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Detection of indoor air pollutants using reactive sputtering/GLAD of tin oxide thin films

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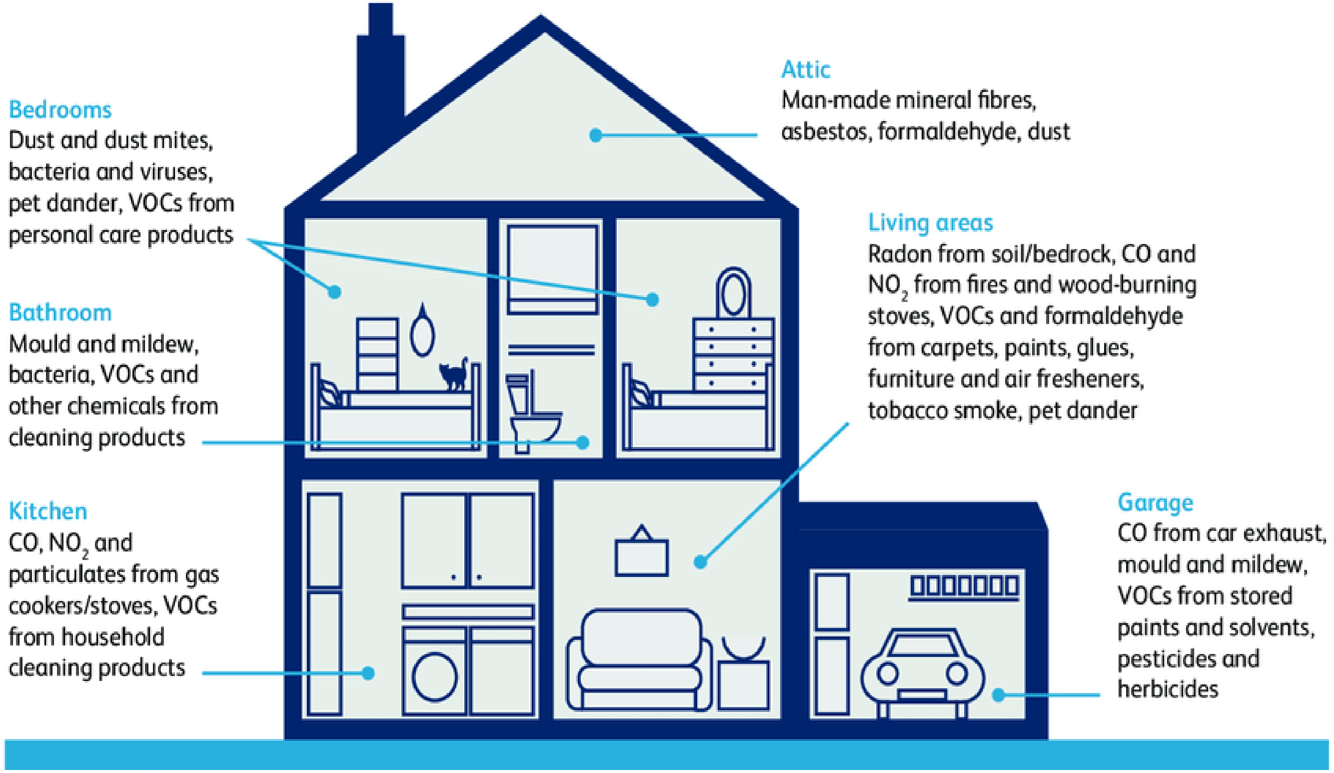
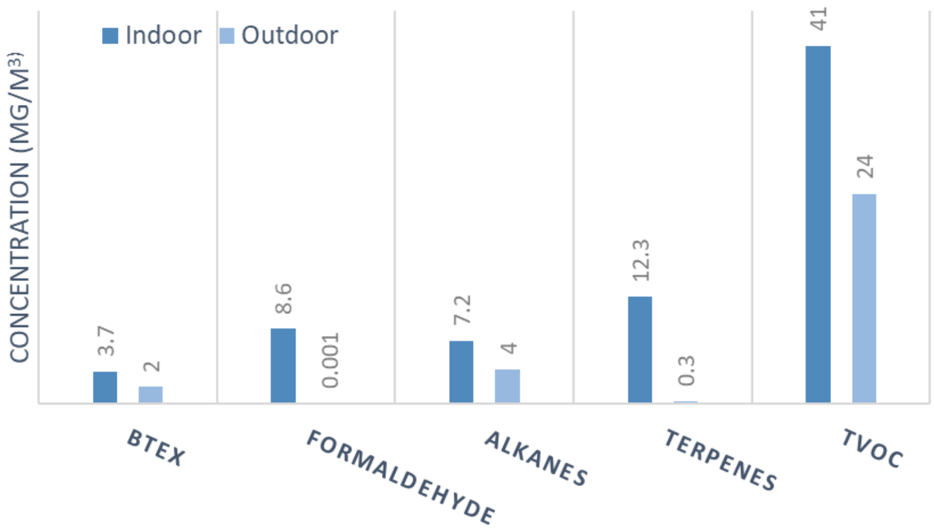
What is Indoor Air Quality ?

Indoor Air Quality (IAQ) refers to the air quality within and around buildings and structures.
IAQ index is used to evaluate the health risks for occupants depending on pollutants levels present indoor.

