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Ozone Sensors Based on WO_3 Sputtered Layers Enhanced by Ultra Violet Light Illumination

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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

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b) Operating principle and sensor structure
c) Ozone detection by sensitive film

II. Thin film deposition and crystalline structure

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I. Context, technology and detection principle

A Gaz to monitor : Ozone

- Ozone presence in troposphere due to human activity :

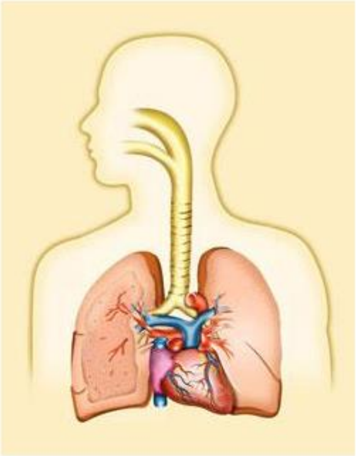
Heat / Solar radiation

VOCs

NOx

Ozone formation

- Ozone has hazardous impact on fauna and flora health



European and american environmental agency report respiratory symptoms for O_3 concentrations > 60ppb

Severity

1 Cough, Wheezing, throat irritation
2 Asthma attack and other respiratory disease
3 Hospitalization

→ Monitor and control O_3 concentration in air

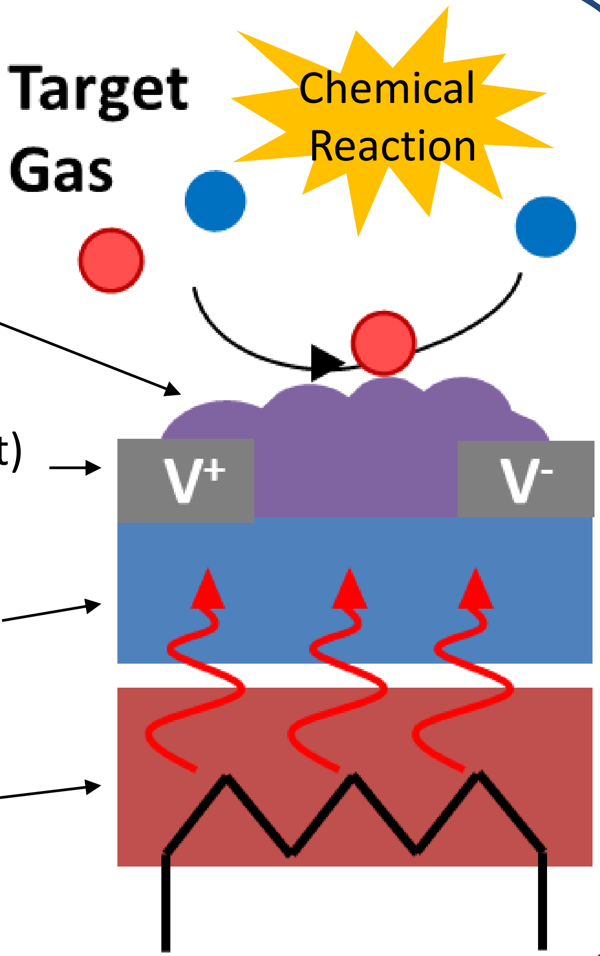
Operating principle and sensor structure

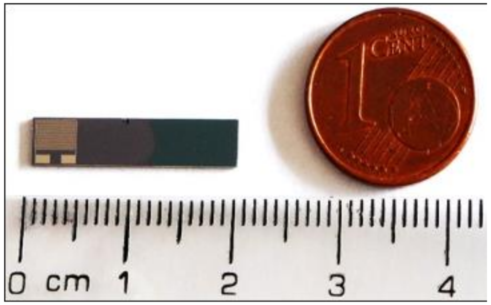
1) Sensitive film (WO_3)
Gas interaction

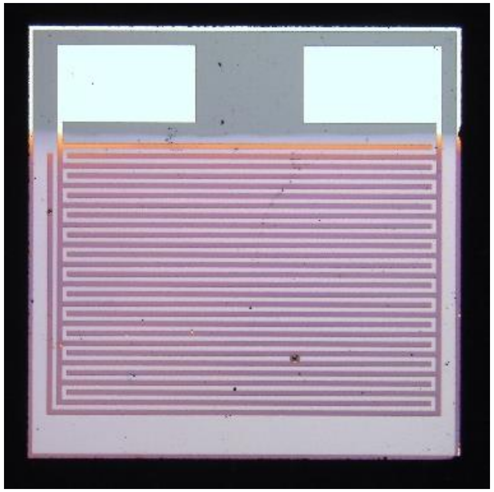
2) Measuring electrode (Pt)
Information reading

