European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

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Year 3: 1 July 2014 - 30 June 2015 (*Ongoing Action*)

Effect of dopants and humidity on NO_2-sensing with semiconducting SnO_2

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DLR

COST EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

EuNetAir European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability

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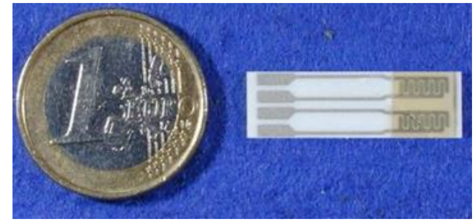
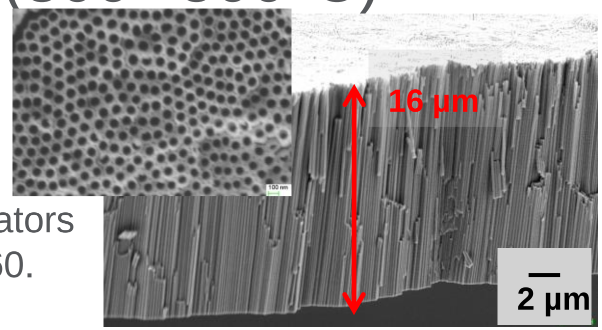
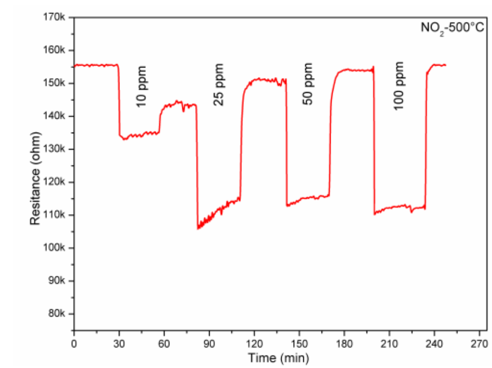
Current research activities at DLR



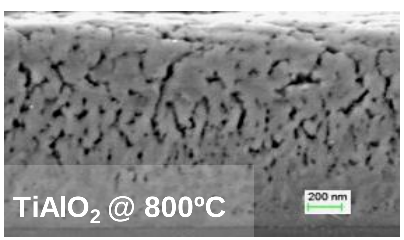
- Nano-tubular TiO_2-sensor electrodes for NO_2 and CO sensing at intermediate temperatures (300°-500°C)

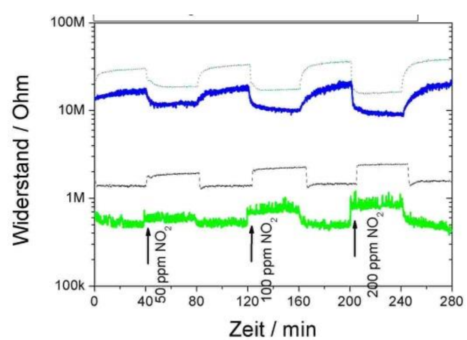
  - Y. Gönüllü, C.G. Mondragón Rodríguez,
  - B. Saruhan, M. Ürgen, Improvement of gas
  - sensing performance of TiO_2 towards NO_2
  - by nano-tubular structuring, Sensors and Actuators
  - B: Chemical, Volume 169 (5 July 2012)151–160.

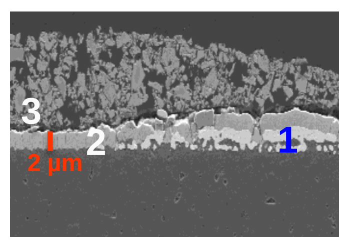


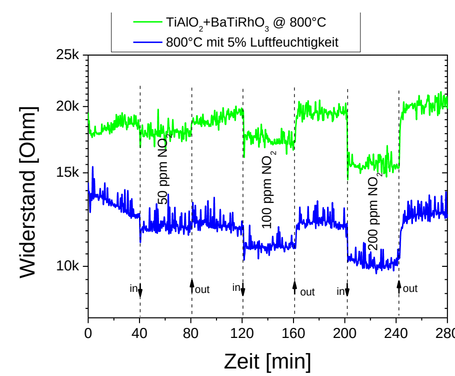


- NO_2 sensing at elevated temperatures (600°-900°C) by the use of doped TiO_2 and catalytic self-regenerative Perovskite layers







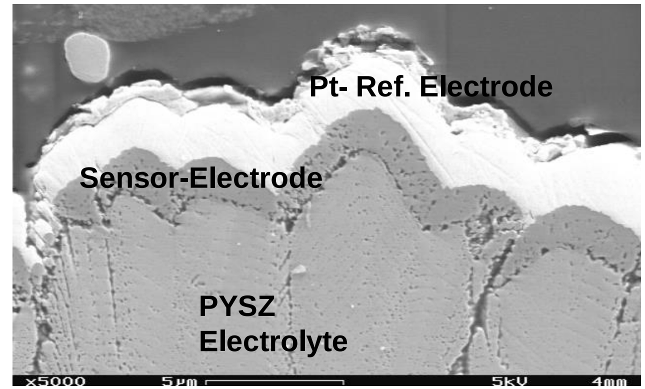


Current research activities at DLR

- Total NO_x sensing by means of component integrated impedance-metric sensors

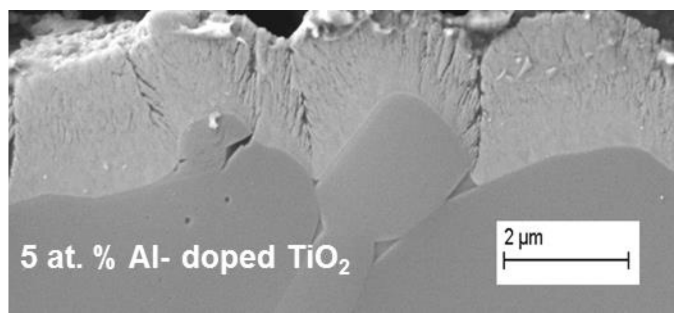
- M. Stranzenbach and B. Saruhan, Equivalent circuit analysis
- on NOx impedance-metric gas sensors, Sensors and Actuators
- B: Chemical, 137(1) 154-163, 2009

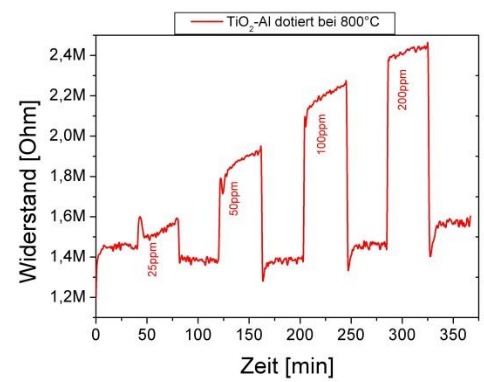
- M. Stranzenbach; E. Gramckow and B. Saruhan, Planar,
- impedance-metric NOx sensor with spinel-type SE for high temperature
- applications, Sensors and Actuators, B, 127, 224-230, 2007