Unexpected indoor sources



Indoor vs outdoor VOC levels

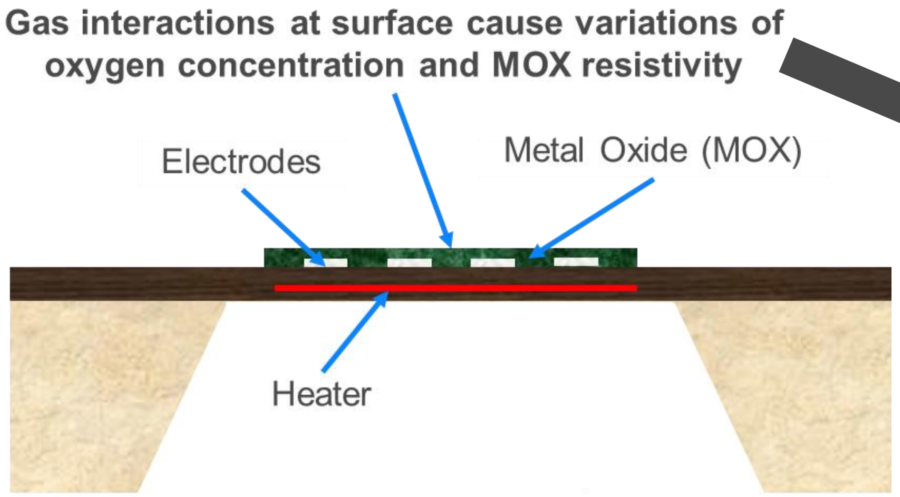


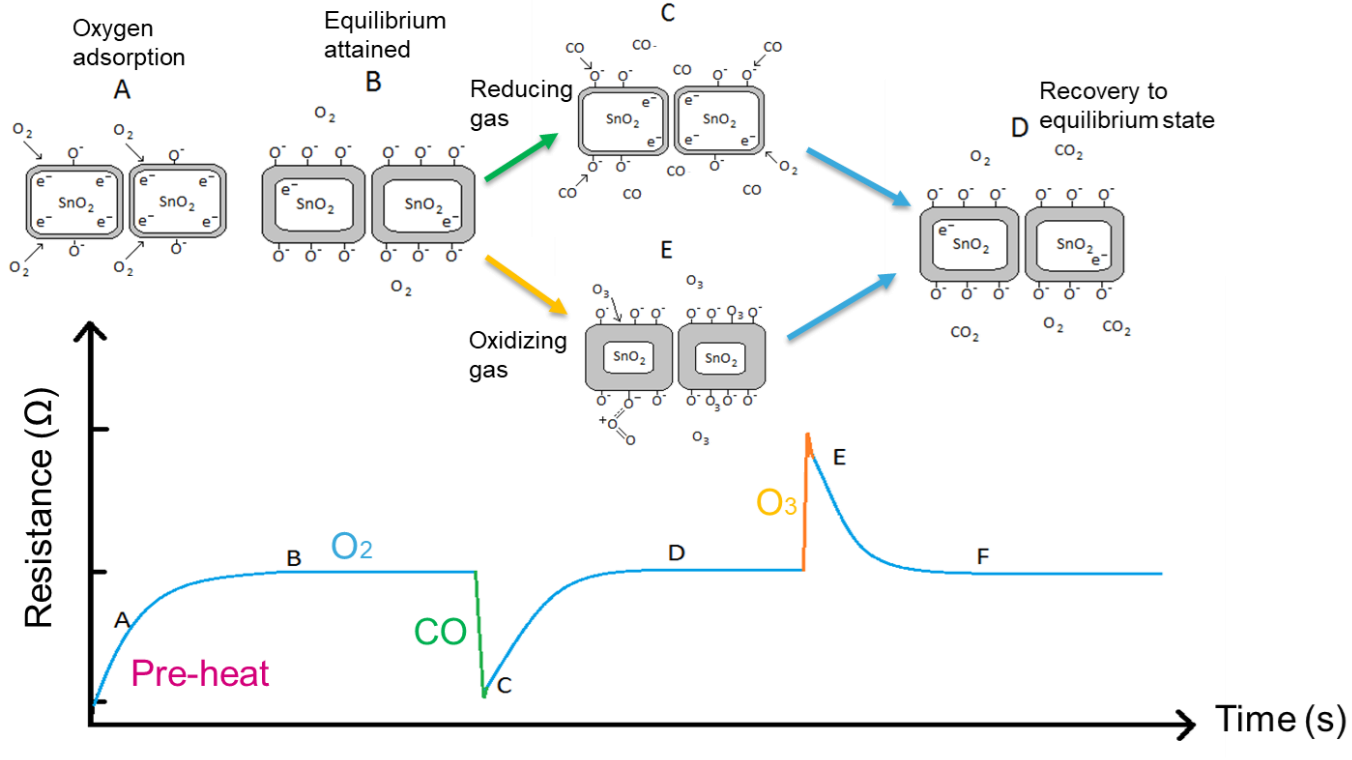
Concentrations of many VOCs are consistently higher indoors (up to ten times higher) than outdoors.

MOX sensors

Metal Oxides are one of the most studied materials in gas sensing applications due to their :