3) Substrate (Si/SiO_2)
Electrical insulation

4) Heating device
Reaction control







Dimension : 4x4mm
Electrode thickness : 100nm
Electrode gap : 50µm

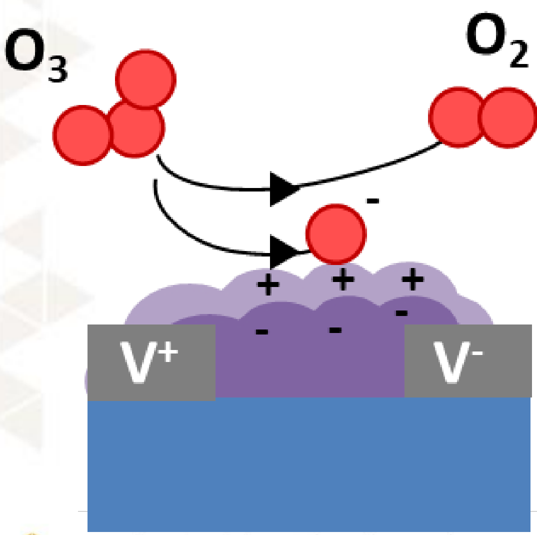
- O_3 decomposes on WO_3 surface by reacting with free charge carriers

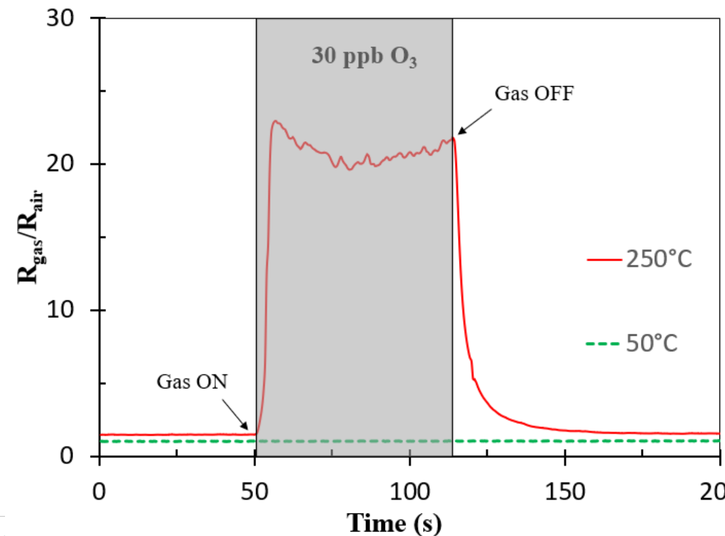
Upon increasing $[O_3]$:	$O_{3\,(gas)} + e^- \rightarrow O^-_{(ad)} + O_{2\,(gas)}$	Resistivity increase
Upon decreasing $[O_3]$:	$2O^-_{(ad)} \rightarrow O_{2\,(gas)} + 2e^-$	Resistivity decrease

Needs elevated temperature **(250-300°C)** to bring energy allowing oxydo-reduction reactions.

Drawbacks : high power consumption, material ageing, no flexible substrate

→ UV illumination creates free charge carriers allowing lower operating temperature