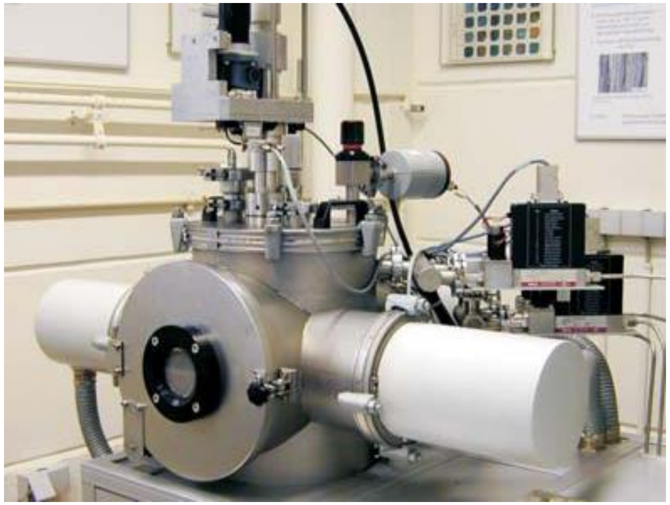
- Effect of Al-doping on high-temperature NO_2-sensing

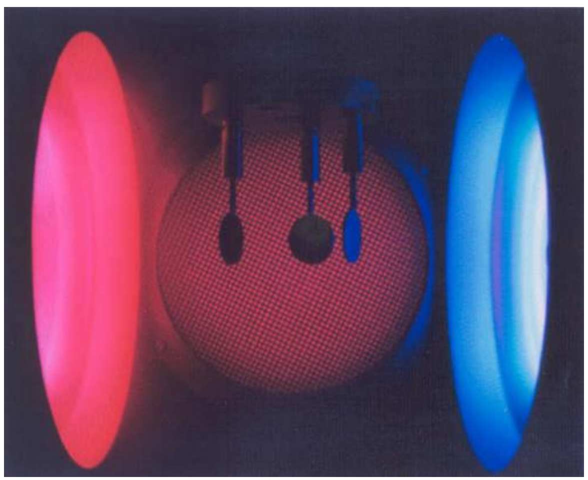
- B. Saruhan A. Yüce, Y. Gönüllü, K. Kelm,
- Effect of aluminium doping on NO_2 gas
- sensing of TiO_2 at elevated temperatures,
- Sensors and Actuators, B 187 (2013)
- 586-597.