- Low cost
- High sensitivity





Example of oxidation pathway for ethanol

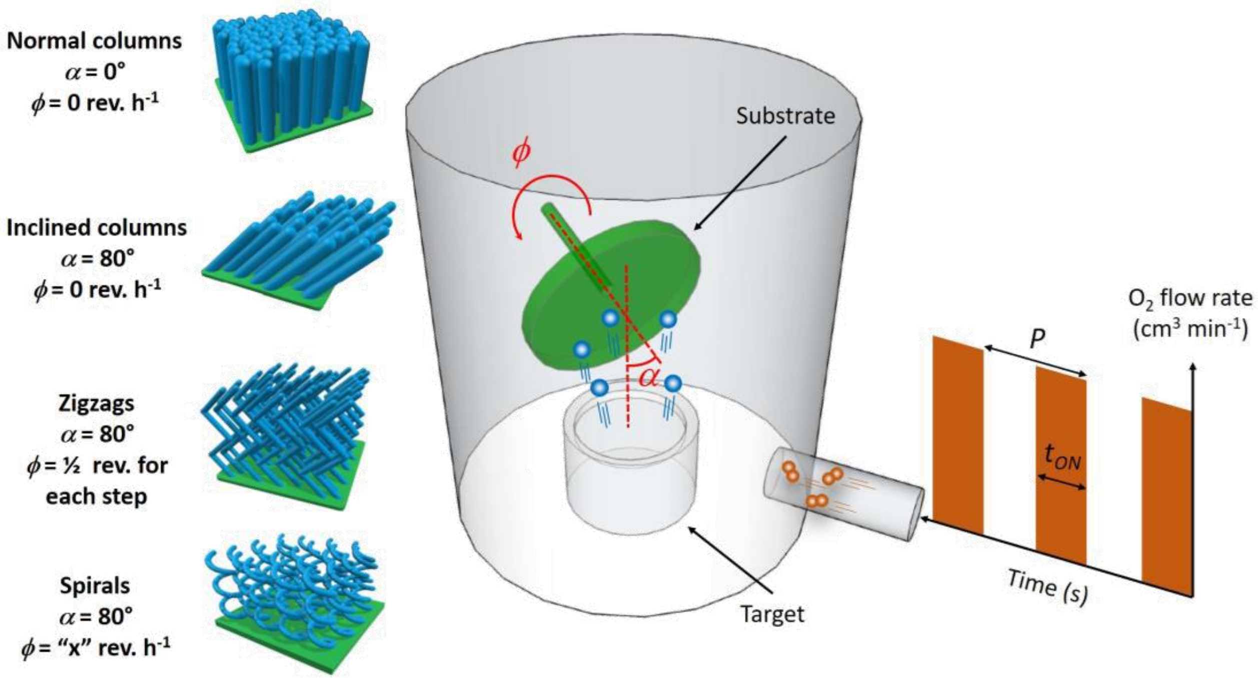
$$CH_3CH_2OH_{(gas)} + [O]_{(ads)} \longrightarrow CH_3CHO_{(ads)} + H_2O$$

Outline

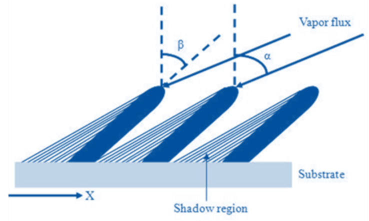
- Introduction to PVD with GLAD (Glancing angle deposition)
- Characterization of tin oxide films
  - Imaging
  - Physicochemical characterization
  - Bulk & surface porosity
- BTEX detection
  - Benzene
  - BTEX & Humidity
  - Selective detection of BTEX
- Conclusion & perspectives

PVD with GLAD (Glancing angle deposition)

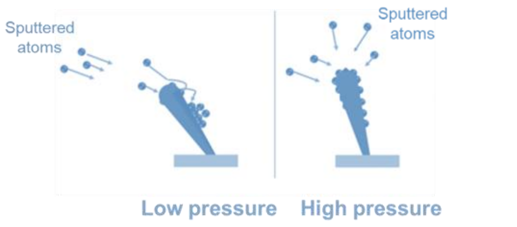
Illustration of the GLAD (Glancing angle deposition) sputtering system. Sn target was DC sputtered, with a constant supply of oxygen and argon



Shadow effect *(Tilting angle)*



Intensified collisions *(Deposition pressure)*



Deposition pressure →

Tilting angle ↓

	C3 • Tilting angle : **0˚** • Deposition pressure: **3.10^{-3} mbar**	**C6** • Tilting angle : **0˚** • Deposition pressure: **6.10^{-3} mbar**
	I3 • Tilting angle : **80˚** • Deposition pressure: **3.10^{-3} mbar**	**I6** • Tilting angle : **80˚** • Deposition pressure: **6.10^{-3} mbar**

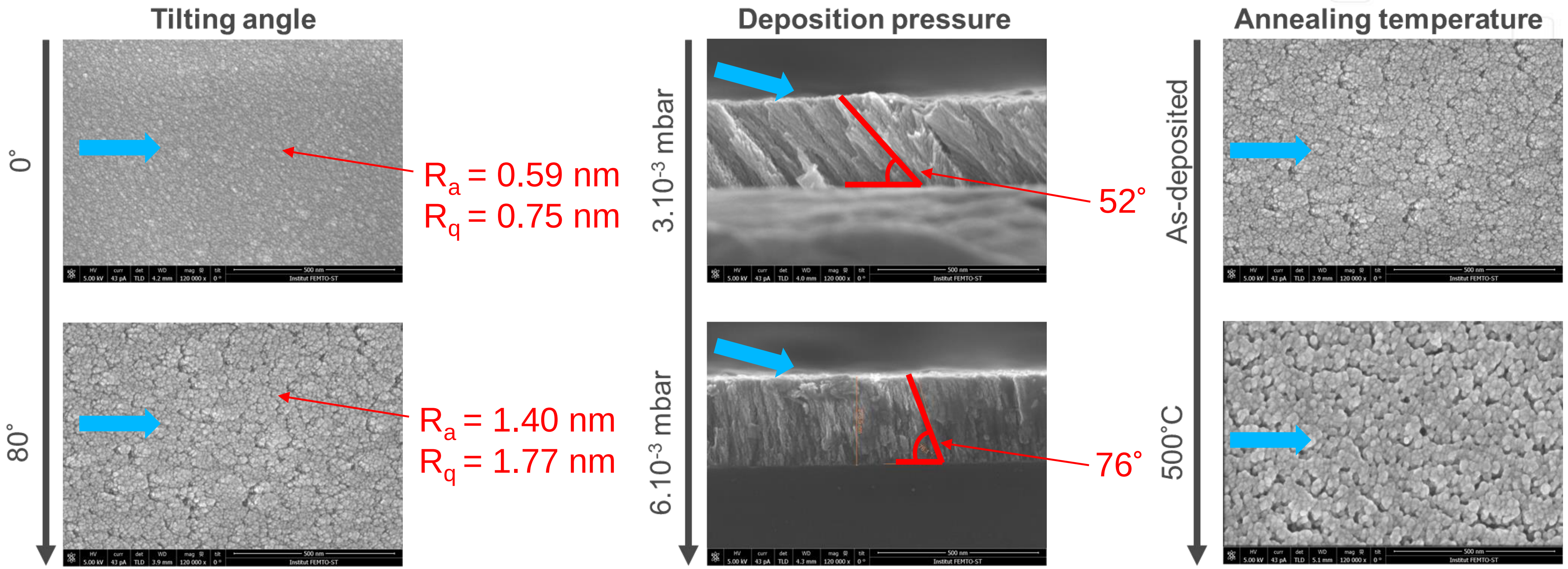
Two parameters were studied, 4 films deposited with a thickness around a thickness of 250nm, and a constant power and oxygen flow :

