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 2$^{nd}$ year Ph.D. student back to the IM2NP Institute, developing hydrogen sensors for anaerobic environment.
I. Context, technology and detection principle
   a) A gaz to monitor: ozone
   b) Operating principle and sensor structure
   c) Ozone detection by sensitive film

II. Thin film deposition and crystalline structure
   a) WO₃ thin film deposition
   b) XRD diffractogram of WO₃ thin film

III. Sensor electrical characterization
   a) Sensor test bench
   b) UV illumination effect
   c) Sensor response for different sputtering parameters
   d) Comparison UV/heating

IV. Conclusion
I. Context, technology and detection principle
- Ozone presence in troposphere due to human activity:

  ![Diagram of Ozone formation](image)

  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

Target Gas

Chemical Reaction

Dimension: 4x4mm
Electrode thickness: 100nm
Electrode gap: 50μm
Ozone detection by sensitive film

- O$_3$ decomposes on WO$_3$ surface by reacting with free charge carriers

Upon increasing [O$_3$]:
\[
\text{O}_3\text{(gas)} + e^- \rightarrow \text{O}^-\text{(ad)} + \text{O}_2\text{(gas)}
\]
Resistivity increase

Upon decreasing [O$_3$]:
\[
2\text{O}^-\text{(ad)} \rightarrow \text{O}_2\text{(gas)} + 2e^-
\]
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
- 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/SiO$_2$)
# and o peaks match Monoclinic WO$_3$ structure
# (002) and o (200) lowest peaks vary with Ar/O$_2$ ratio $\rightarrow$ grain growth influence
III. Sensor electrical characterization
Sensor test bench

Dry Air Generator → MFC → Ozone Generator → Sensor Chamber → Exhaust

Data Acquisition System → Sourcemeter

Dry air flow rate: 500 sccm
O₃ 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) $\rightarrow$ creation of free electrons $\rightarrow$ reaction

O$_3$ gas reacts even at low temperature $\rightarrow$ response amplitude remains low

Need to improve sensor response ... !!!

\[ E = \frac{h \times c}{\lambda} = 3.16 \text{ eV} \]

UV illumination at 50°C
Sensor response for different sputtering parameters

✓ O₃ detection for all 3 samples at 50°C

✓ Best response for Ar/O₂ ratio of 3:2

No stabilization in 60s O₃ 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 O₃ detected for all samples

Under UV and low temperature: best response for Ar/O₂ ratio of 3:2

Under Dark and high temperature: best response for Ar/O₂ ratio of 1:1
IV. Conclusion
Ar/O₂ sputtering gas ratio affects the film microstructure

Optimization of sensor performance through Ar/O₂ ratio during sputtering

✓ UV illumination enables low temperature operating
  → Power consumption decreases

✓ Best results under UV for Ar/O₂ ratio of 3:2

✓ O₃ detection for 30, 65 and 120ppb

Ozone decomposition on WO₃ remains a slow process
• No response stabilization
• Long response and recovery time
• Small response amplitude

For better understanding → complementary measurements of microstructure
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Thank you for your attention

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