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

COST Action TD1105

WGs and MC Meeting at LINKOPING, 3 - 5 June 2015

Action Start date: 01/07/2012 - Action End date: 30/06/2016

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

EFFECT OF SENSOR CONFIGURATION FOR LOW TEMPERATURE GAS DETECTION WITH SEMICONDUCTING OXIDES

Bilge Saruhan-Brings

WG 1 Member

Institute of Materials Research, German Aerospace Center, 51147 Cologne/Germany

EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

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

COST is supported
by the EU Framework Programme

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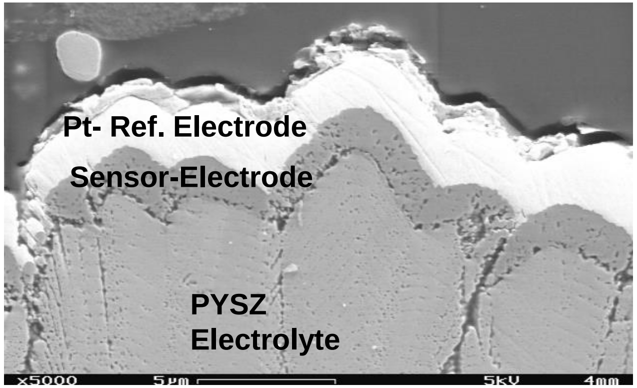
Research activities at DLR

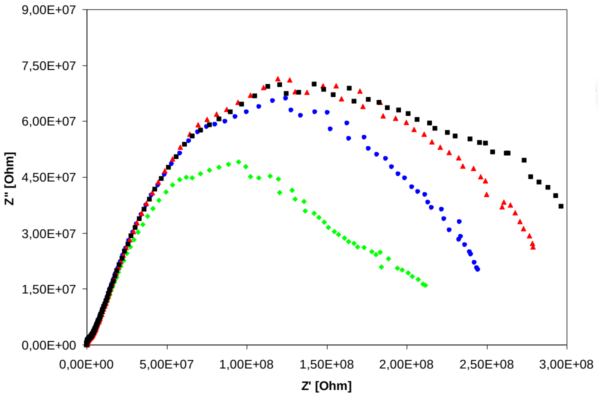
- Total NO_x sensing by means of component integrated impedance-metric sensors

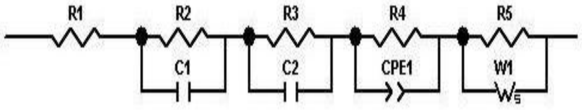
M. Stranzenbach and B. Saruhan, Equivalent circuit analysis on NOx impedance-metric gas sensors, Sensors and Actuators B: Chem., 137(1) 154-163, 2009

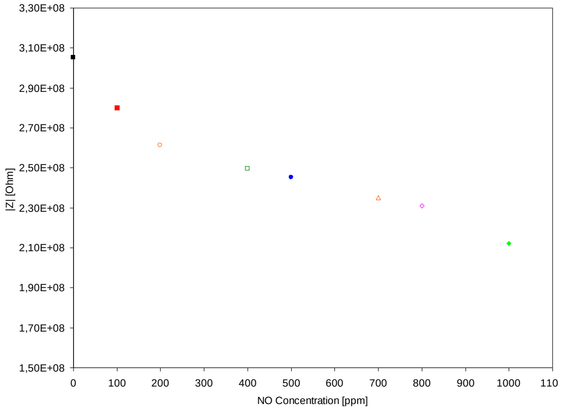
M. Stranzenbach; E. Gramckow and B. Saruhan, Planar, impedance-metric NOx sensor with spinel-type SE for high temperature applications, Sensors and Actuators, B: Chem., 127, 224-230, 2007



- Impedance-metric sensors having NiO and Ni-spinel-SE and YSZ-electrolytes has a great potential as high temperature total NOx sensors for use in and harsh environment gas sensing applications. The applicability of the total impedance is proven to yield reliable sensor signal.