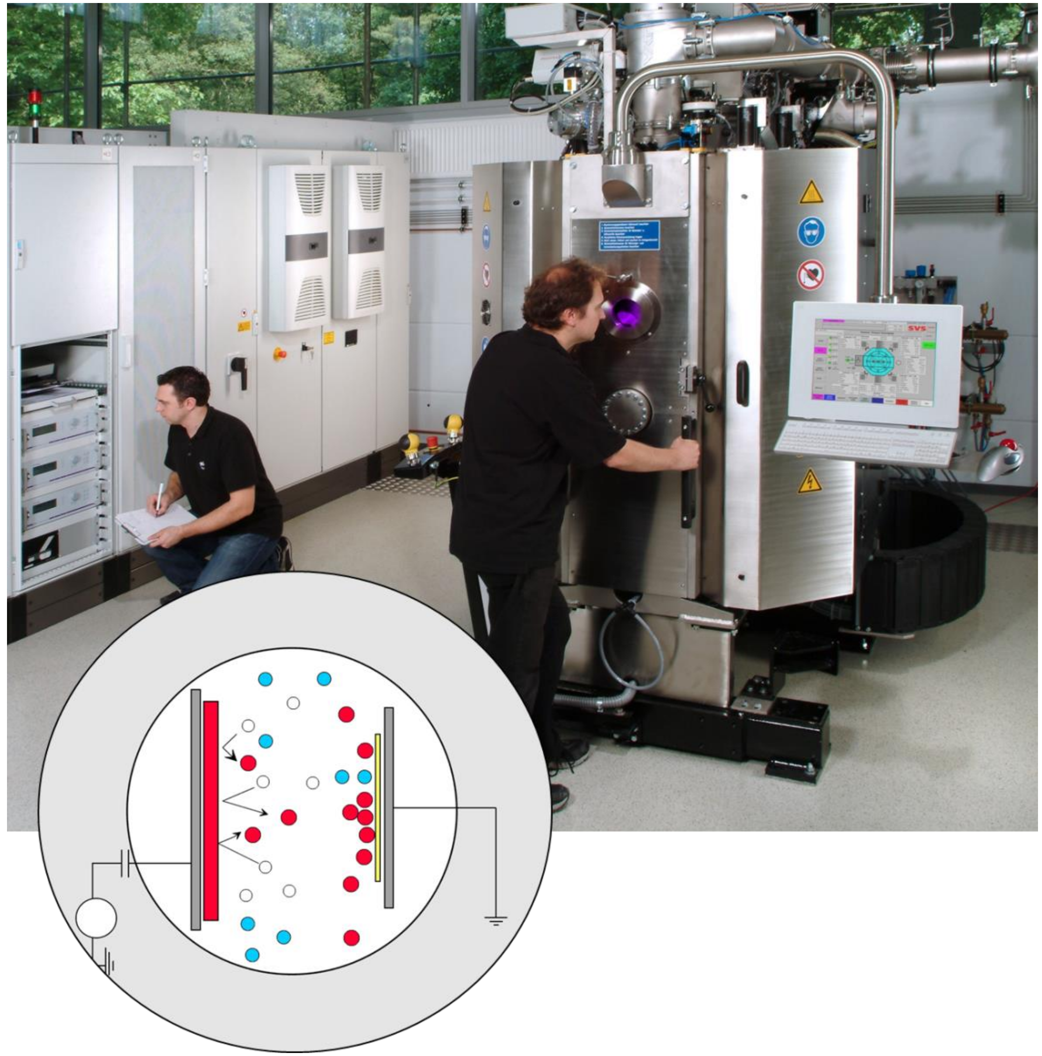




Research Facilities: Coating





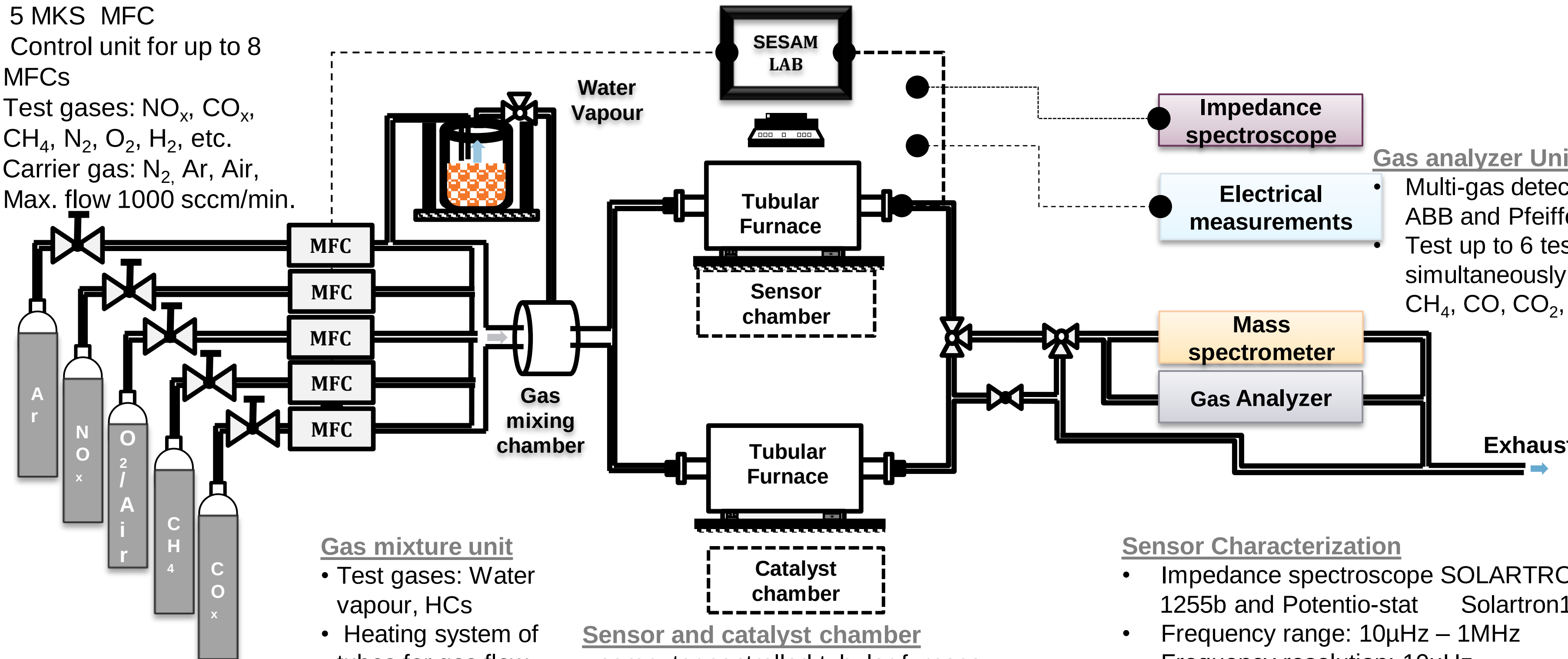


Research Facilities

SESAM – Sensor and Catalyst Test Unit

Gas mixture unit

- 5 MKS MFC
- Control unit for up to 8 MFCs
- Test gases: NO_x, CO_x, CH_4, N_2, O_2, H_2, etc.
- Carrier gas: N_2, Ar, Air,
- Max. flow 1000 sccm/min.



Gas analyzer Unit

- Multi-gas detector from ABB and Pfeiffer
- Test up to 6 test gases simultaneously: NO, NO_2, CH_4, CO, CO_2, H_2,

Gas mixture unit

- Test gases: Water vapour, HCs
- Heating system of tubes for gas flow

Sensor and catalyst chamber

- computer controlled tubular furnace (CARBOLITE) up to 1200 °C,
- Quart-glass recipient stable up to 1300 °C,
- 3 m for heating of gas mixture
- Flexible sample geometry (max. ∅50 mm) with variable interior

Sensor Characterization

- Impedance spectroscope SOLARTRON 1255b and Potentio-stat Solartron1286
- Frequency range: 10µHz – 1MHz
- Frequency resolution: 10µHz
- Impedance range: 0 – 100 MΩ
- DC- Bias range: ± 50V
- Computer controll over IEEE 488 Interface

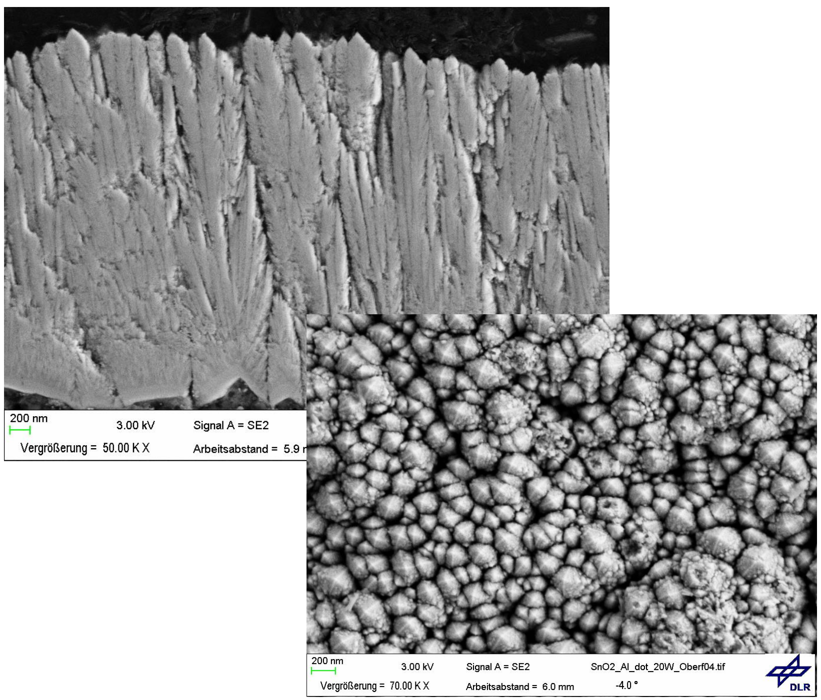
Motivation and objectives

- The main disadvantages of cheap semiconductor oxides are
  - The lack of sensitivity to monitor dilute NOx,
  - Need of long-term stability under fluctuating environments
  - Signals from interfering gases
- This work suggests and evaluates
  - The use of sputter technique for deposition of sensing layers based on SnO_2
  - Effect of dopants on NO_2-sensing of SnO_2
  - Sensing property of SnO_2 in the presence humidity

