Screen Printed $BaTiO_3$ for CO_2 Gas Sensor

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Author presentation

Fabien LE PENNEC is a Ph.D. student (3rd year) in the Microsensors and Instrumentation team at IM2NP laboratory, Marseille, France. The research performed within the framework of his thesis concerned the realization and the characterization of the sensitive layer (based on metal oxide) as a CO_2 sensor.

Ph.D Student
LE PENNEC Fabien

Introduction to the MOX and $BaTiO_3$

- Introduction & context
- Operating principle of MOX
- Sensitive material: $BaTiO_3$ & Structural study $BaTiO_3$

Electrical sensor characterization

- Experimental setup: sensor test bench
- Resistance response for 1000 ppm CO_2
- Optimal operating temperature of $BaTiO_3$ Sensor
- Sensitivity response of $BaTiO_3$ to CO_2
- Repeatability of $BaTiO_3$ sensor to one concentration of CO_2
- Sensitivity response to different relative humidity

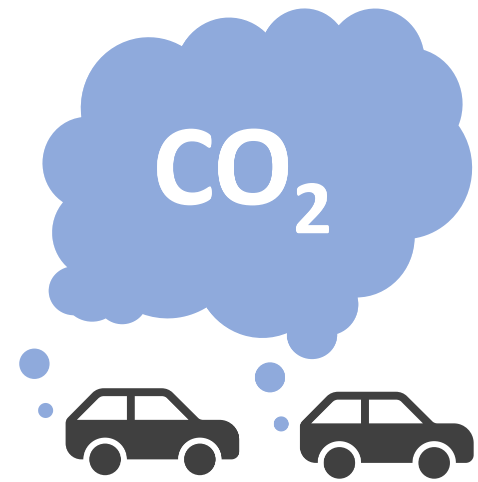
Conclusion and prospective

Introduction to the MOX and $BaTiO_3$

Introduction & context

The carbon dioxide (CO_2) are:

- High thermal stability
- Odorless
- Colorless
- Average concentration ≈ 400 ppm



The CO_2 interest:

- Greenhouse effect (contribution: 9-26%)
- The global warming
- The outdoor air monitoring is a major social issue

≈0.04% (400ppm):

average concentration of CO_2 in the air

0.3% to 2%:

several symptoms are felt depending on the CO_2 concentration (i.e. difficult breathing)

>10%:

risk of death after prolonged exposure to CO_2

} effects of various levels of CO_2 in the air

The commercial instruments for CO_2 sensing

The technologies based on IR detection are the most used for CO_2 sensing:

- Selectivity to CO_2
- High performance

However, their **drawbacks** are:

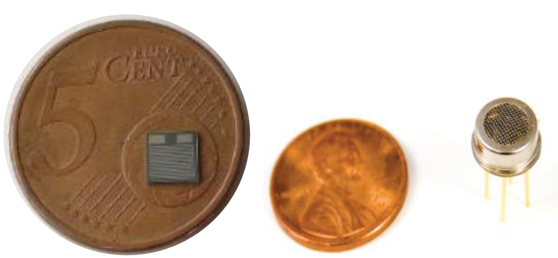
- Cost of a few hundred euros
- Incompressible size of the sensor
- High power consumption

Analyzer CO/CO_2 Fuji Electrics

EE894 Elektronik

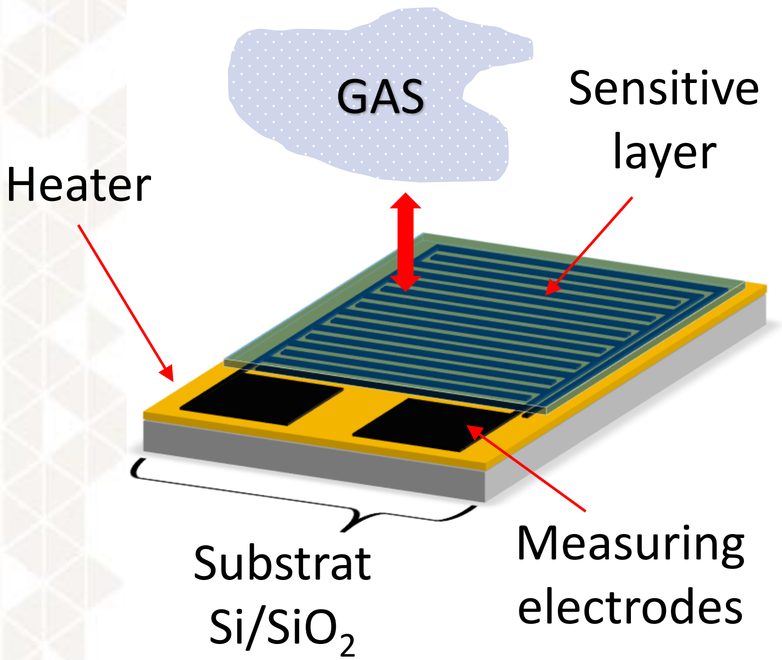
→ The MOX gas sensors respond to these disadvantages:

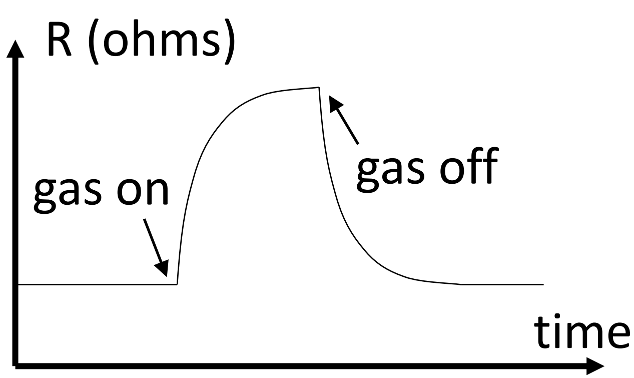
- High sensitivity
- Low cost
- Small size
- Low electrical consumption (<25 mW)



MOX

Operating principle of MOX microsensors





Interaction gas-semiconductor + **Energy supply**

Charge transfer

Resistance variations

For an n-type semiconductor (ex: WO_3):

→ Increase of resistance in presence of oxidizing gases (i.e.: O_3, NO_2, …)

Examples of metal oxide materials:

SnO_2, WO_3, ZnO, $BaTiO_3$, …

Sensitive material: $BaTiO_3$

State of the art:

material	Operating T° (°C)	Measurement method	response	$[CO_2]$ (%)	[Ref]
$CuO-BaTiO_3-Ag$(1mol%)	470	Capacitive	**7.74**	2% (20000 ppm)	[1]
$BaTiO_3-LaCl_3$ (10%wt)	400	Resistance	**1.57**	1% (10000 ppm)	[2]
$BaTiO_3$	200	Resistance	**1.1**	0.05% (500 ppm)	[3]
$CuO-BaTiO_3$	412	Capacitive	**2.34**	2% (20000 ppm)	[4]
$BaTiO_3$	280	Resistance		0.5% (500 ppm)	This work

[1] T. Ishihara, Sensors and actuators 1995

[2] M.S. Lee, Sensors and actuators 2000

[3] S.B. Rudraswamy, IEEE 2012

[4] B. Liao, Sensors and actuators 2001

→ First step : study of $BaTiO_3$ material alone

Sensitive material: $BaTiO_3$

Process of deposited $BaTiO_3$:

Need to have a quick validation of the material

→ $BaTiO_3$ nanopowder from Sigma-Aldrich®

→ Process of $BaTiO_3$ depositing: **screen printing**

Sensitive film deposition process:

- Mixture:

  → 4 g of $BaTiO_3$ + 1.5 g of glycerol

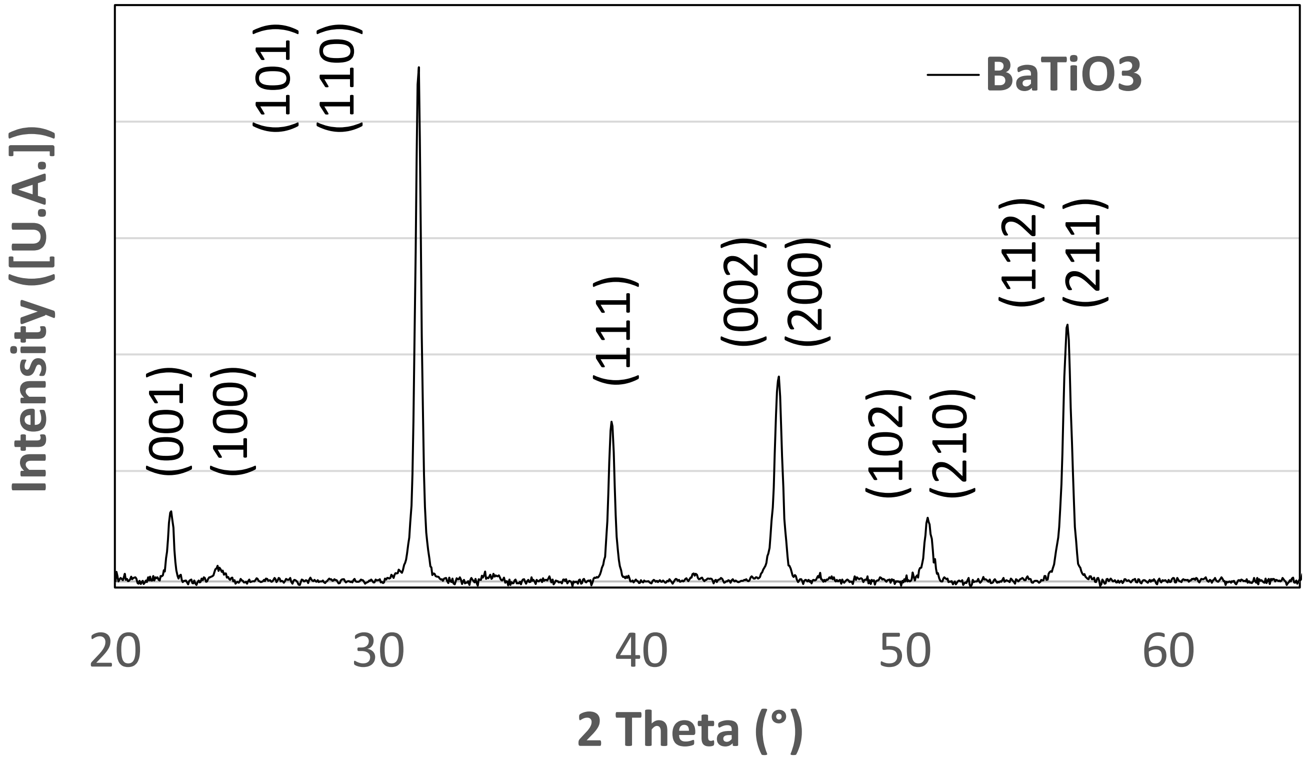
- Annealing:

  → On **plate 3 min**, at **450°C** for $BaTiO_3$

- Thick layer ≈ 7µm

Structural study $BaTiO_3$

The XRD diffractogram of $BaTiO_3$ thick film:



Determined by X-ray Diffraction (XRD) with a Philip's X'Pert MPD equipment (l = 1.54Å)

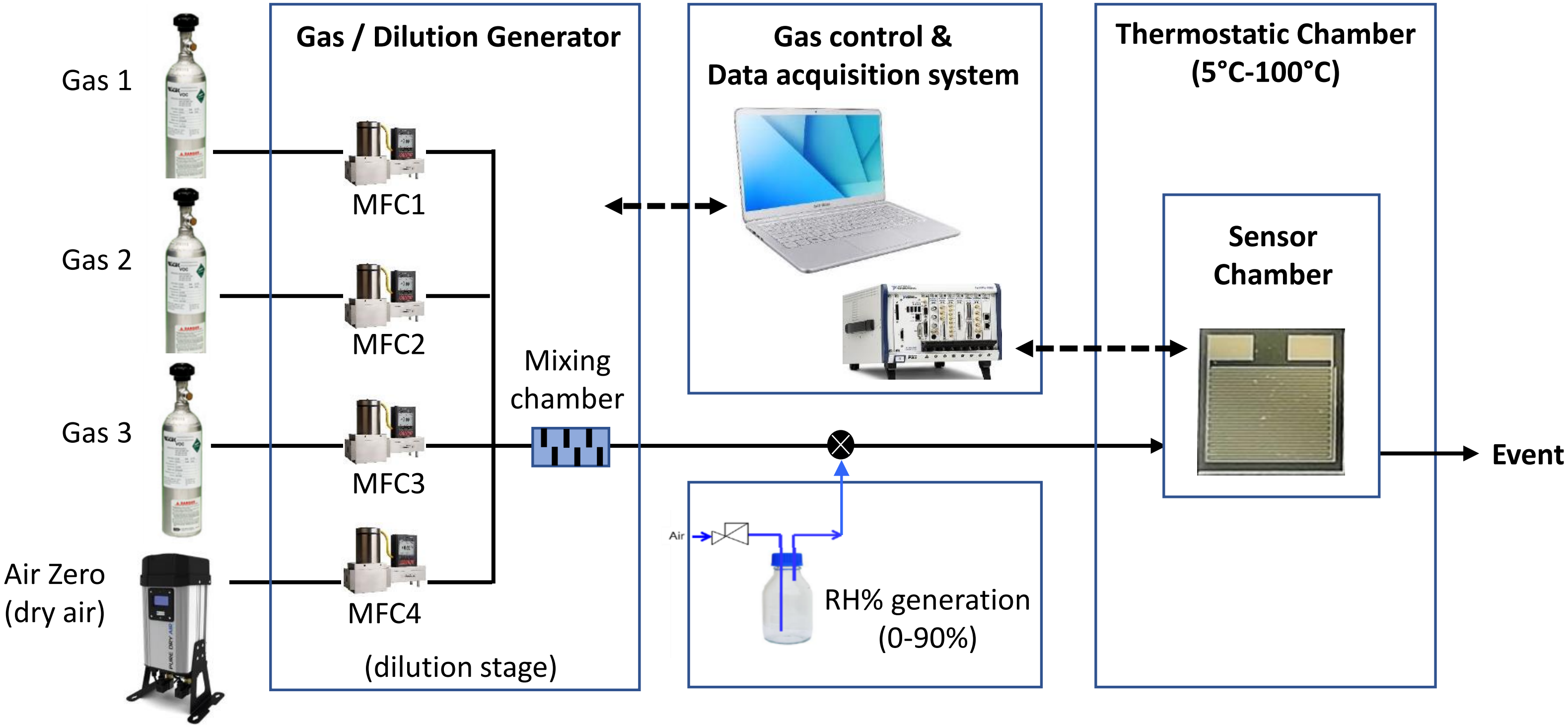
Phase of $BaTiO_3$ → Tetragonal

Electrical Sensor characterization