II. Thin film deposition and crystalline structure

WO_3 thin film deposition

- **Film Deposition**

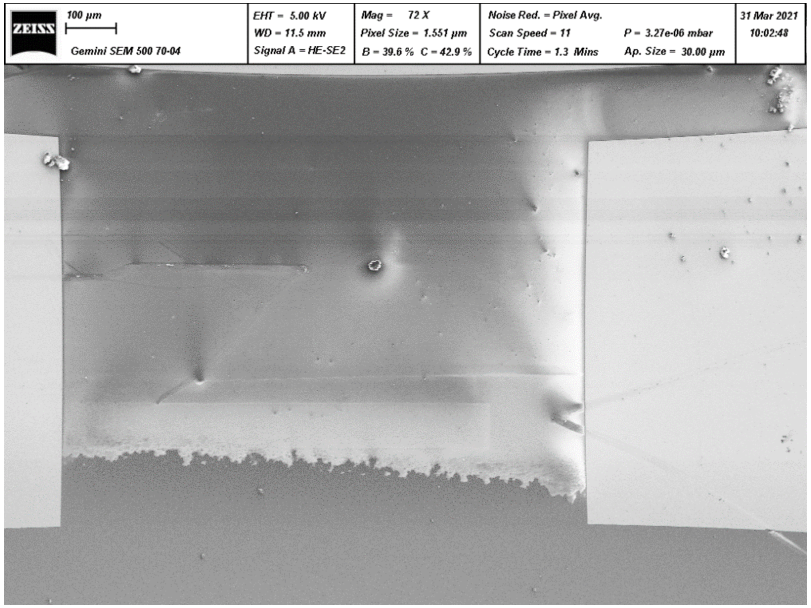
Reactive RF magnetron sputtering
Argon/oxygen ratio → **3:2 ; 1:1; 2:3**
Thin layer : 50nm

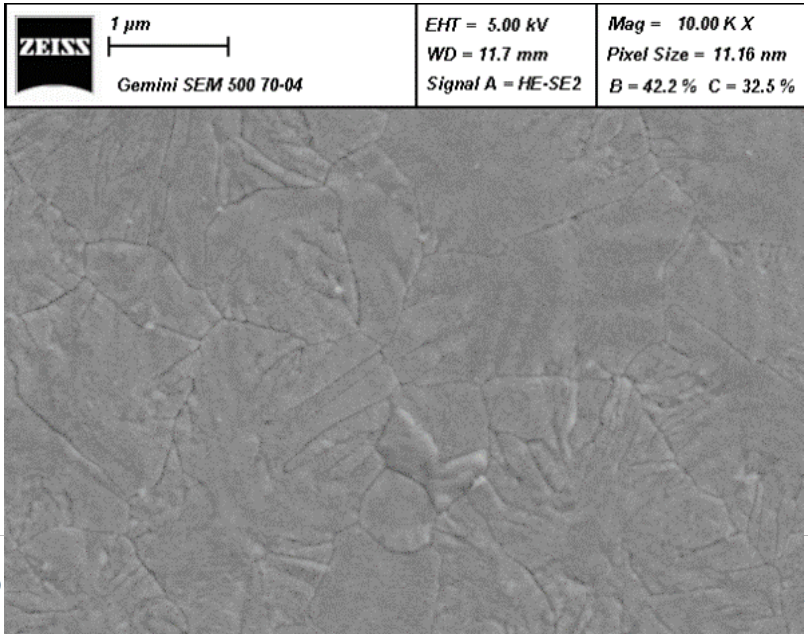
- **Annealing**

On plate 2h at 400°C in air,

- **EDXS measurements** (after annealing)

Identical chemical composition for all 3 samples
Quasi stoichiometric : 77%O ; 23%W