- Tilting angle α (0˚ & 80˚)
- Deposition pressure (3.10^{-3} mbar & 6.10^{-3} mbar)

SEM imaging

Sputtering direction

Imaging was done to study the nanostructured films as well as their surface roughness and the impact of annealing.



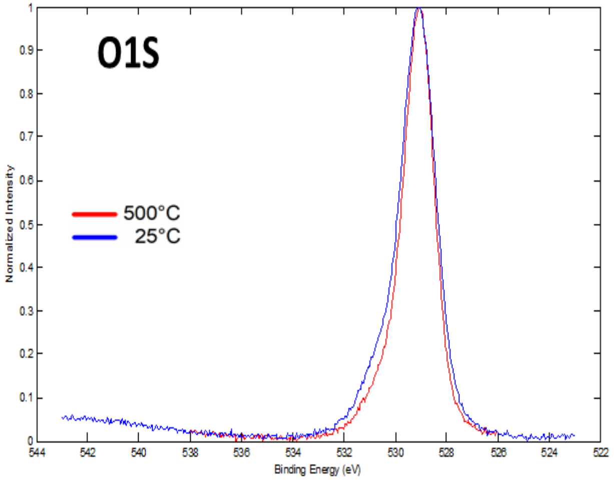
- Tilting the substrate leads to columnar structures due to the shadow effect
- Increasing the deposition pressure straightened the columnar structures
- The architectures of the material were maintained with post-deposition annealing treatment

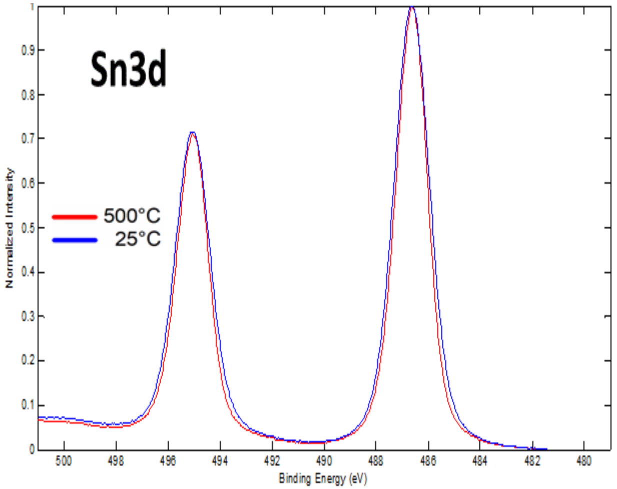
Physicochemical characterization

Surface chemical composition data obtained from XPS

Surface concentration (%)

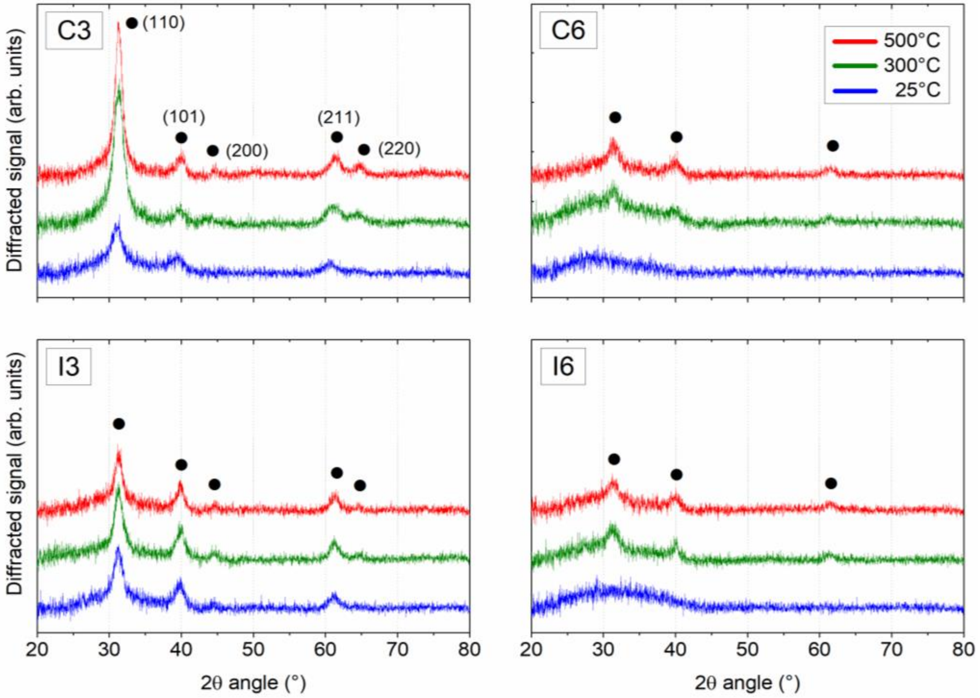
Annealing temperature (˚C)	O	Sn
25˚C	52.86	47.14
500˚C	54.18	45.82