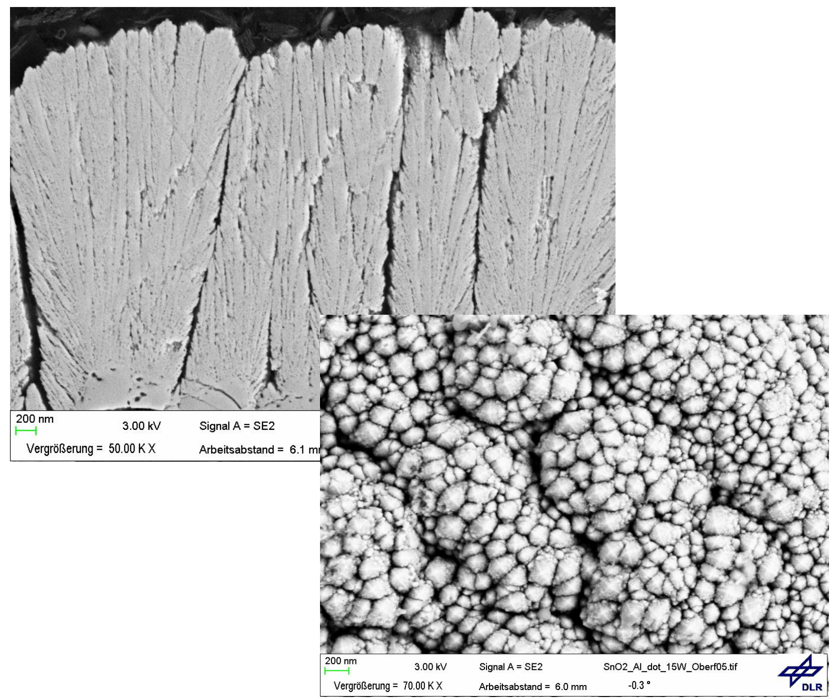
Morphology of undoped SnO_2 layers

	Power	Structure	Coating	Annealing
Undoped SnO_2	150 W	Crystal feather structure	Rotated	800°C in air, 5 h