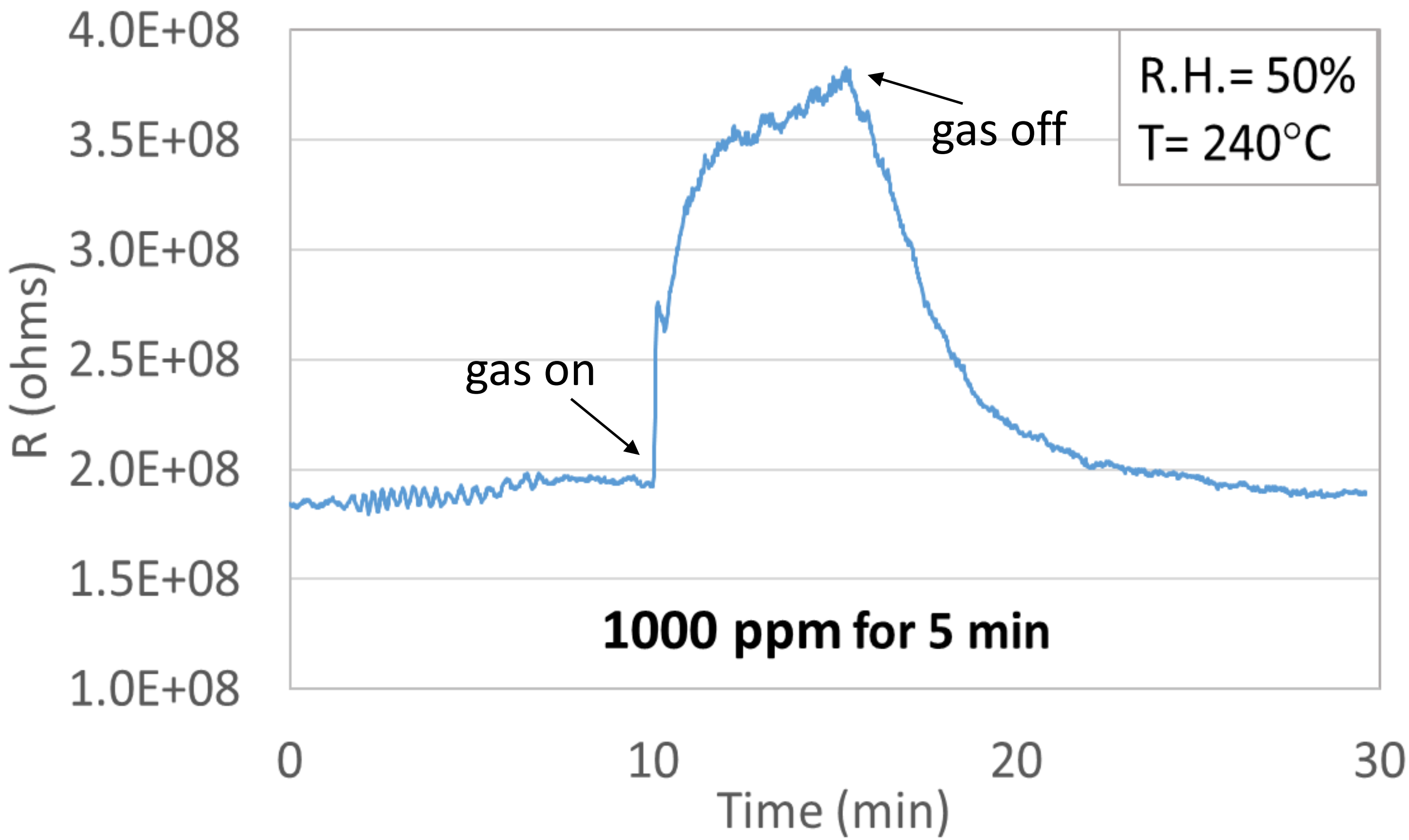
Experimental setup: sensor test bench

Our automated bench:

- Generation system (3 channels = 3 gases: CO_2 / CO / NO_2) and dilution (ppb / ppm / %)
- Climatic chamber: controlled environment (T °: 5 to 100 ° C / RH: 0% to 90%)
- Test chamber linked to multichannel acquisition system