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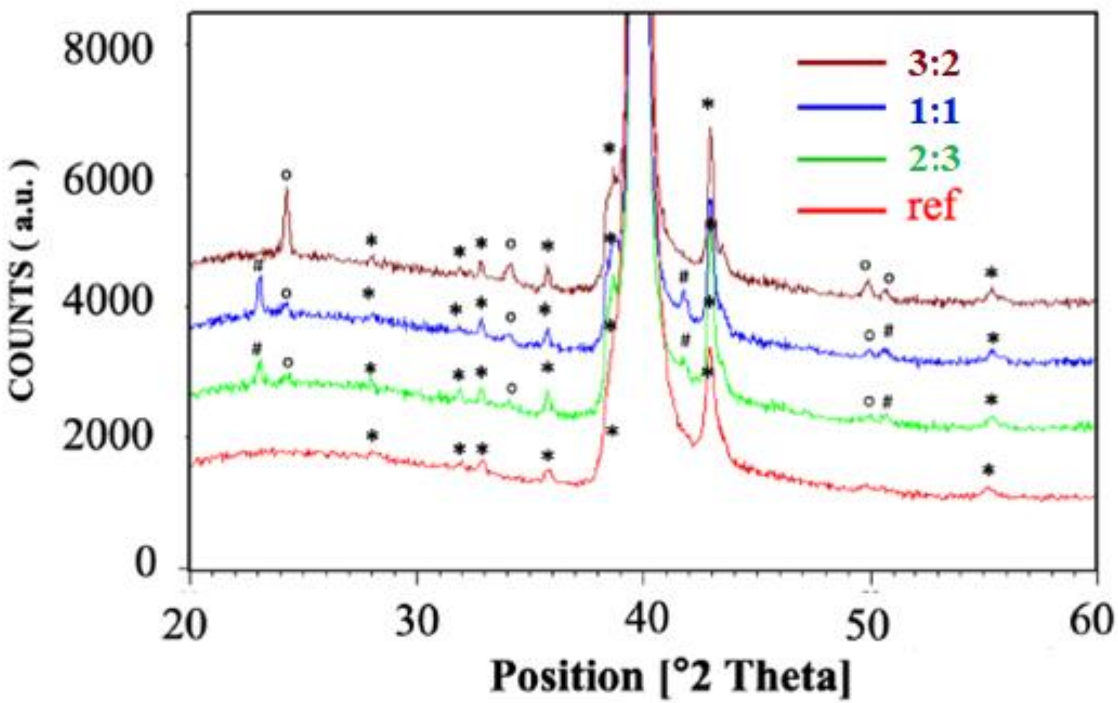
XRD diffractogram of WO_3 thin film

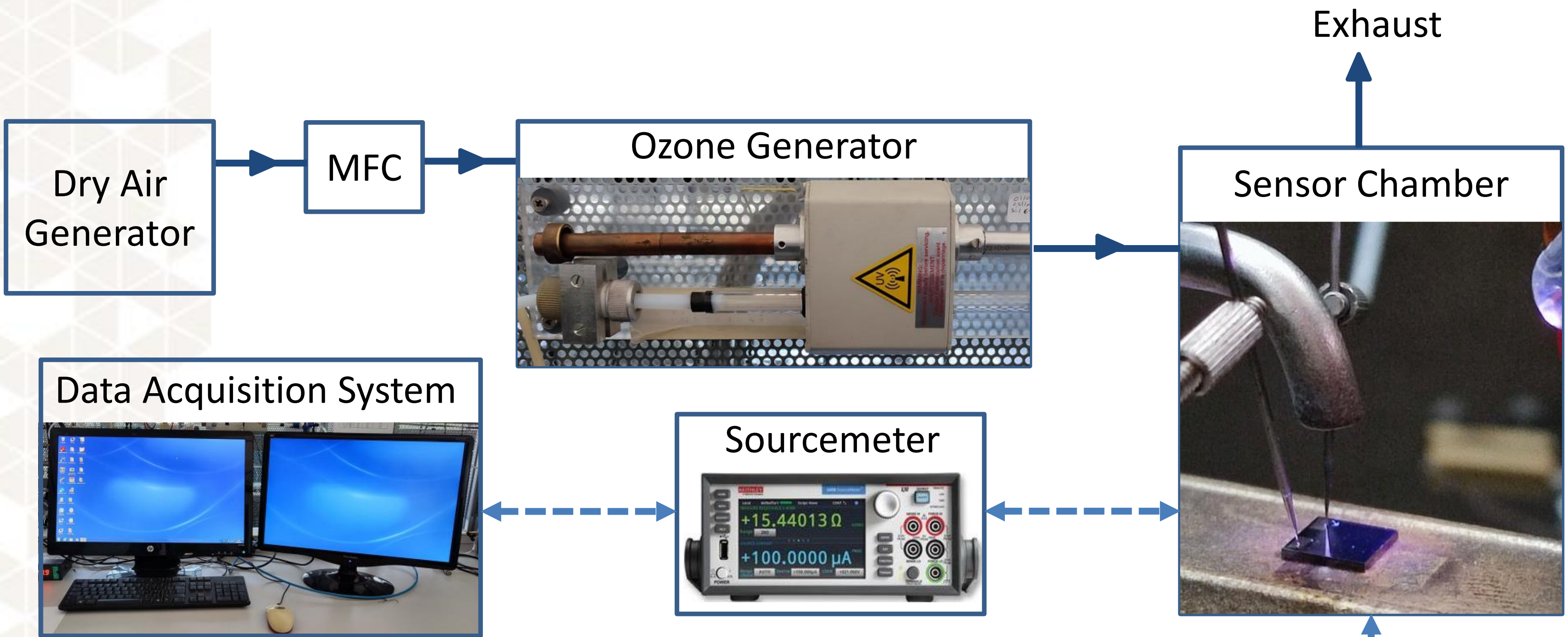
- Analyse of transducer without and with WO_3 films
- Comparison between 3 samples with different Ar/O_2 deposition ratio