- Sub-stochiometric tin oxide SnO_{2-x}
- Slight variation of the chemical composition with an annealing at 500˚C

X-Ray Diffraction for each annealing temperature

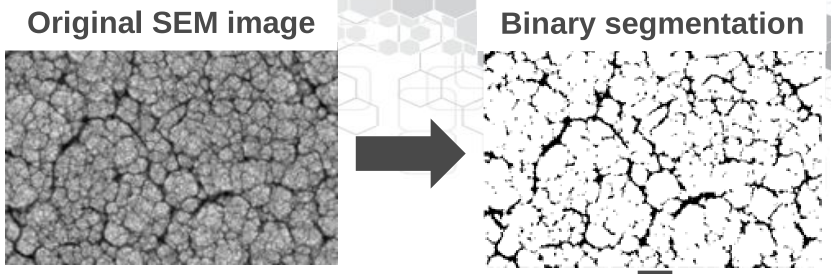


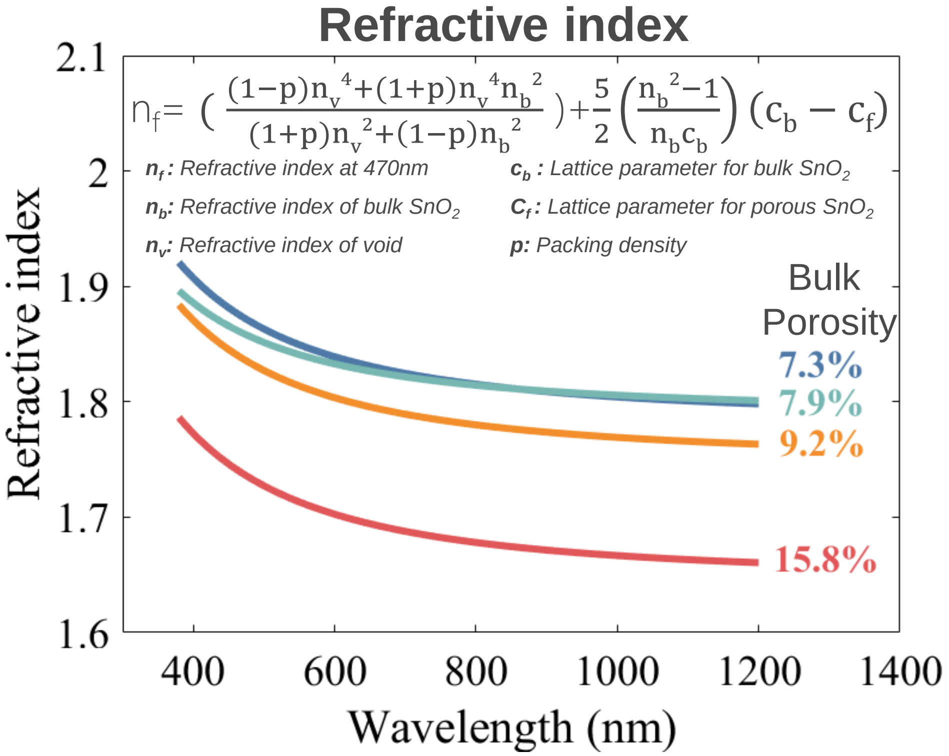
Films deposited at higher pressure require annealing at 500˚C to achieve crystallization