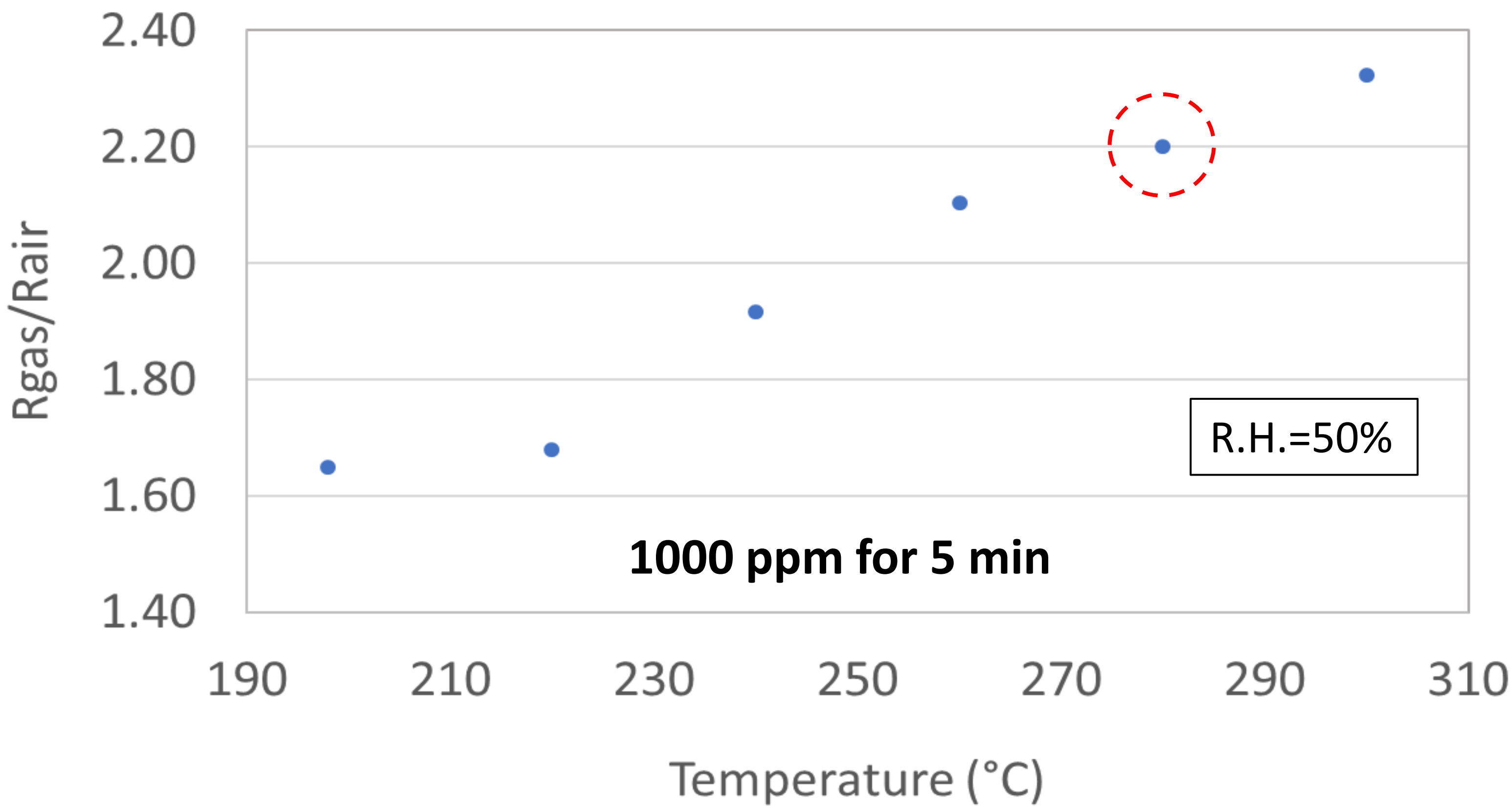


Resistance response for 1000 ppm CO_2



→The sensitive response agrees with the literature:

- CO_2 are an oxidizing gas
- $BaTiO_3$ are a n-type semiconductor

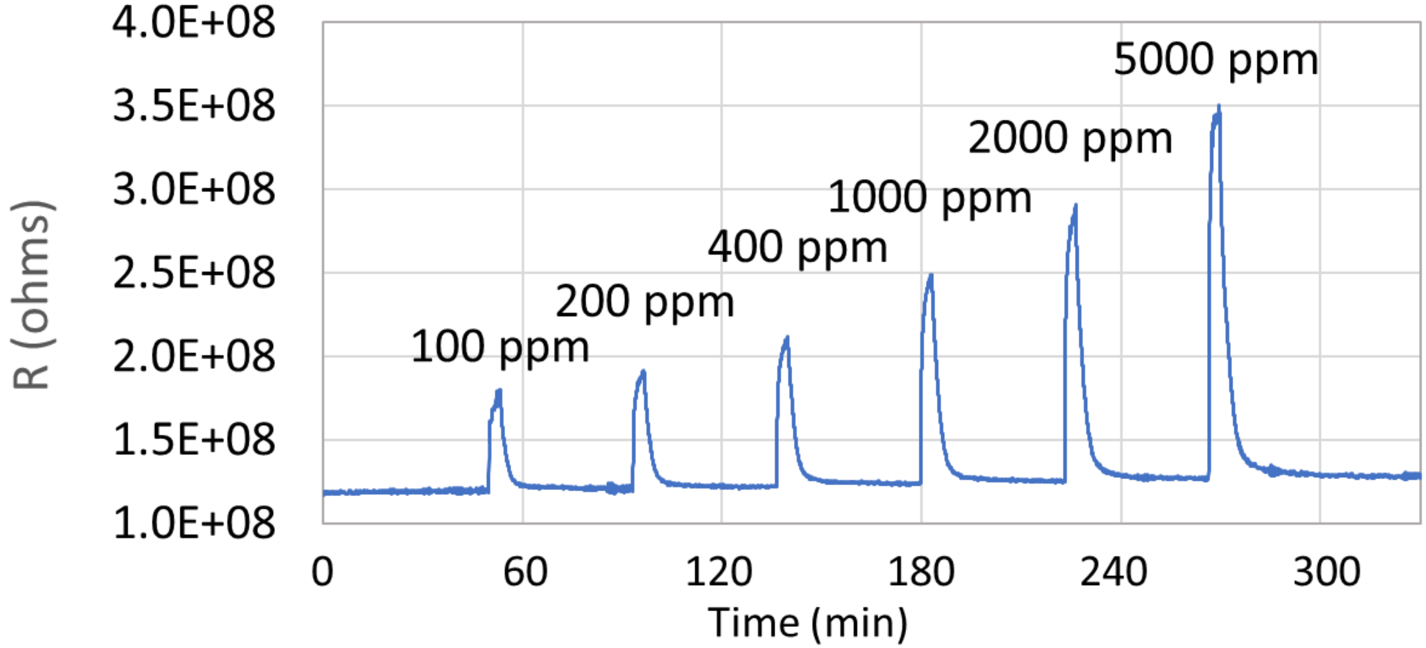


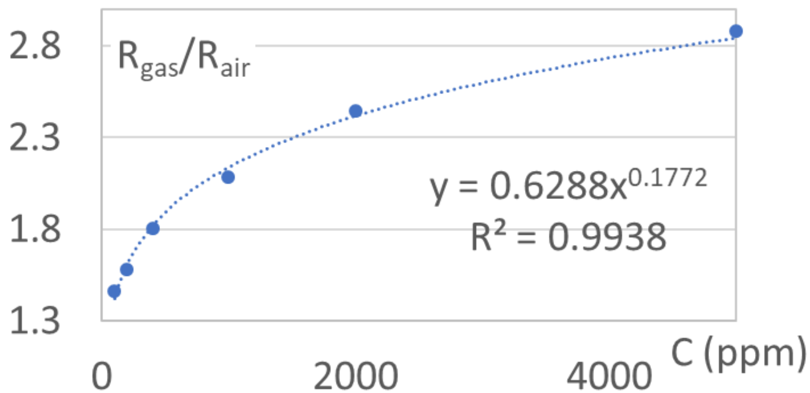
→The sensor responses increase with the temperature

→We carried out our measurements at **a temperature of 280°C** which is a good compromise between the sensitivity and the heater electrical consumption