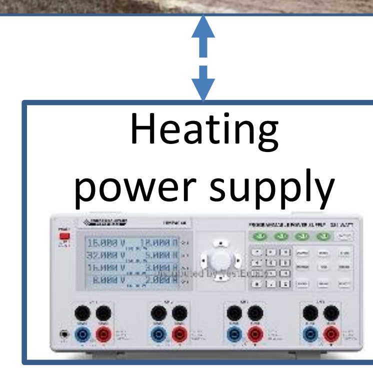
* Peaks correspond to the ones on reference spectra (Pt and Si/SiO2)
# and o peaks match Monoclinic WO_3 structure
# (002) and o (200) lowest peaks vary with Ar/O_2 ratio → grain growth influence



III. Sensor electrical characterization

Sensor test bench





Dry air flow rate : 500 sccm

O_3 in dry air : 30 ppb; 65 ppb; 120 ppb

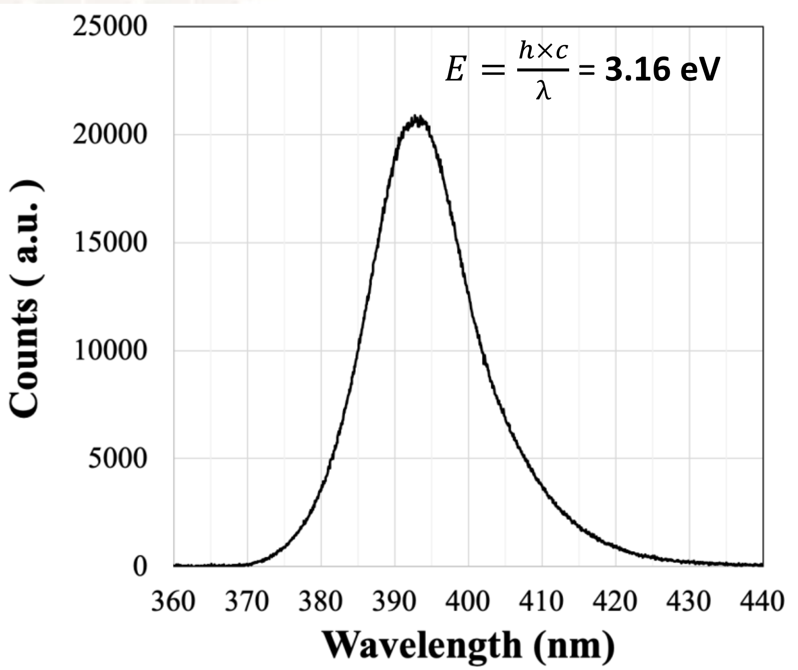
Operating temperature : 50°C

UV illumination effect

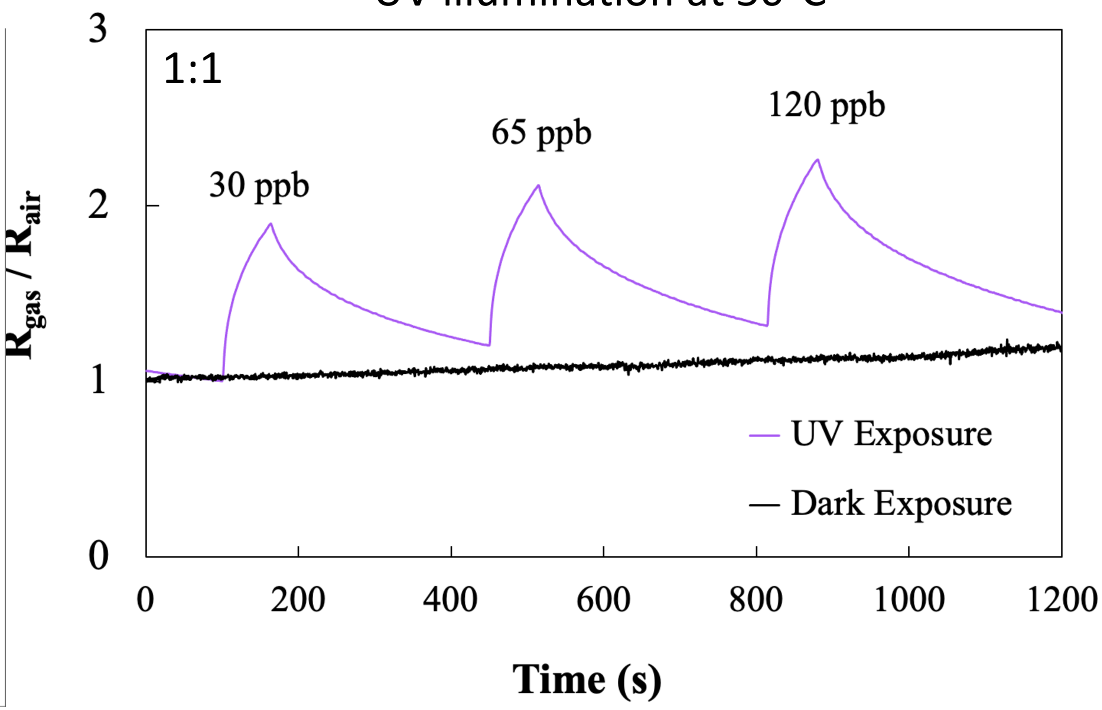
- Illumination of WO_3 with photon energy higher than indirect band gap (2.6-2.8 eV) → creation of **free electrons** → reaction

O_3 gas reacts even at low temperature → response amplitude remains low

Need to improve sensor response … !!!