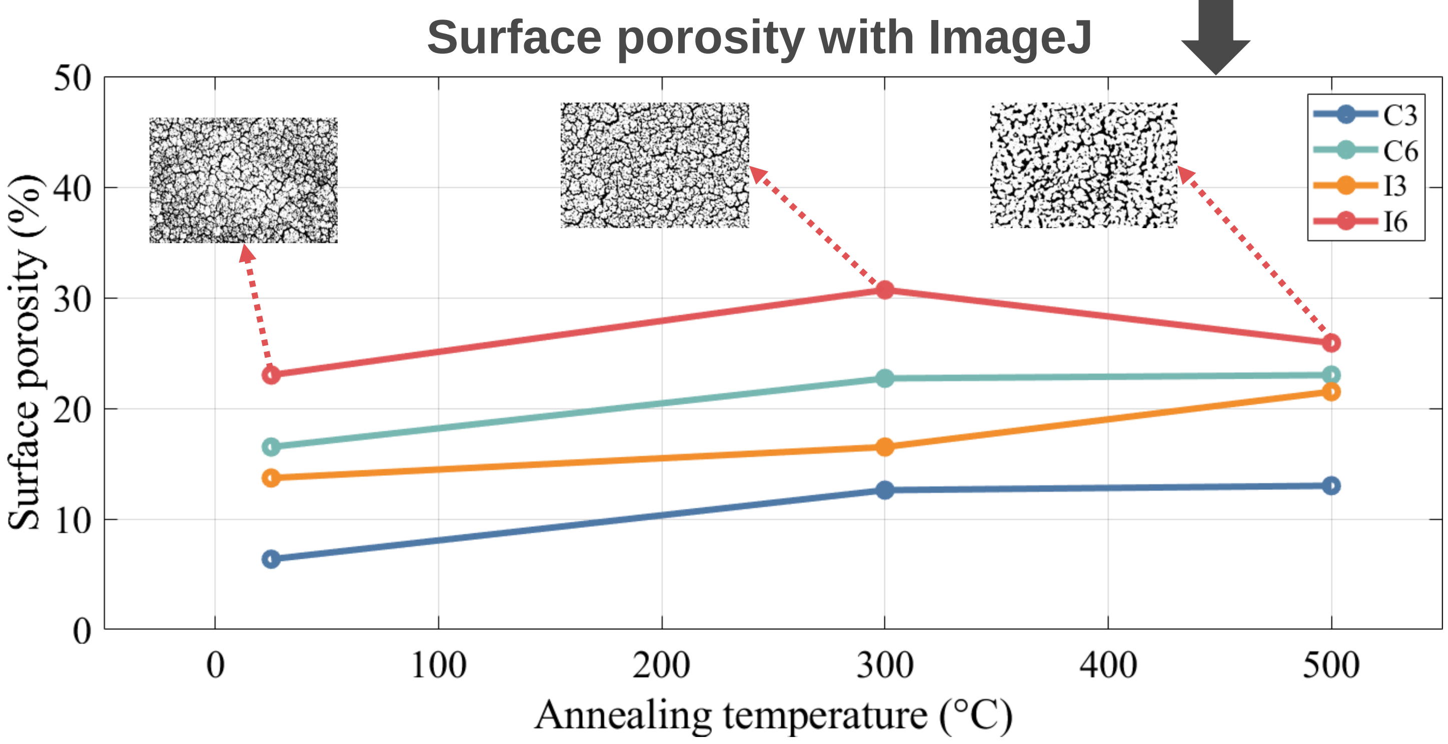
Optical characterization

Bulk & surface porosity were studied with different techniques:

- Bulk porosity : Optical approach based on refractive indices
- Surface porosity : Image processing of binarized SEM images







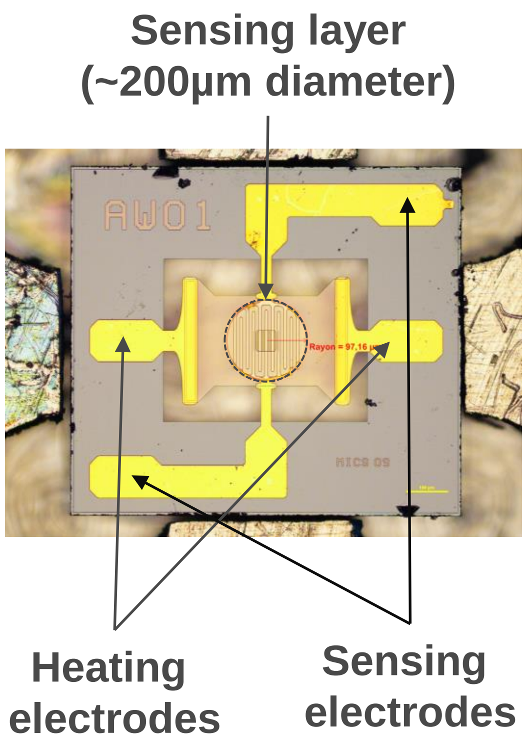
Tilted depositions & higher deposition pressures were found to increase the bulk and surface porosity resulting in higher surface areas

Micro-hotplate testing : Benzene detection

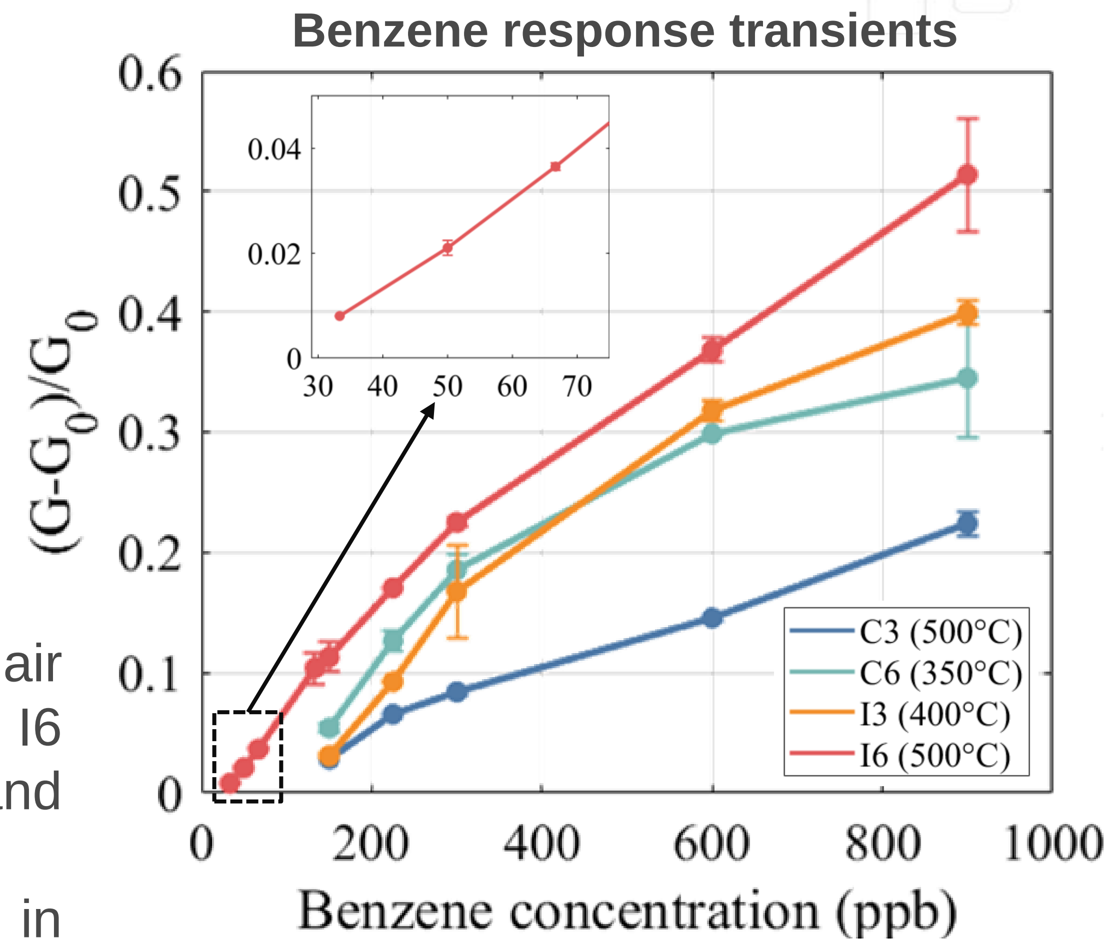
Tin oxide thin films, were deposited on a SGX micro-hotplate silicon-based sensor.