As coated

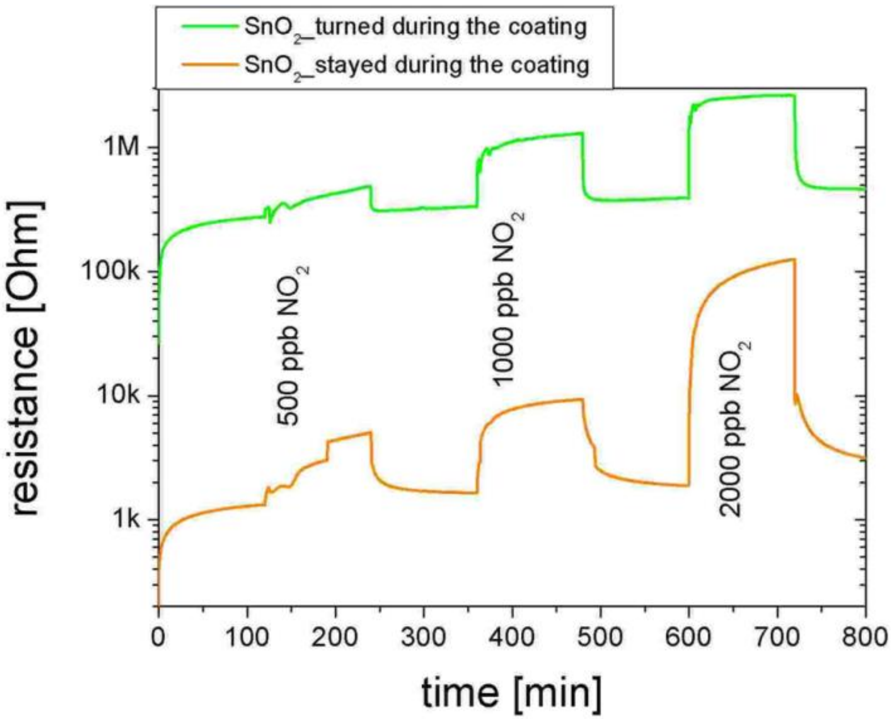


Annealing after 800°C for 5 hours

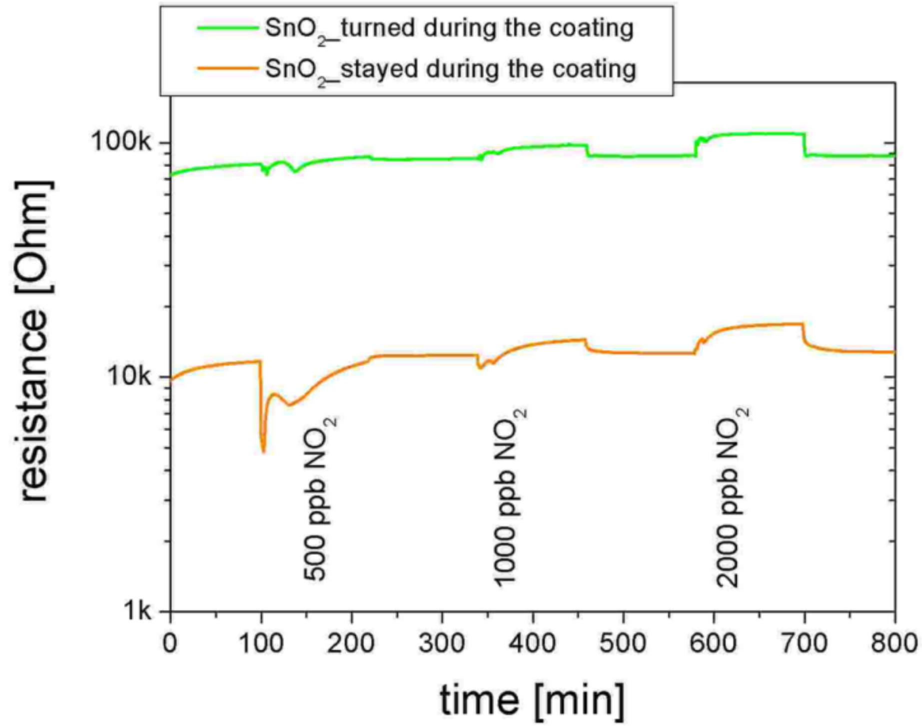


NO_2-sensing of un-doped SnO_2

Under low concentrations 500-2000 ppb NO_2



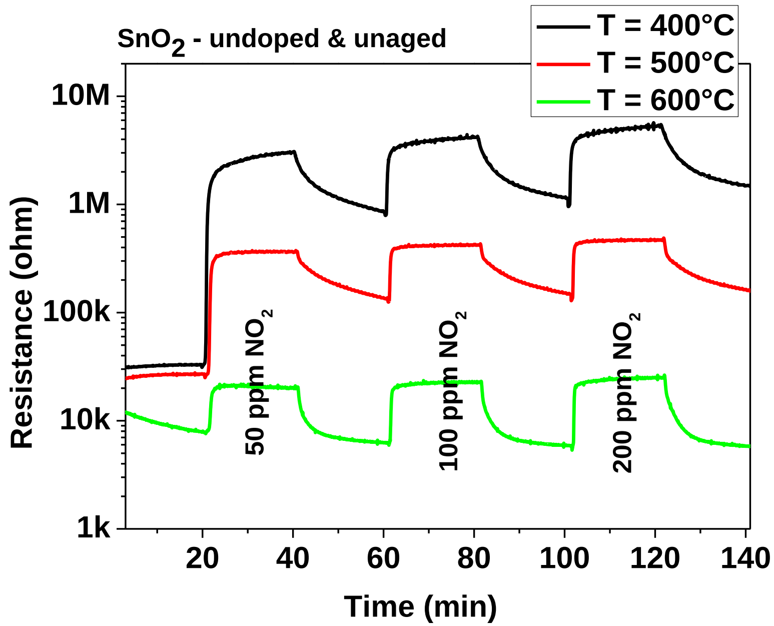
at 300°C, synt. air + 50% humidity



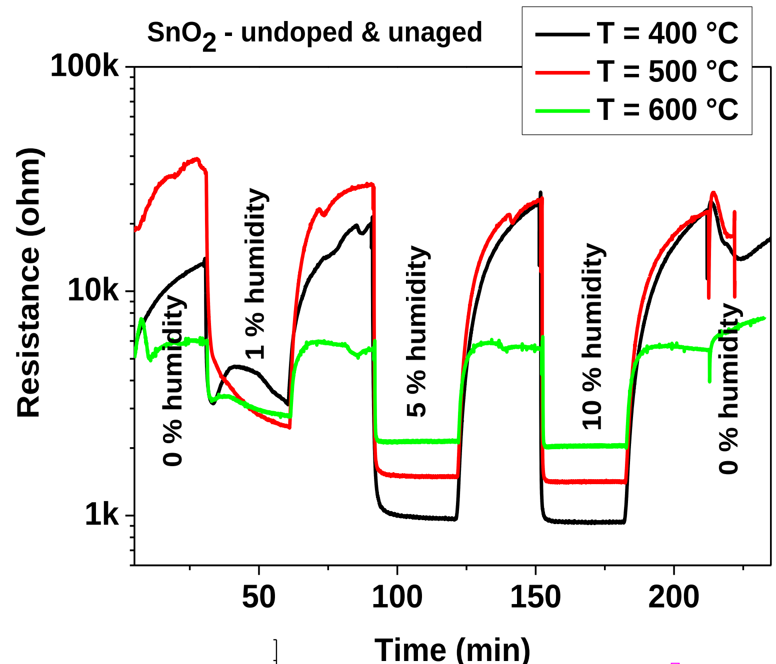
at 400°C, synt. Air + 50% humidity

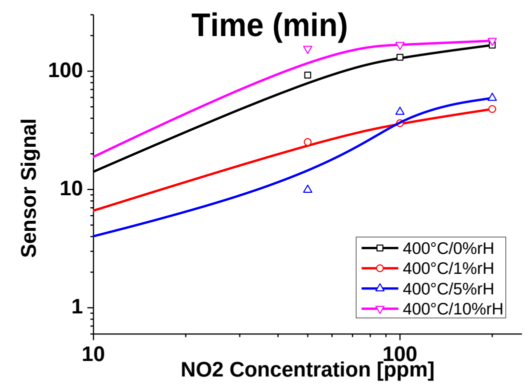
NO_2-sensing of un-doped SnO_2

at 400°C - 600°C, Dry Argon



at 400°C - 600°C, Humid Argon

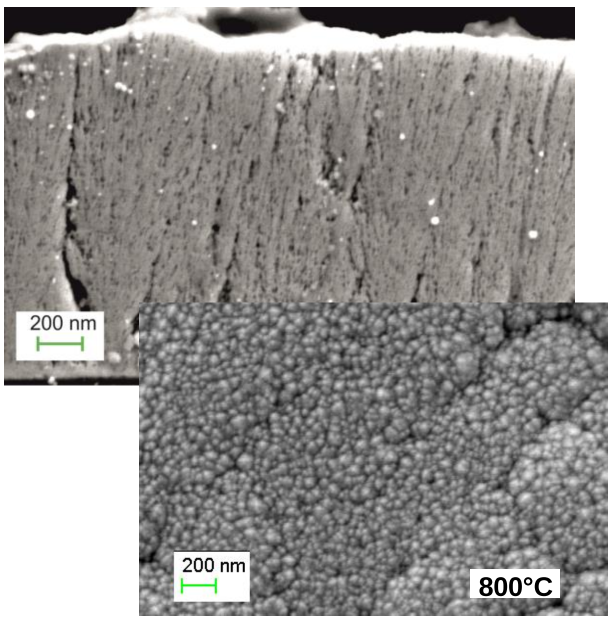


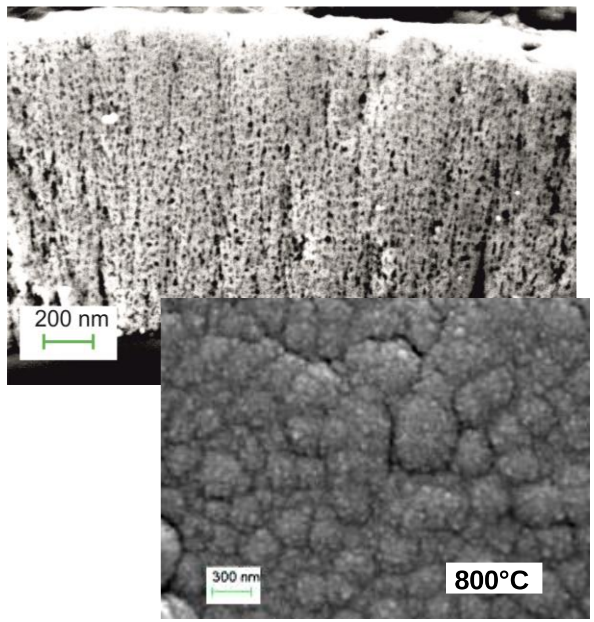


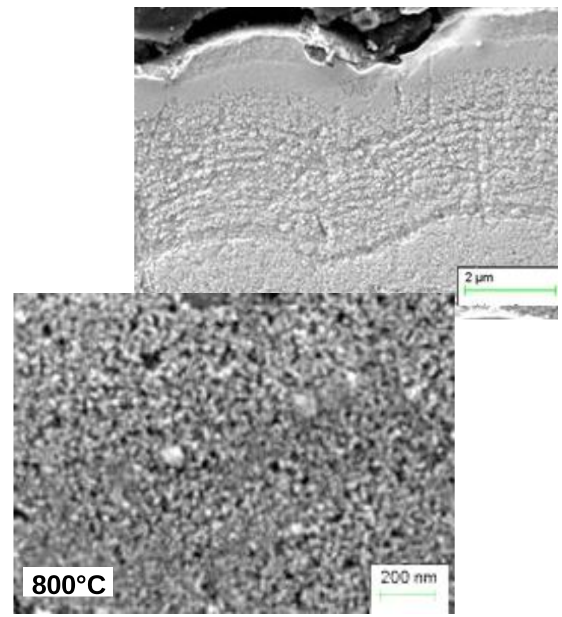
Under higher concentrations 50-200 ppm NO_2

Effect of Dopant on Morphology

	Sn-Power	Doped Power	Atm. % of doped materiel	Ar / O_2 ‰	Structure	Annealing
Al-doped SnO_2	100 W	80 W	1,6 at. %	70 / 30	Cassiterite	800°C in atm 5 St.
Cr-doped SnO_2	100 W	65 W	6 at. %	70 / 30	Cassiterite	800°C in atm 5 St.
W-doped SnO_2	100 W	130 W	8 at. %	70 / 30	Amorphous	800°C in atm 5 St.