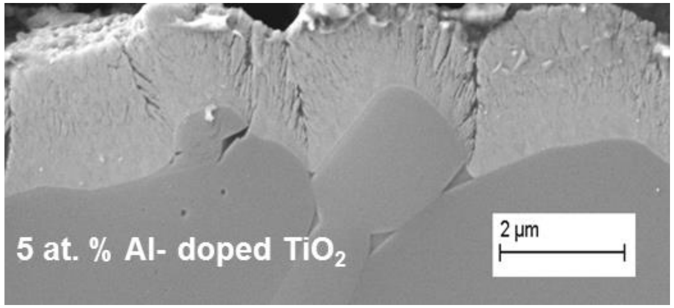


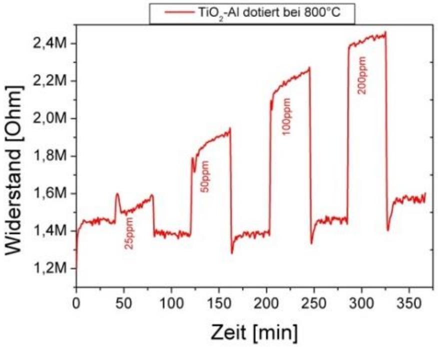


Research activities at DLR

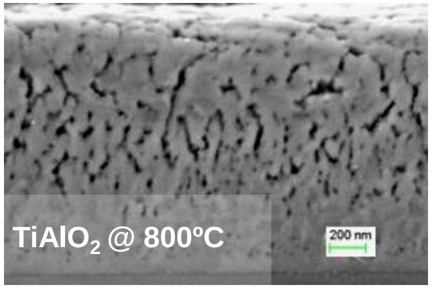
- Effect of Al-doping of TiO_2 on high-temperature NO_2-sensing

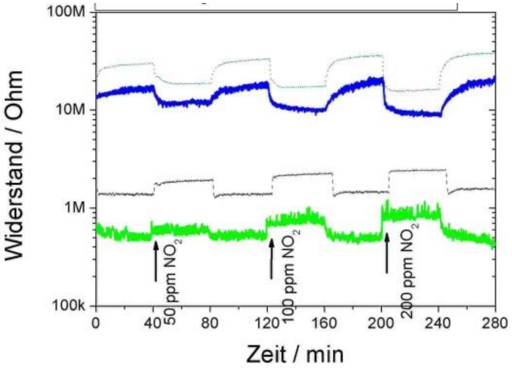
B. Saruhan A. Yüce, Y. Gönüllü and K. Kelm, *Effect of aluminium doping on NO_2 gas sensing of TiO_2 at elevated temperatures*, Sensors and Actuators, B 187 (2013) 586-597.

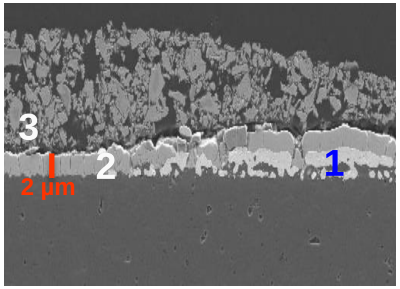


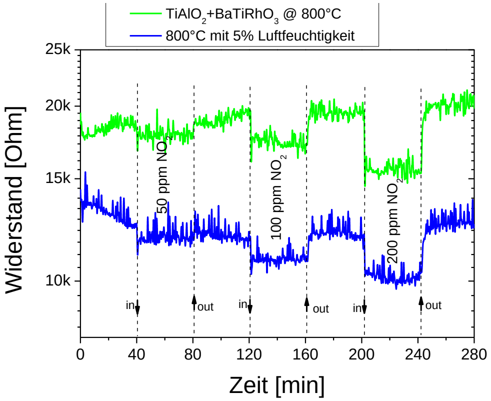


- NO_2 sensing at elevated temperatures (600°-900°C) by the use of Al-doped TiO_2 sensing layers and catalytic self-regenerative Perovskite layers





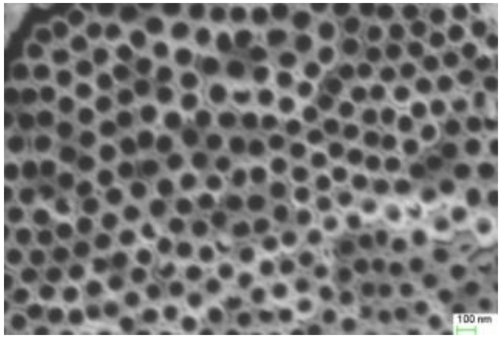


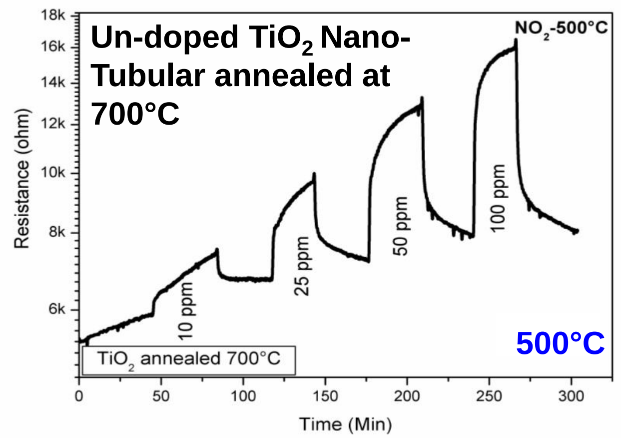


Research activities at DLR

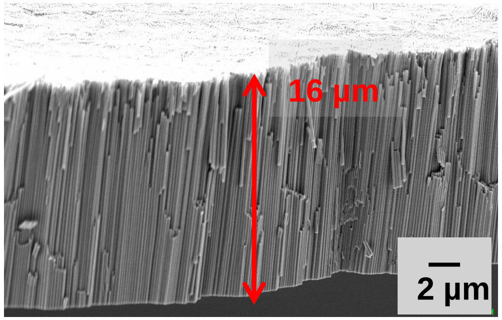
- Nano-tubular TiO_2-sensor electrodes for NO_2 and CO sensing at intermediate temperatures (300°-500°C)