UV illumination at 50°C

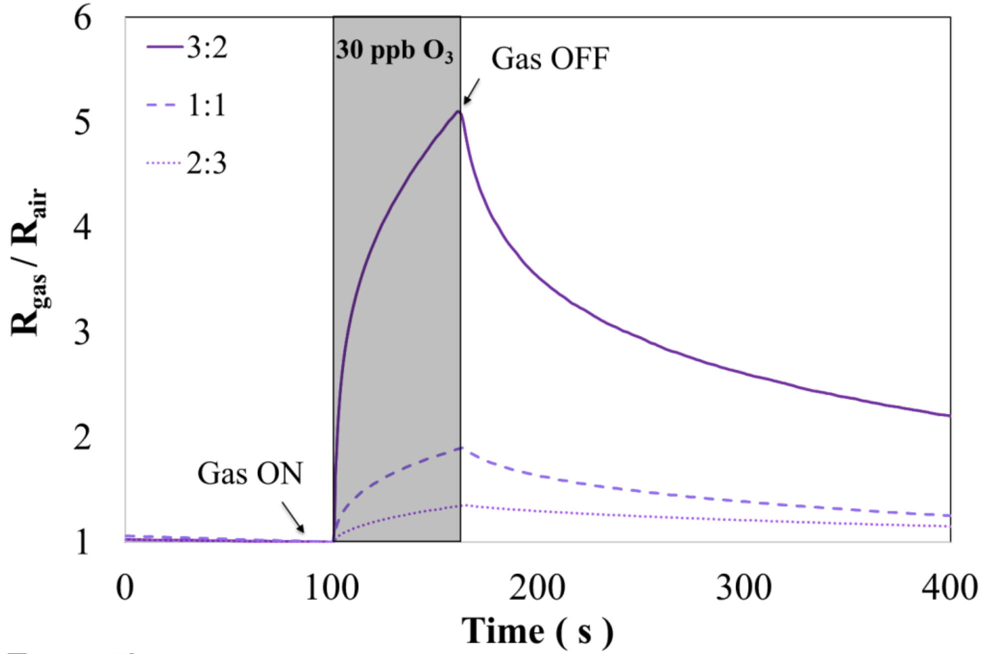


Sensor response for different sputtering parameters

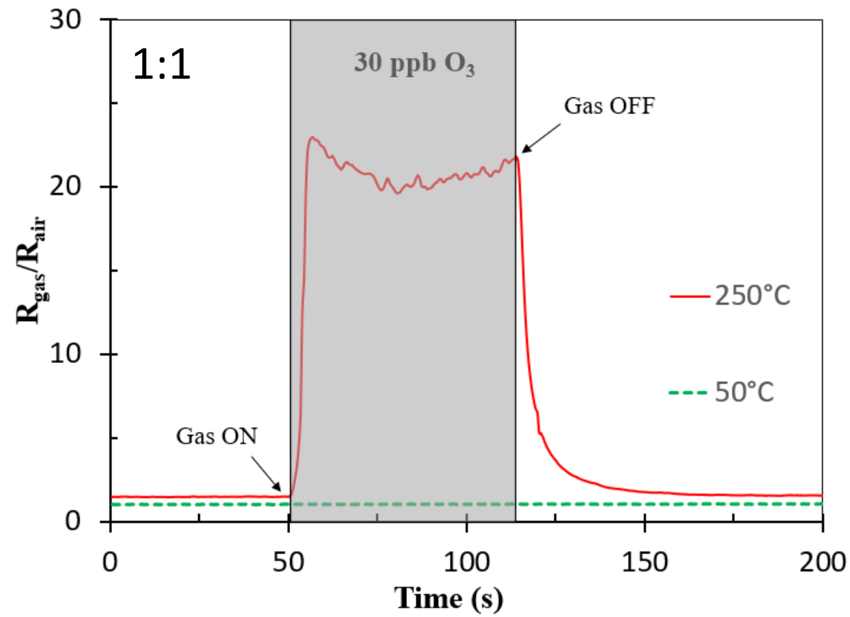
- ✓ O_3 detection for all 3 samples at 50°C
- ✓ Best response for Ar/O_2 ratio of 3:2

No stabilization in 60s O_3 exposure nor complete desorption in 240s
→ slow process compared to high temperature operating

