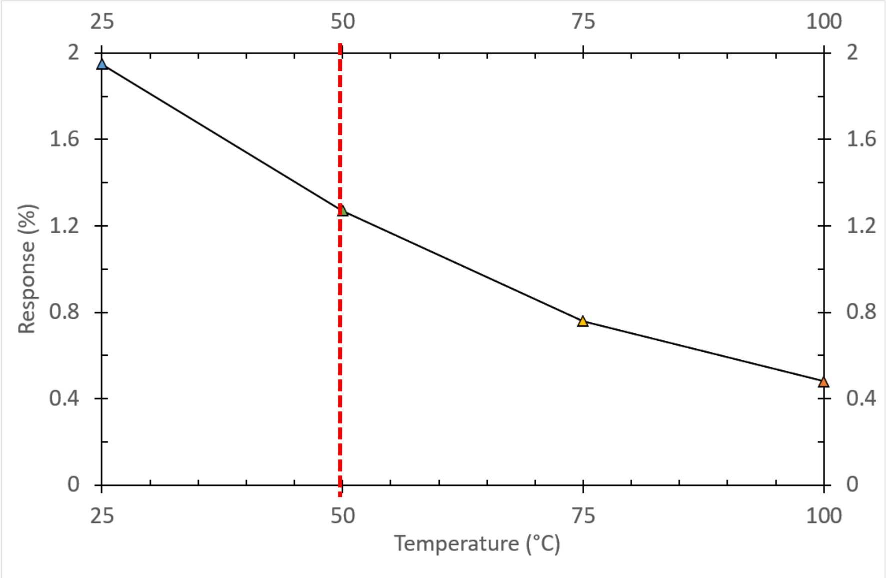
- Detection is effective at all temperatures
- Response diminishes with increasing temperature
- Response and recovery time diminish with increasing temperature
- Signal tends to be noisy at elevated temperature

Best operative temperature

T_{90} and T_{10} at various temperatures



R_s at various temperatures



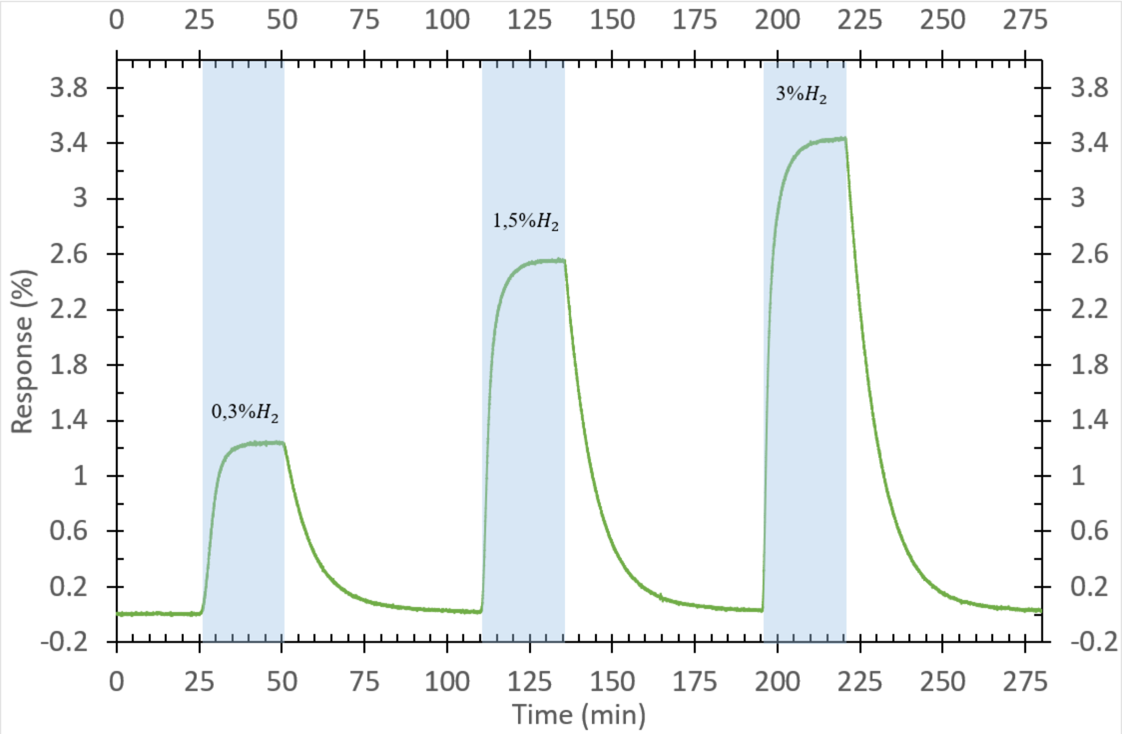
Best compromise at 50°C :

- Good response and recovery time (6 min 20s & 21 min 40s)
- Good sensitivity (1.3% for 0.3% H_2)
- Clear signal

Sensor testing at various hydrogen concentrations

Sensor tested for 3 H_2 concentrations at 50°C

Sensor response at 50°C for various H_2 concentration exposure



- All 3 concentrations detected
  - 1.3% for 0.3%H_2
  - 2.6% for 1.5%H_2
  - 3.4% for 3%H_2
- Stabilization of response
- Baseline recover without H_2

Sensor was able to detect various concentrations of hydrogen in N_2 with a stable baseline

IV. Conclusion

Hydrogen micro-sensor fabricated :

- Radio frequence, magnetron sputtering
- Based on a $Pd_{0.8}Au_{0.2}$ thin film
- Thermal annealing at 200°C
- Preferential growth along the (111) plane

Hydrogen sensor performance :

- Best operating condition at 50°C
- Detection from 0,3 to 3%H_2 in anaerobic environment

➔Long response and recovery time are due to filling time of the test chamber

Next step of the study :

- Characterisation of the sensitivity and selectivity in natural gas
- Use of a smaller test chamber
- Testing the effect of different Au contents in the alloy

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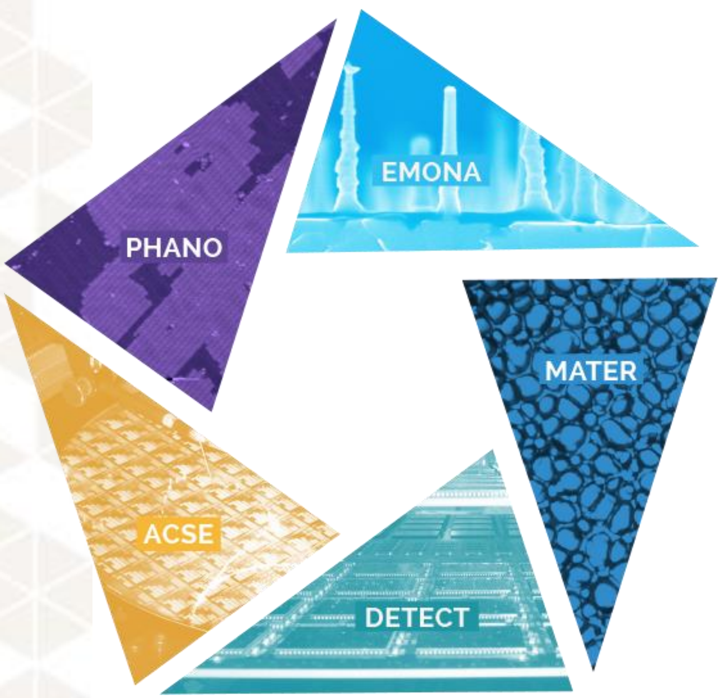
Thank you for your attention



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