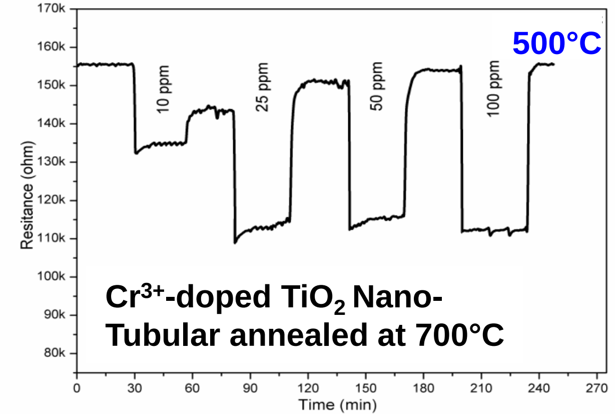
Y. Gönüllü, C.G. Mondragón Rodríguez, B. Saruhan, M. Ürgen, Improvement of gas sensing performance of TiO_2 towards NO_2 by nano-tubular structuring, <u>Sensors and Actuators B: Chem.</u>, Vol.:169, 2012,151–160





Y. Gönüllü, A.A. Haidry, B. Saruhan, Nanotubular Cr-doped TiO_2 for use as high-temperature NO_2 gas sensor, <u>Sensors and Actuators B: Chem.</u>, in press, online available since Nov. 2014





Content

- Objectives of the present work
- Research facilities at DLR-WF (Cologne)
- Applied sensor configurations
- Reactive sputtering of doped TiO_2
- Microstructure and Phase conditions
- NO_2-sensing of TiO_2 and Cr-doped TiO_2 with three different configurations
    - On interdigital Electrodes (IDE)
    - With Top-Bottom Electrodes (TBE i.e. resistive switching)
    - By nanostructuring and parallel top electrodes

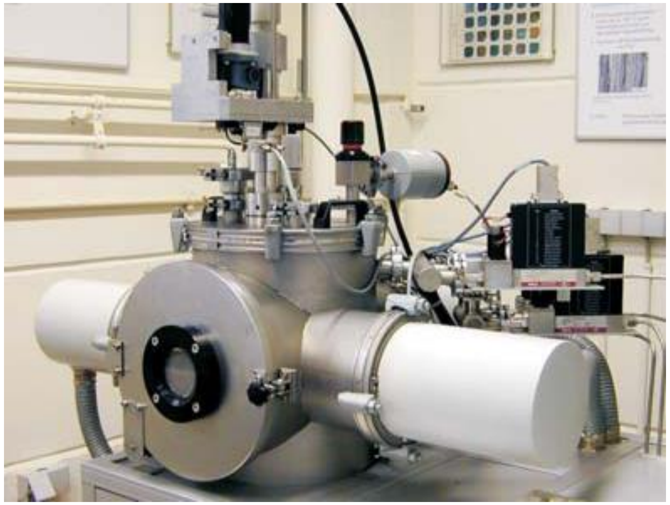
- Past research activities at DLR-WF on gas sensors