UV illumination at 50°C



Dark at 250°C

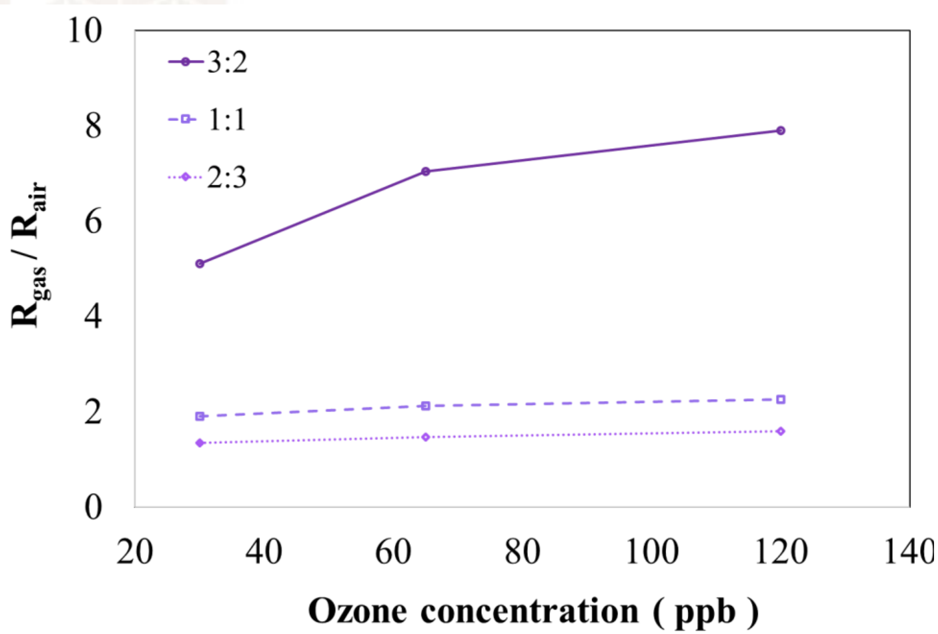


✓ 30, 65 and 120 ppb O_3 detected for all samples

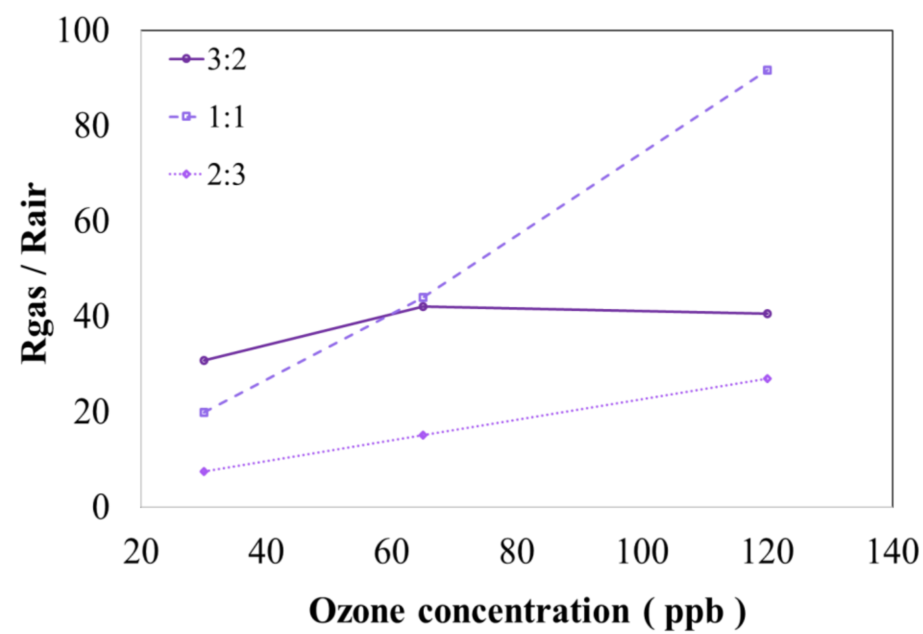
Under UV and low temperature : best response for Ar/O_2 ratio of 3:2

Under Dark and high temperature : best response for Ar/O_2 ratio of 1:1

UV illumination at 50°C



Dark at 250°C



IV. Conclusion

Conclusion

Ar/O_2 sputtering gas ratio affects the film microstructure

Optimization of sensor performance through Ar/O_2 ratio during sputtering

✓ UV illumination enables low temperature operating
→ Power consumption decreases