Main features of micro-sensors are :

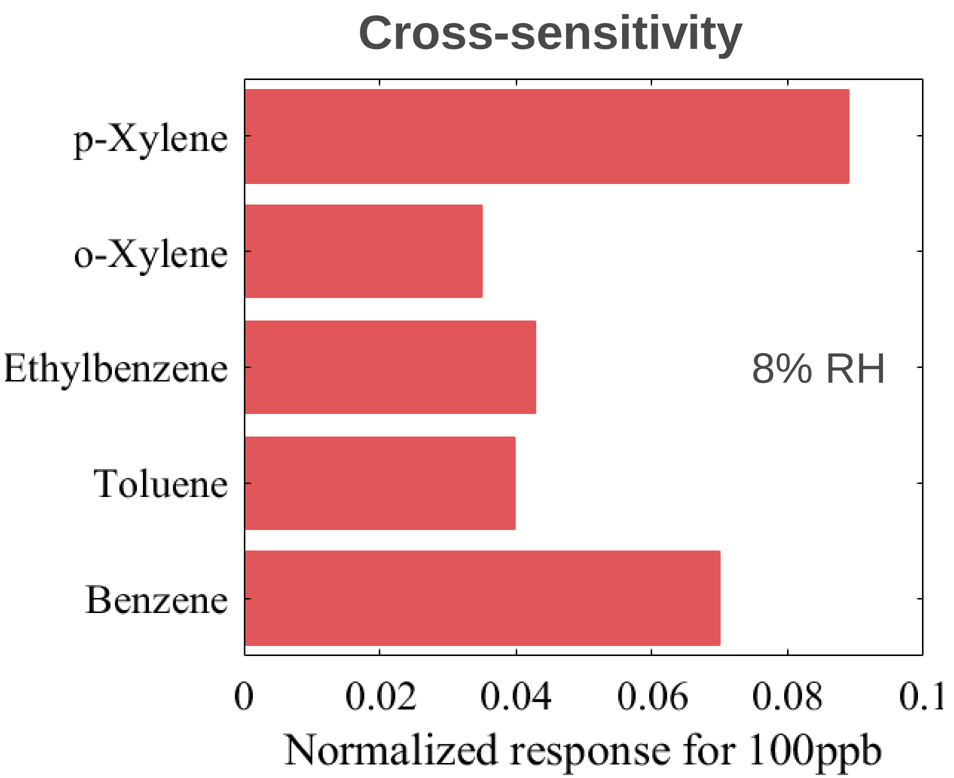
- Localized deposition
- High thermal uniformity
- Low power consumption
- Highly stable heater resistance

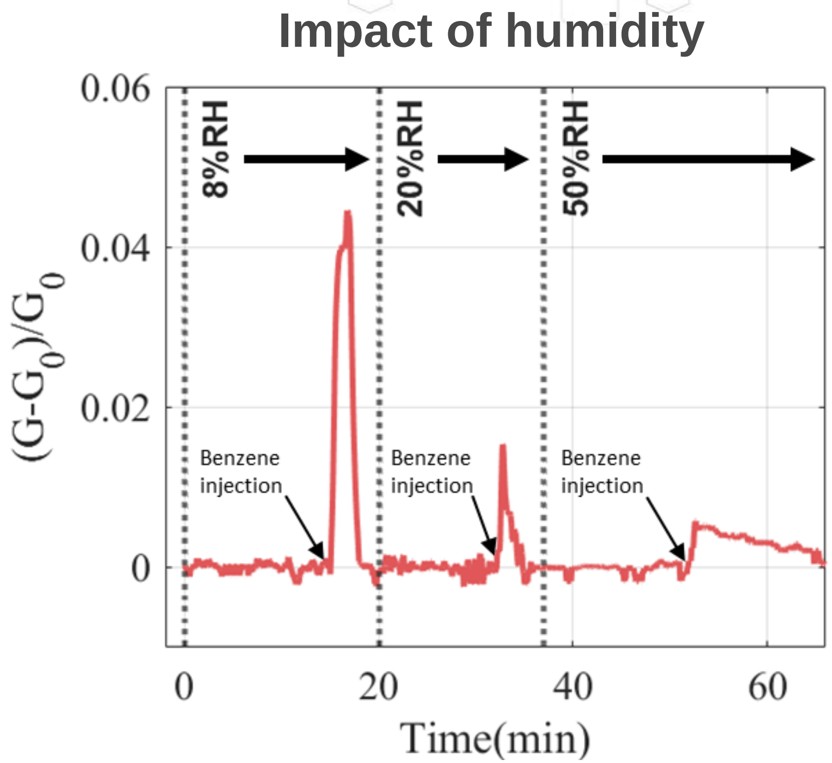


With Benzene tests (2min exposition) under nearly dry air (8% RH) at each sensor's optimum temperature, I6 showed the highest responses due to its high bulk and surface porosity.
I6 sensor was the only sensor able to detect benzene in concentrations as low as 25 ppb.