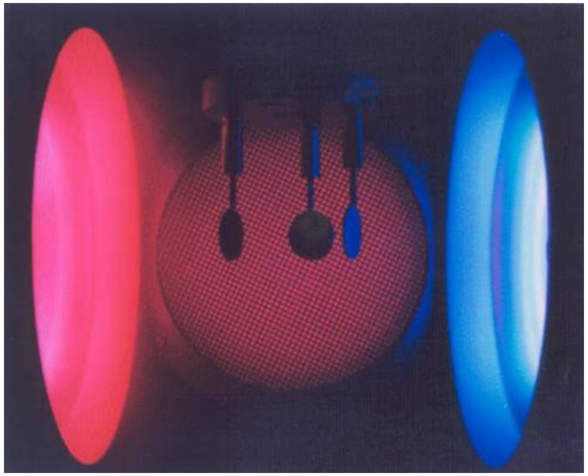
Objectives of the present work

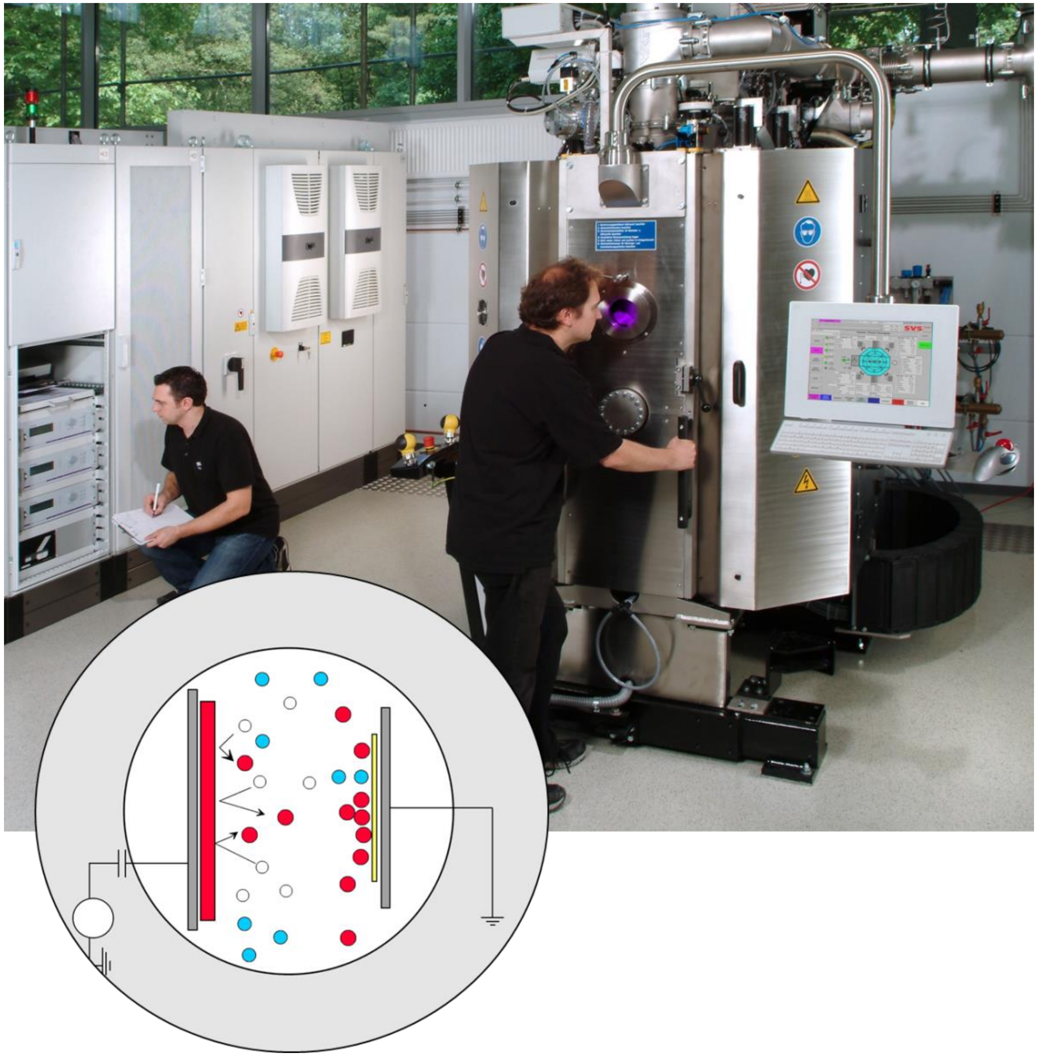
- TiO_2 is a n-type semiconductor and can be used for gas sensing
- But there are problems in terms of sensor response and sensitivity towards oxidizing gas NO_2
- Doping with M^{3+} (Al, Cr) improves sensor signal and sensitivity yielding a p-type sensor response
- However
  - Higher temperatures are needed for reasonable signal (>>400°C)

- This work deals with
  - Application of different sensor designs
  - Effect of sensor layer type on NO_2-sensing (semiconductor, dopant, nanostructuring)
  - Low temperature NO_2 sensing with semiconductor undoped and doped TiO_2