Sensitivity response of $BaTiO_3$ to different concentrations of CO_2

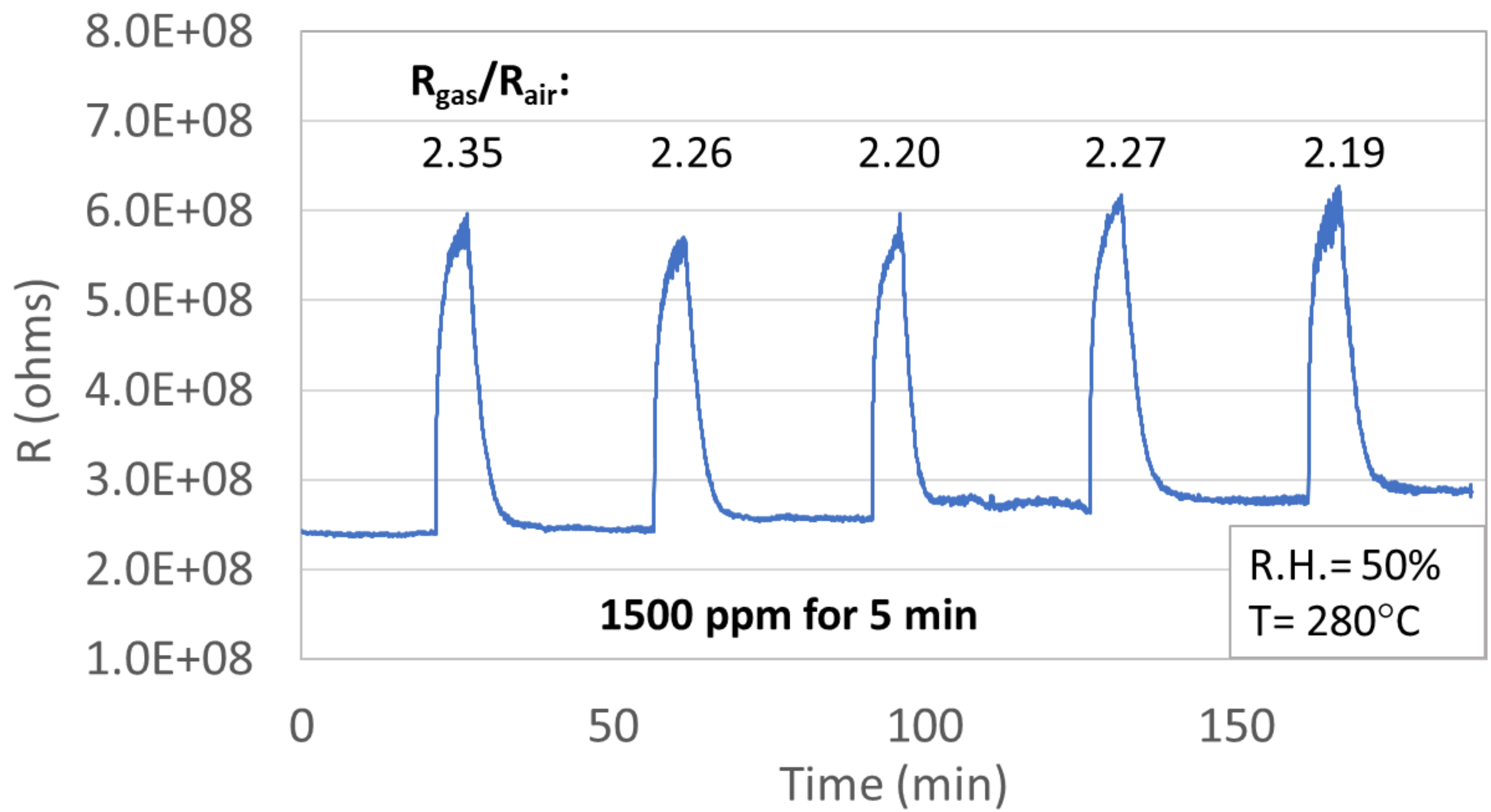
Resistance variation depending on the CO_2 concentration:





Operating parameters:
R.H.= 50%
T= 280°C
Exposure time = 5 min

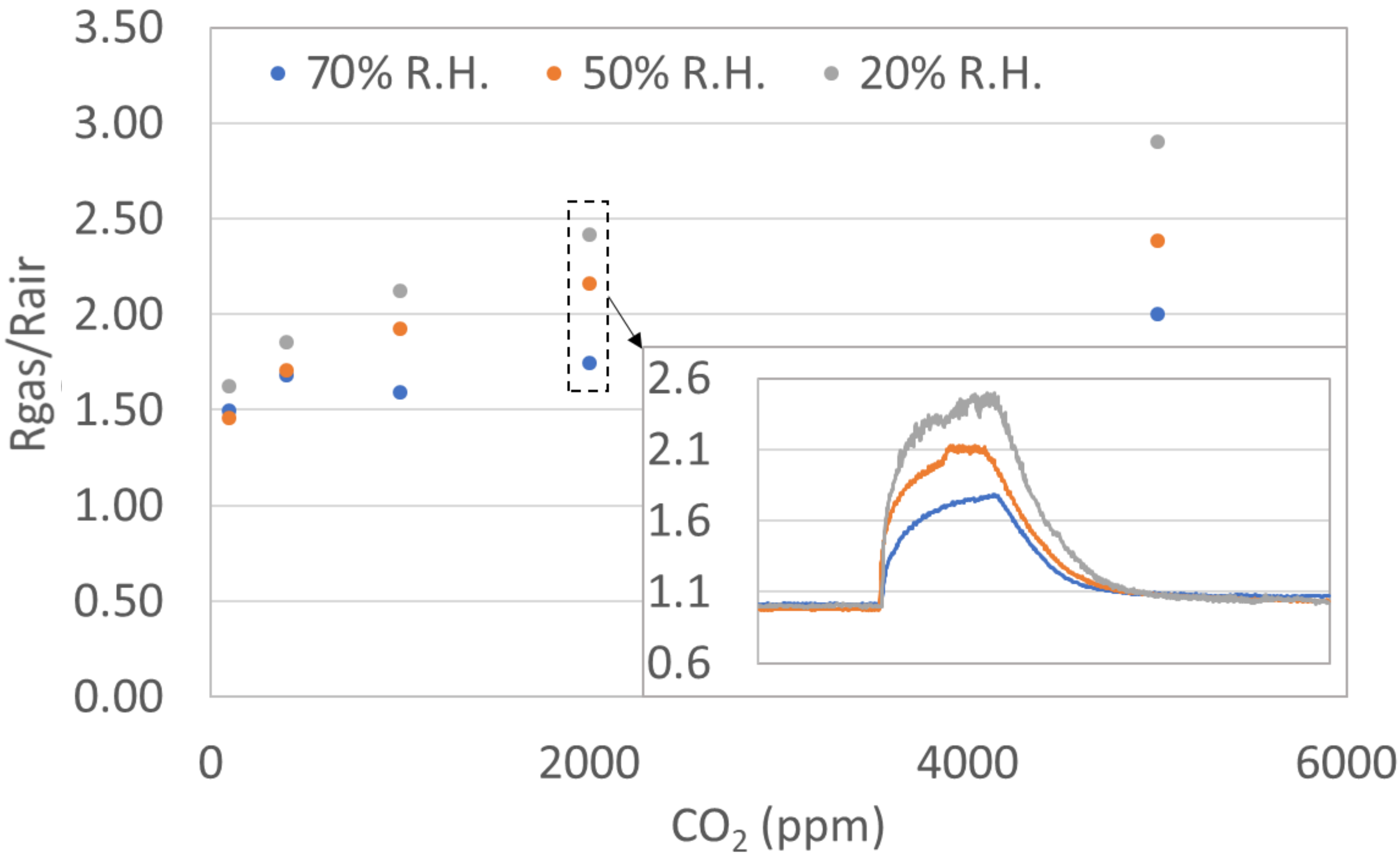
Repeatability of $BaTiO_3$ sensor to one concentration of CO_2



→The sensor response presents a stable behavior

→We obtained a good sensitive response with a good repeatability

Sensitivity response to different relative humidities



→The highest responses were obtained for the lowest R.H.

Conclusion and prospective

Conclusion:

→ We have determinated the operating temperature (280°C) and the relative humidity influence

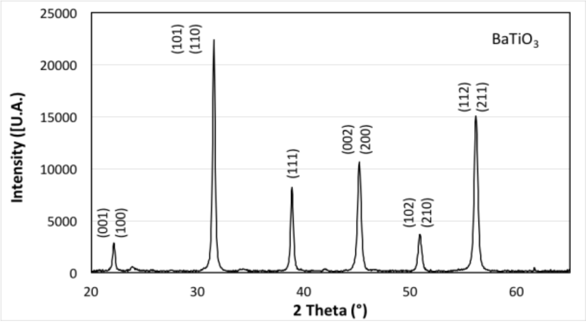
→ We developed a sensor based on $BaTiO_3$ with a high sensitivity to CO_2 and respond as n-type for oxidizing gas

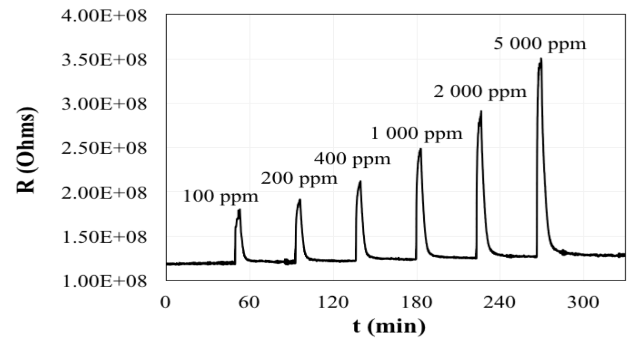
→ We notice a repeatability behavior for a CO_2 concentration equals to 1500 ppm

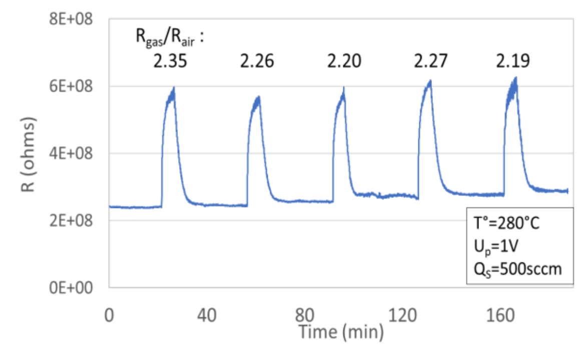
Prospective:

→ Study of several depositing methods of $BaTiO_3$ to enhance the aging of the sensor

→ Study of $BaTiO_3$ composite films







Acknowledgments

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Thank you for your attention !