Micro-hotplate testing : Cross-sensitivity & humidity for BTEX





Cross-sensitivity tests with I6 for BTEX showed great sensitivity for all compounds with an enhanced response for para-Xylene

Humidity hindered the performances of I6 :

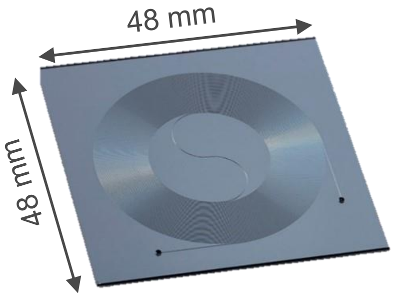
- Lower sensitivity
- Longer response & recovery times

Coupling with GC µColumn : Selectivity at 60% RH

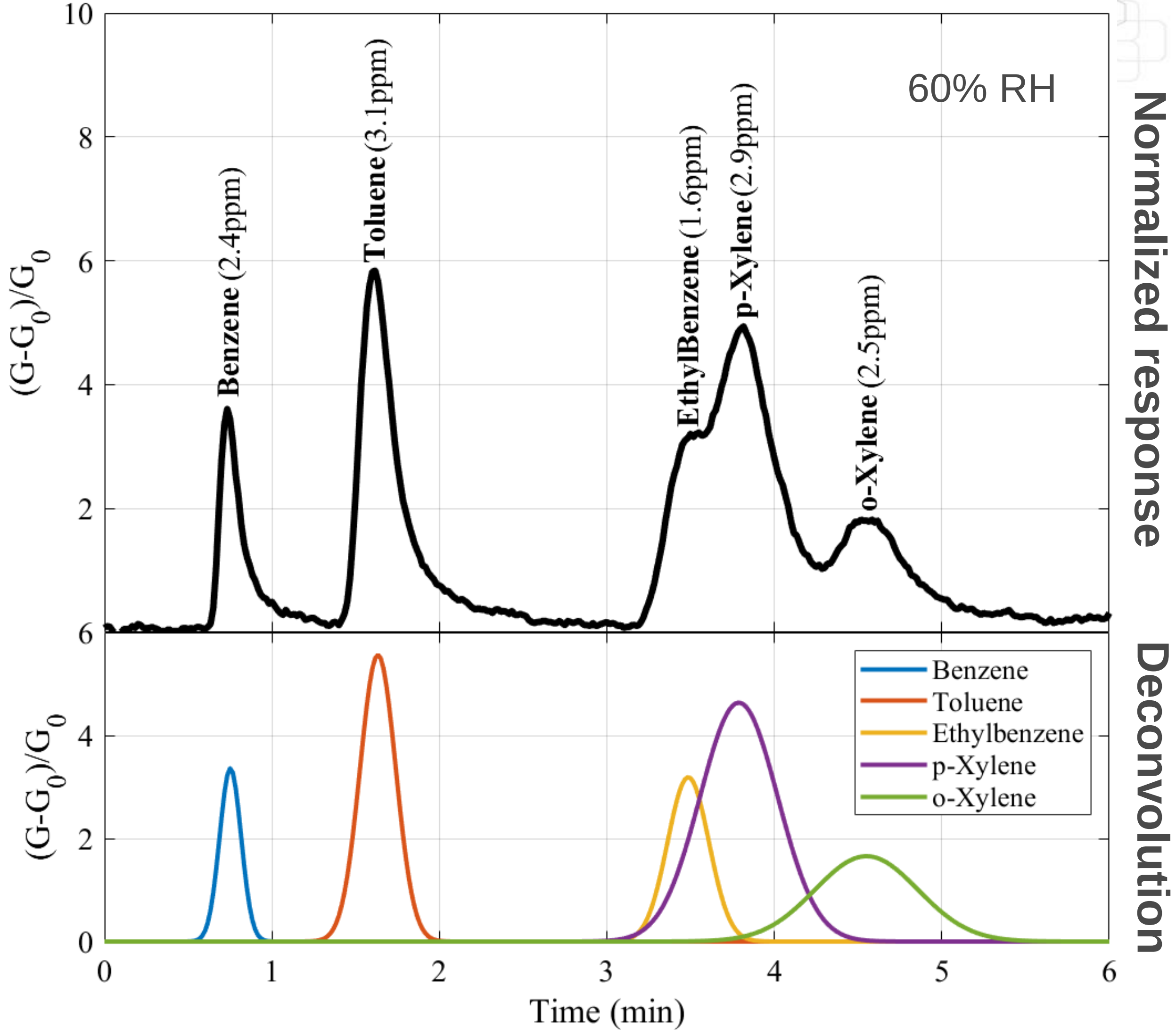
MOX sensors suffer from poor selectivity and are massively impacted by high values of humidity

Our team have recently been working on miniaturized device to selectively detect VOCs present in mixtures.

GC µcolumn



MOX sensor



By adding a GC micro-column in front of the MOX sensor, we are able to selectively detect BTEX compounds in a mixture, and under high relative humidity values (60%).

Conclusion & perspectives

- Successful synthesis of nanostructured thin films of tin oxide
- Tuning of porosity for enhanced sensing performances
- Selective detection of BTEX in humid environments

What's next ?

- Identifying preconcentration adsorbents to reach trace level BTEX in indoor air
- Integration of the miniaturized system
- Target other VOCs present in indoor air

Thank you for your attention !