Research Facilities at DLR: Coating





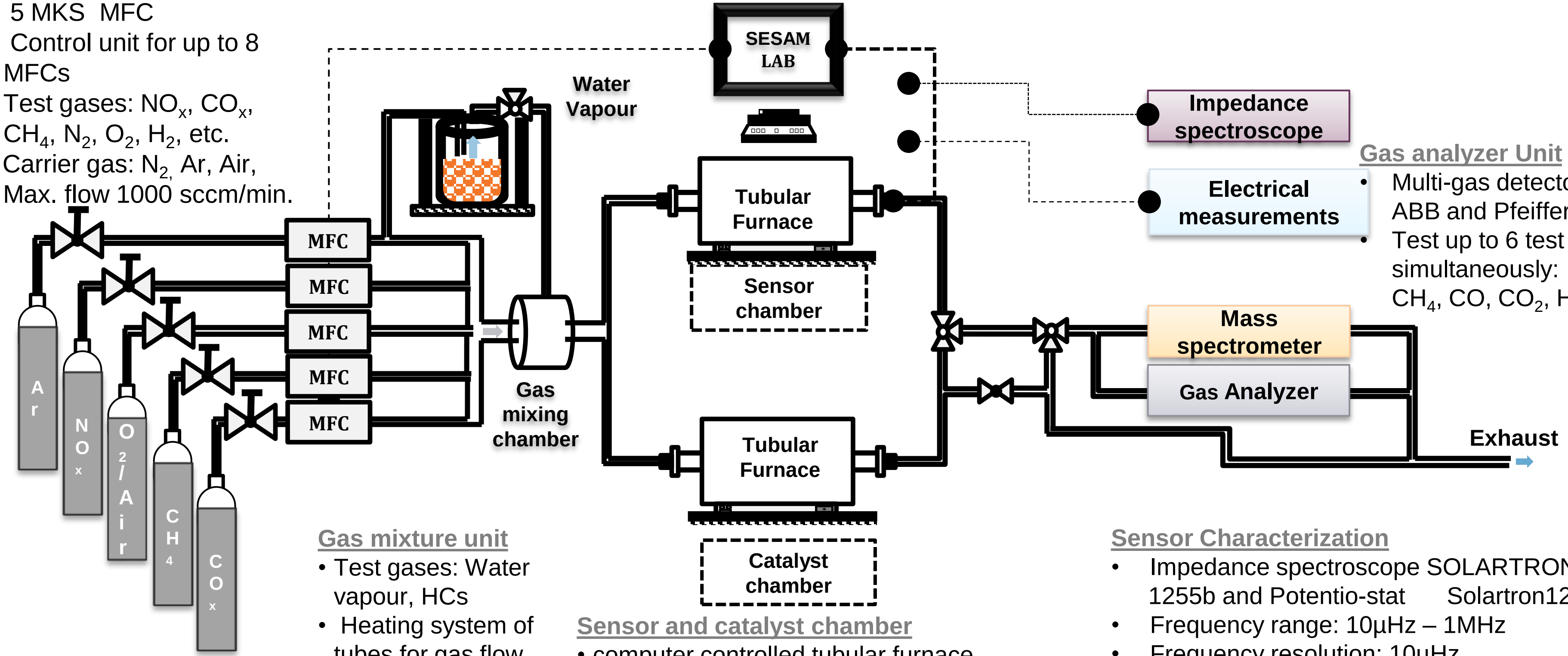


Research Facilities at DLR: Sensor testing

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

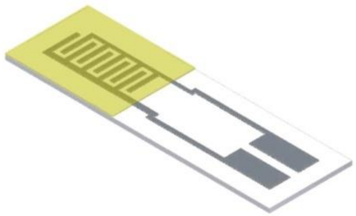
- computer controlled tubular furnace (CARBOLITE) up to 1200 °C,
- Quart-glass recipient stable up to 1300 °C,
- 3 m for heating of gas mixture
- Flexible sample geometry (max. ∅50 mm) with variable interior

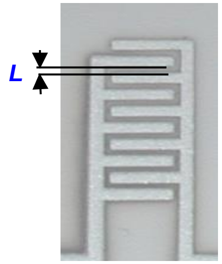
Sensor Characterization

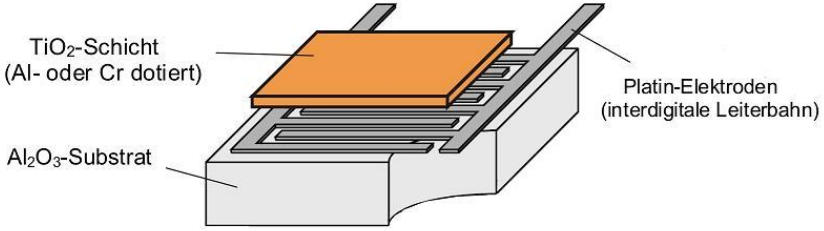
- Impedance spectroscope SOLARTRON 1255b and Potentio-stat Solartron1286
- Frequency range: 10µHz – 1MHz
- Frequency resolution: 10µHz
- Impedance range: 0 – 100 MΩ
- DC- Bias range: ± 50V
- Computer controll over IEEE 488 Interface

Applied Sensor Electrode Configurations

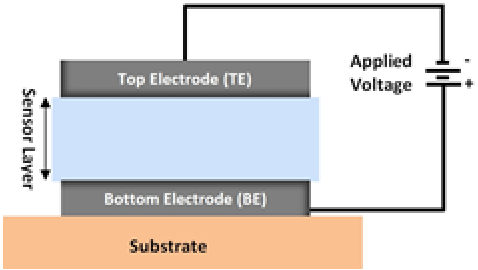
- Pt-InterDigital sensor Electrode (IDE)