✓ Best results under UV for Ar/O_2 ratio of 3:2

✓ O_3 detection for 30, 65 and 120ppb

Ozone decomposition on WO_3 remains a slow process

- No response stabilization
- Long response and recovery time
- Small response amplitude

For better understanding → complementary measurements of microstructure

Acknowledgments

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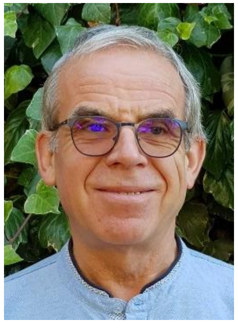

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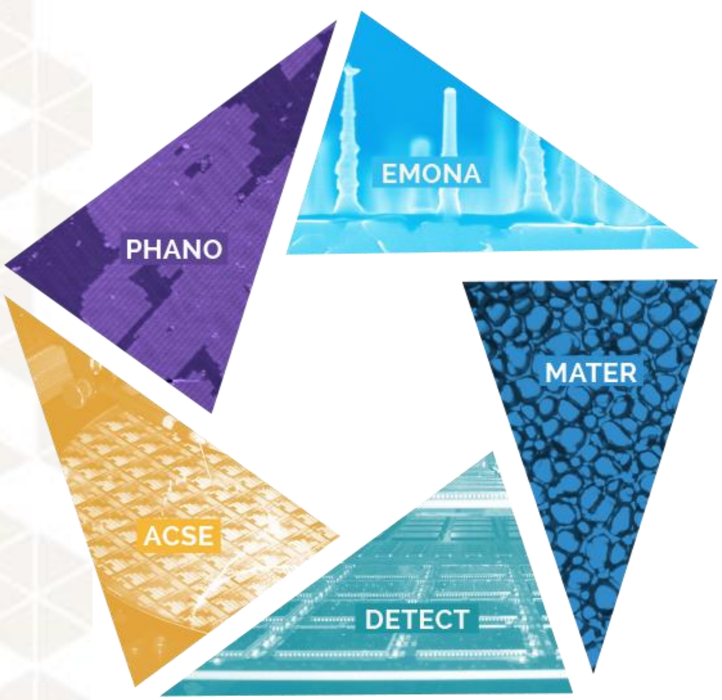
Thank you for your attention



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