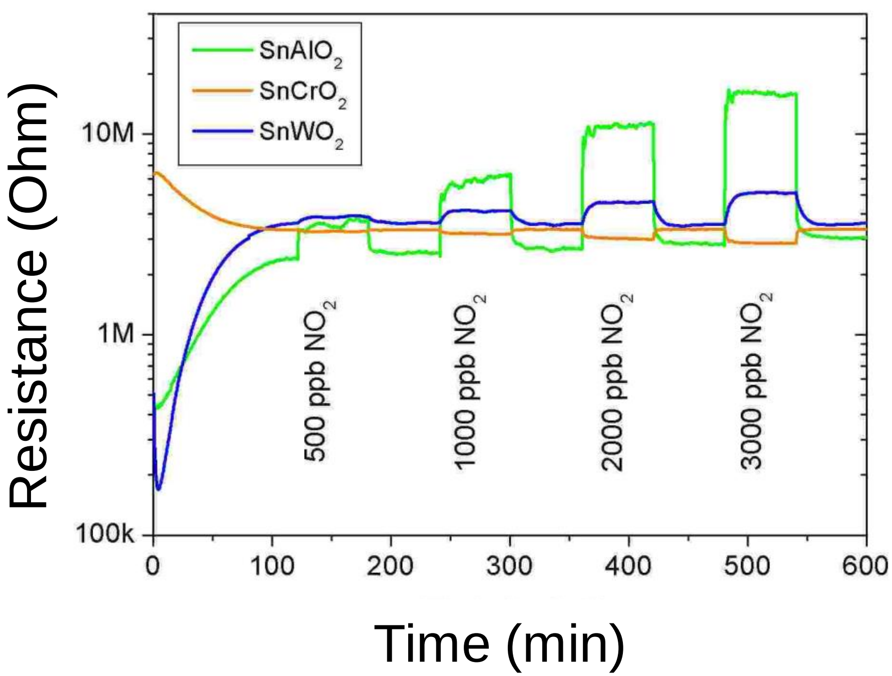




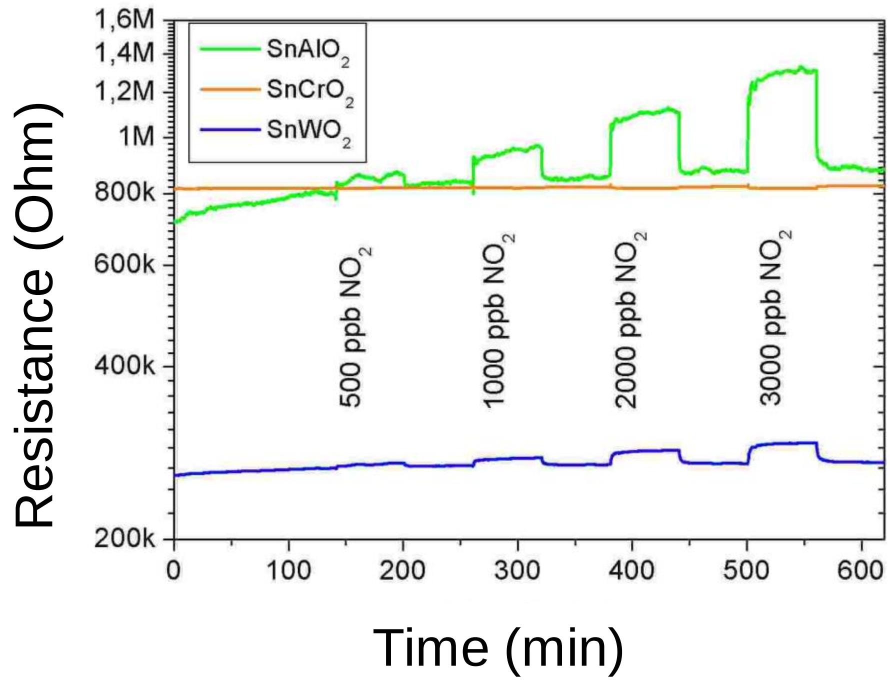


Effect of dopants on NO_2-sensing of SnO_2

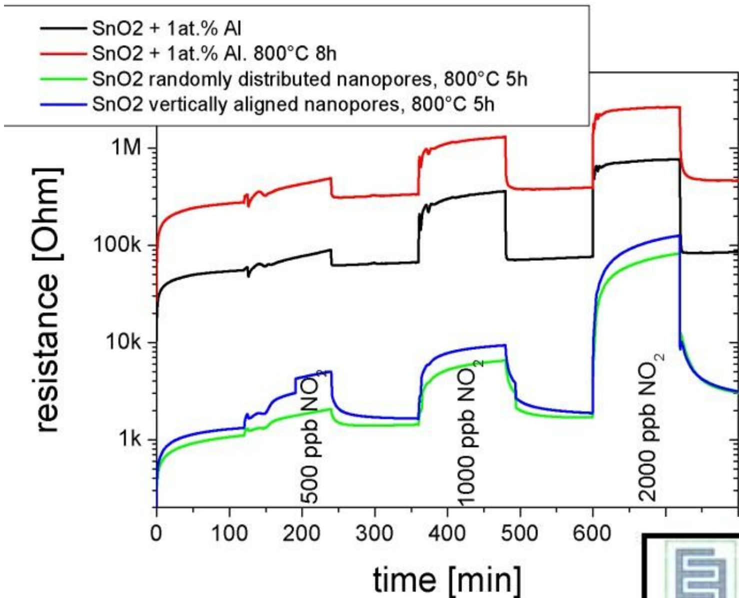
at 300°C, synt. air + 50% humidity

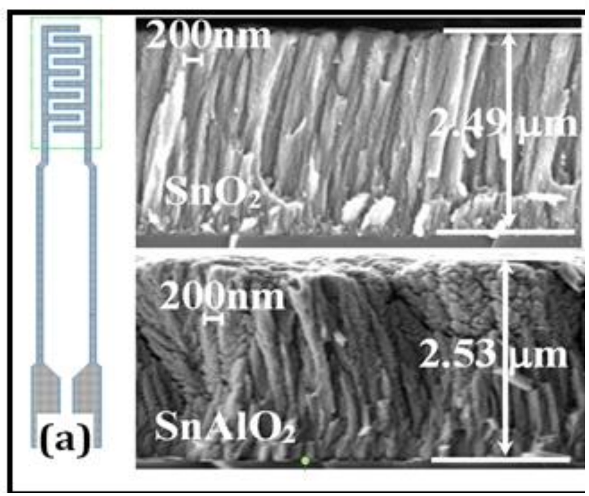


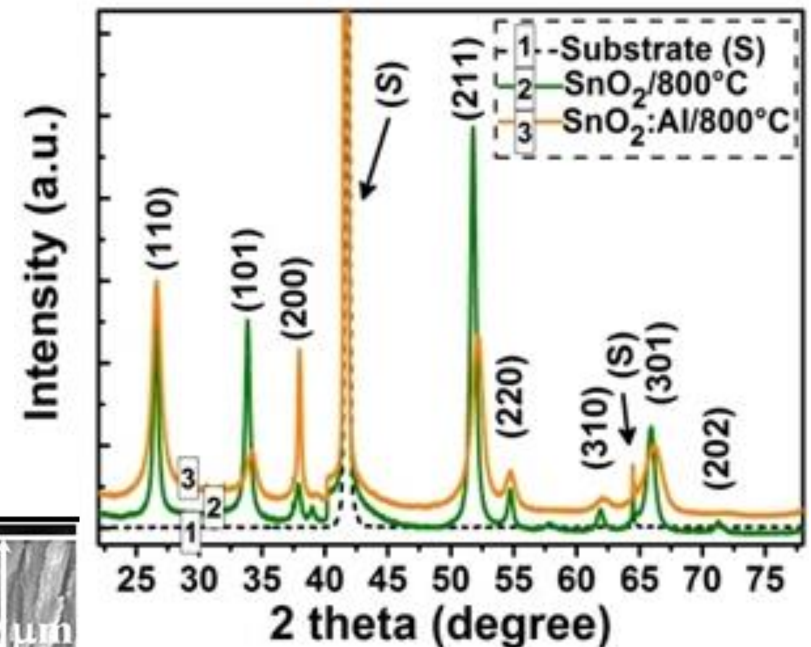
at 400°C, synt. Air + 50% humidity



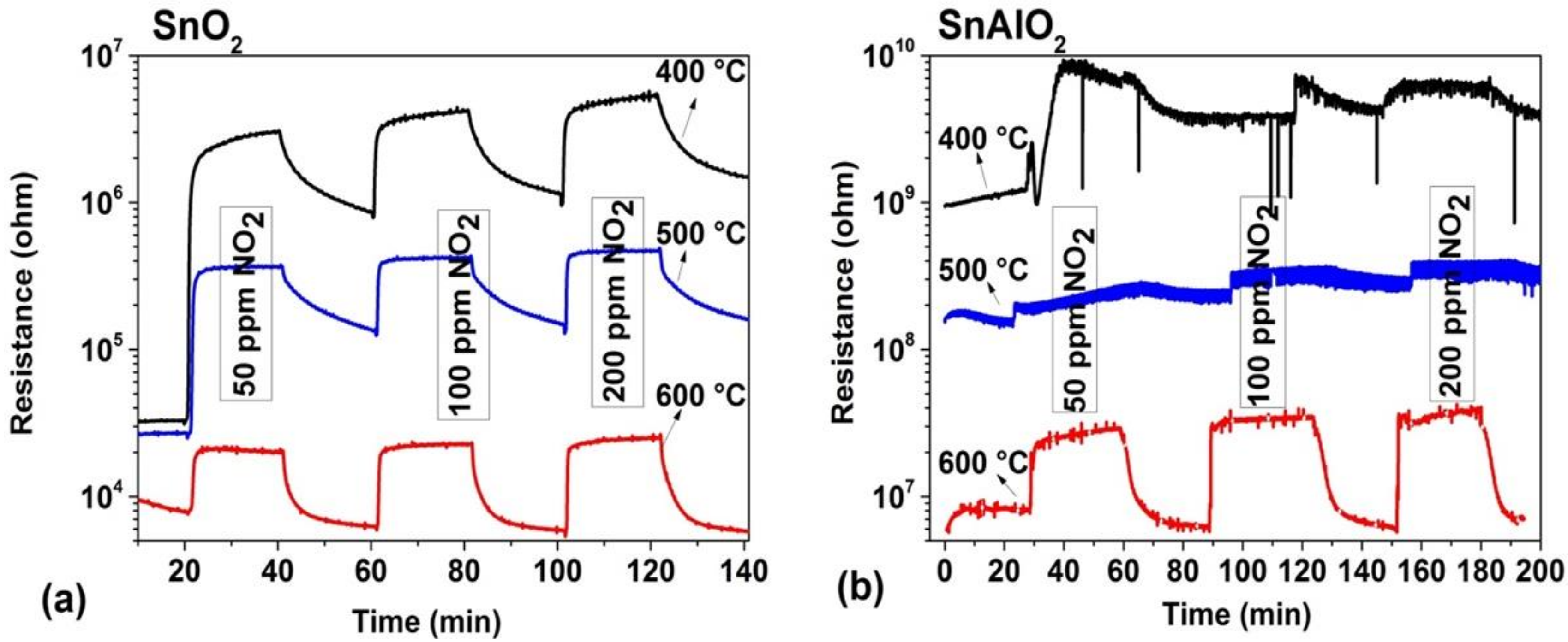
NO_2-sensing with Al-doped SnO_2







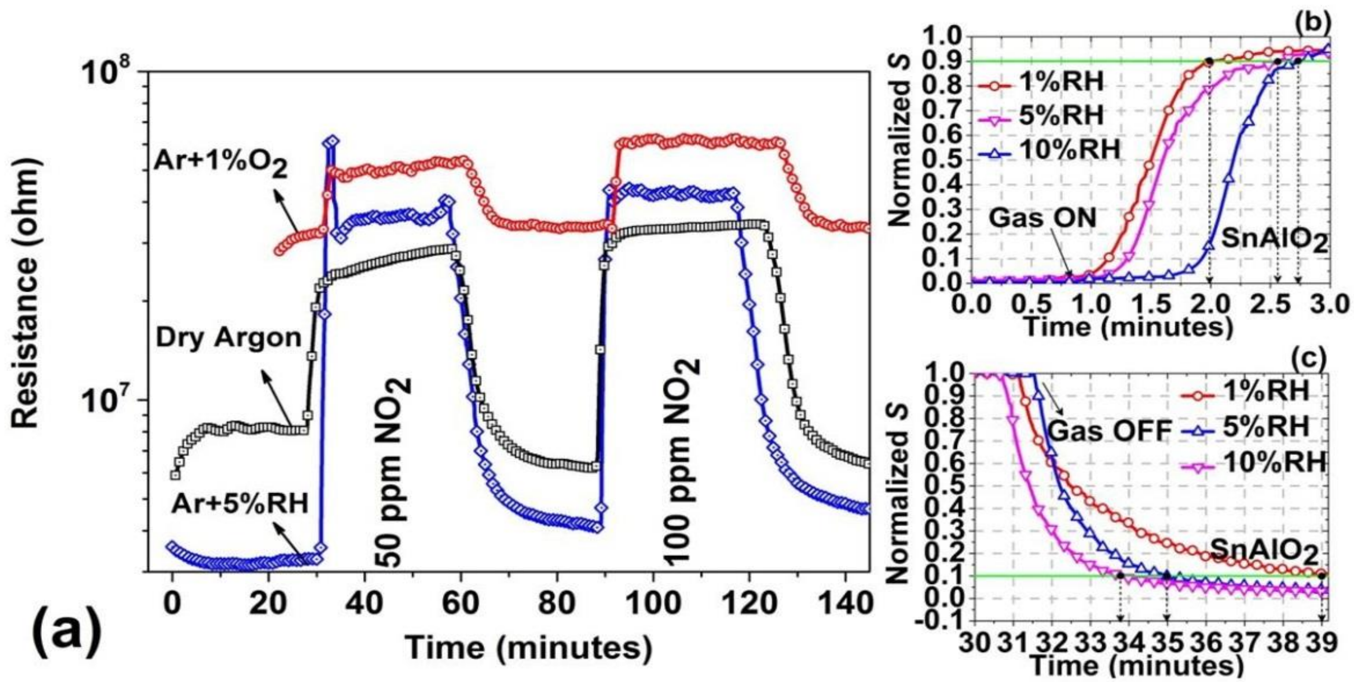
Dynamic response towards NO_2



(a) Sputtered SnO_2 (b) SnO_2:Al sensors
when exposed to 50, 100 and 200 ppm of NO_2 gas concentrations in dry argon carrier gas and at T = 400°, 500° and 600°C