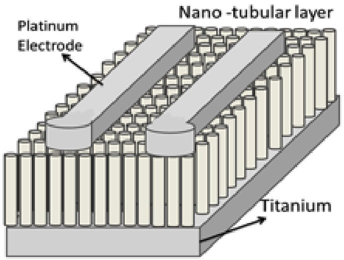


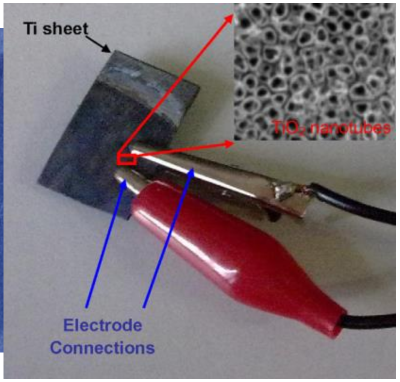


- Pt Top Bottom Electrode (TBE)



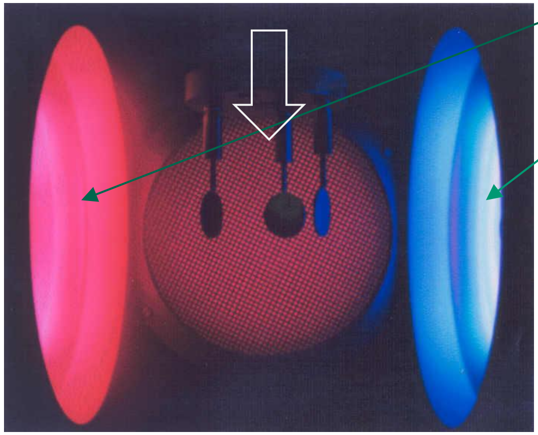
- // Pt sputtered Electrode (PE)





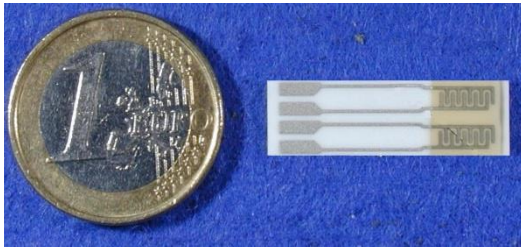
Reactive Sputtering of undoped and doped TiO_2 layers

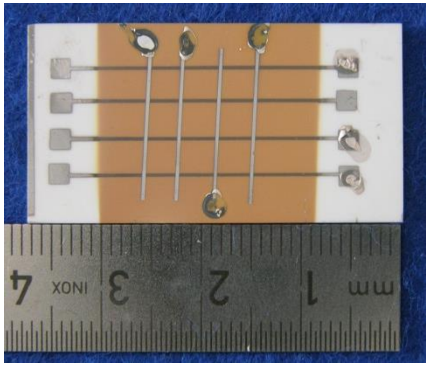
Oxygen gas as
reactive source



Reactive Magnetron Sputter Chamber

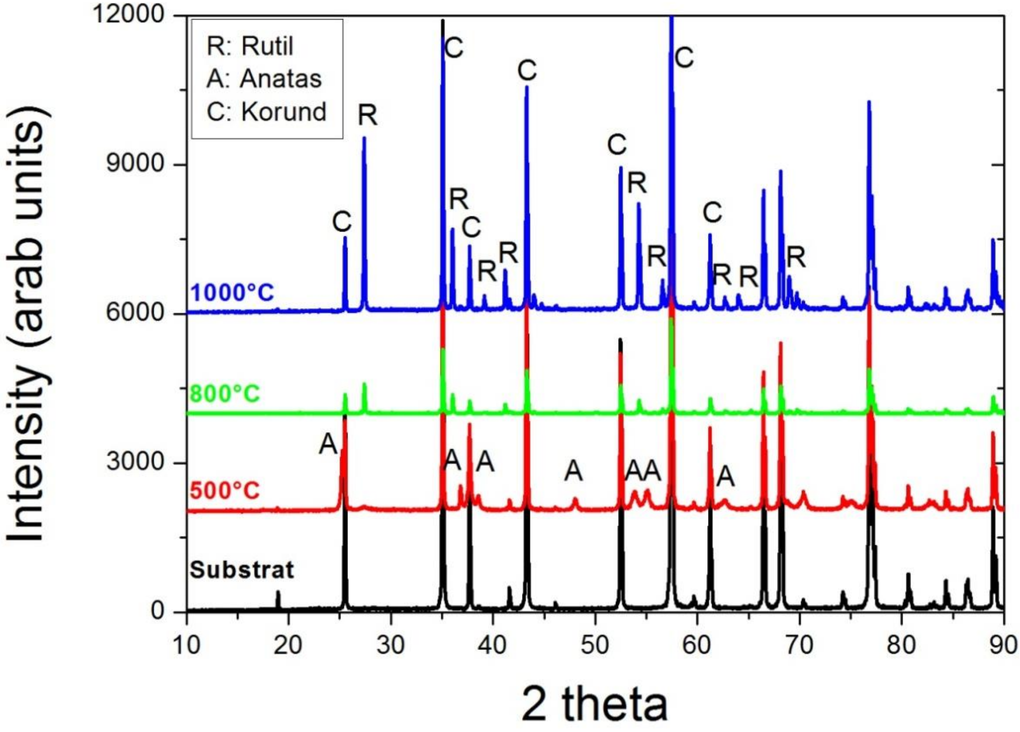
Sensing layers
on screen printed
interdigital electrodes





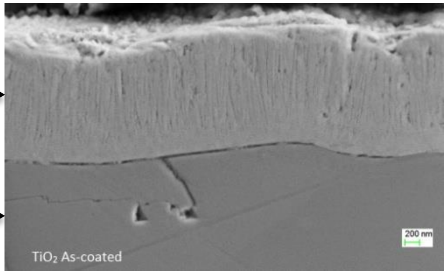
Sensing layers
between Pt Top
Bottom Electrodes

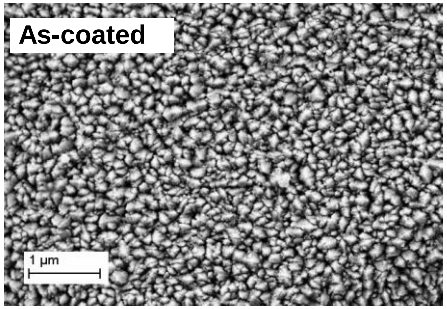
Microstructure and phase conditions of sputtered undoped TiO_2



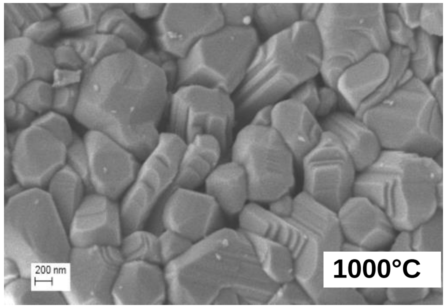
TiO_2 -Layer

Al_2O_3 -Substrate



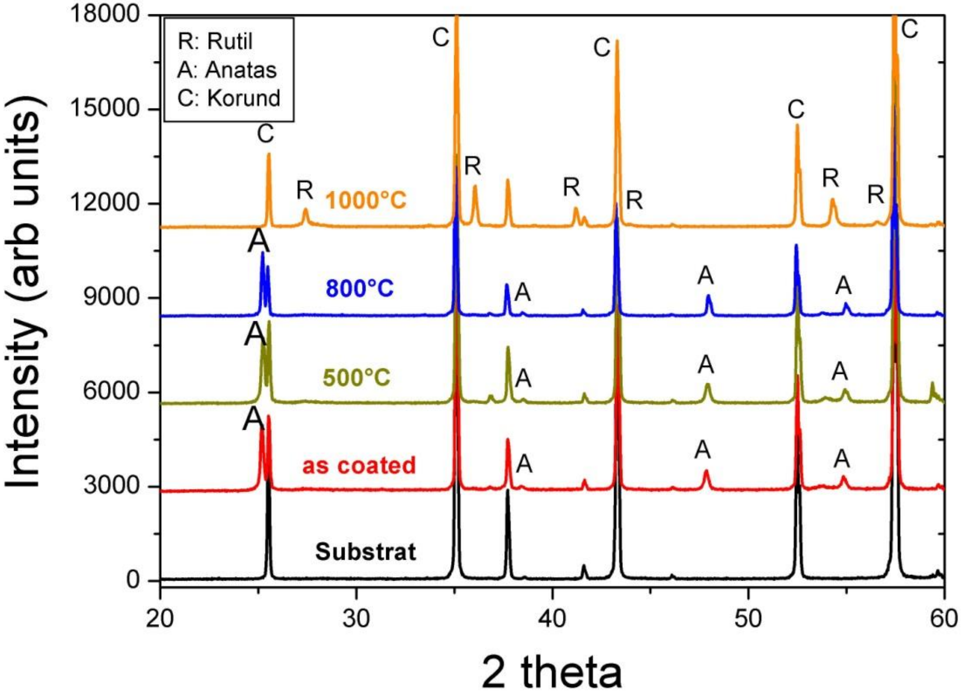


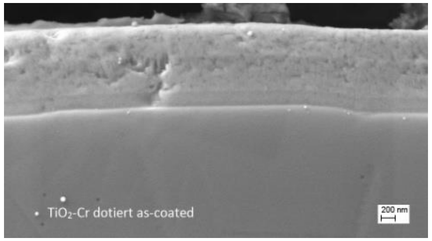
As-coated



1000°C

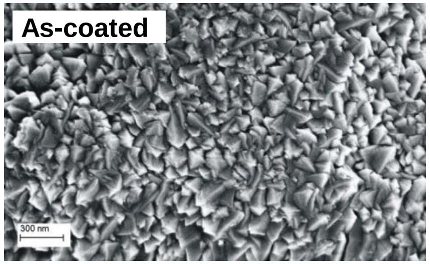
Microstructure and phase condition of sputtered Cr-doped TiO_2 (TiO_2:Cr)