Dynamic response of SnO_2:Al sensors

Normalized $S = [\{R_{(t)} - R_{(Ar)}\} / \{R_{(NO2)} - R_{(Ar)}\}]$ $R_{(t)}$, $R_{(Ar)}$ and $R_{(NO2)}$ designate real time resistance, resistance in argon and NO_2 gas, respectively.

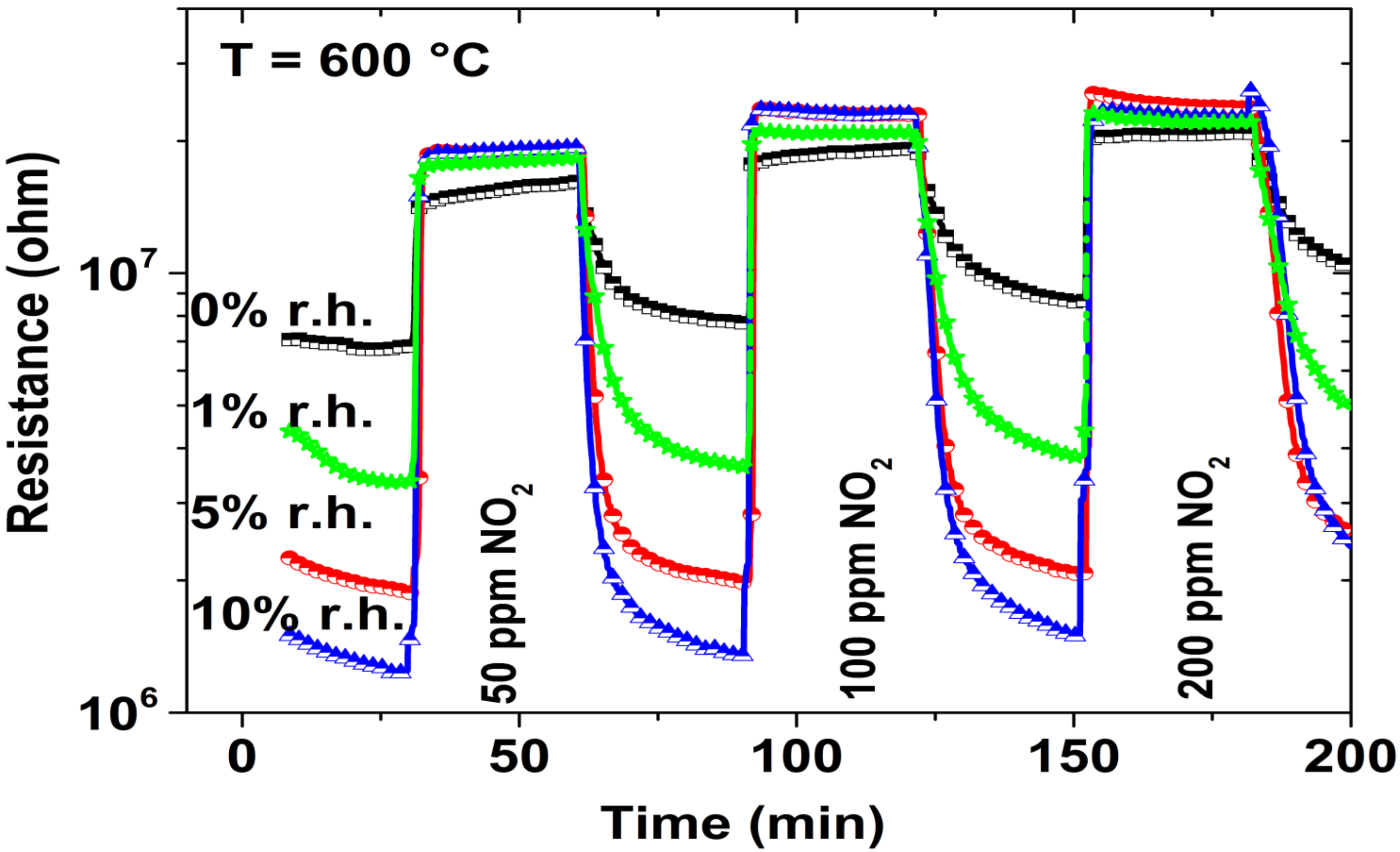


Exposure to 50 and 100 ppm of NO_2 gas concentrations

- in Dry Argon,
- in Argon with 1% O_2
- in Argon with 5% RH

} measured at T_w = 600 °C

Response of Al-doped SnO_2 towards NO_2 in the presence of humidity



Conclusions

- NO_2 sensing of SnO_2 sensors
  - is reasonable well with sputtered thin layers under low concentrations and at lower temperatures (250°-400°C)
  - Al-doping improves sensor signal up to 600°C
    - yielding more selective sensing towards NO_2 in $CO+NO_2$ gas mixtures
  - the presence of humidity (up to 10% RH) shortens the response and recovery times drastically and improves NO_2-sensing at 600°C
    - indicating a change in adsorption kinetics probably due to change in sensing mechanism.

- Thank you very much for your attention

Suggested R&I Needs for future research

- Development of SO_2 sensors for use at severe environments (e.g. volcano ash detection in atmosphere)

- Nanostructured ultra-thin sensing films and top/bottom circuitry for room temperature sensing