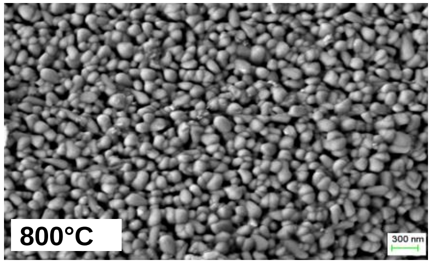


Cr-doped TiO_2 -Layer →

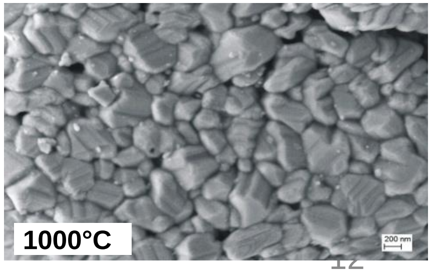
Al_2O_3 -Substrate →



As-coated

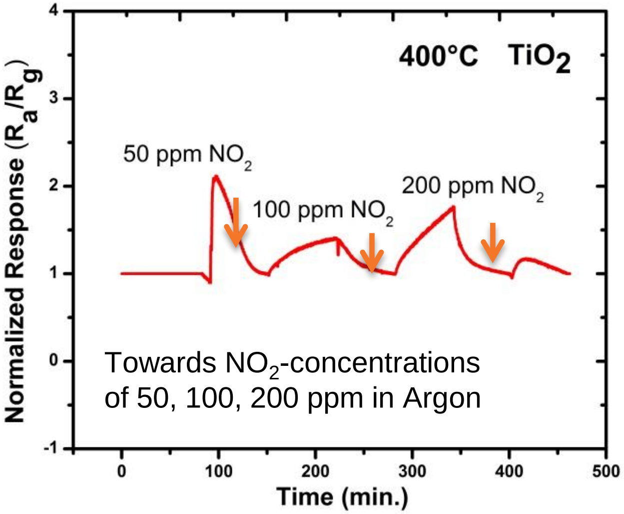


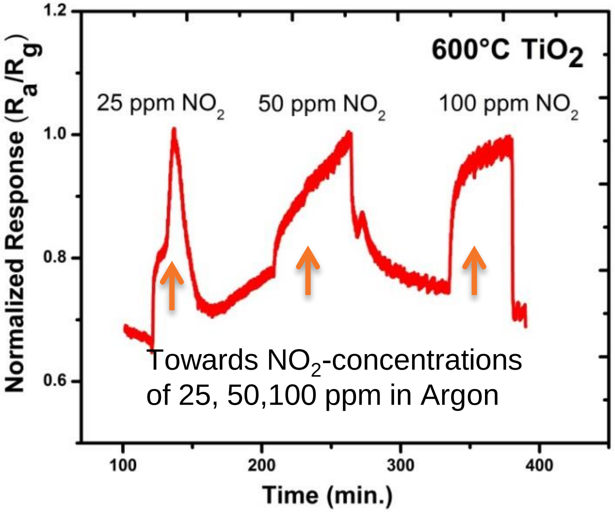
800°C

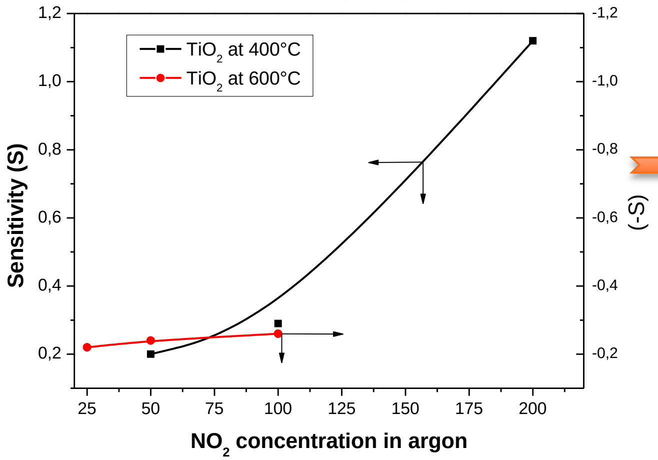


1000°C

NO_2-response of TiO_2-layer sputtered on IDE







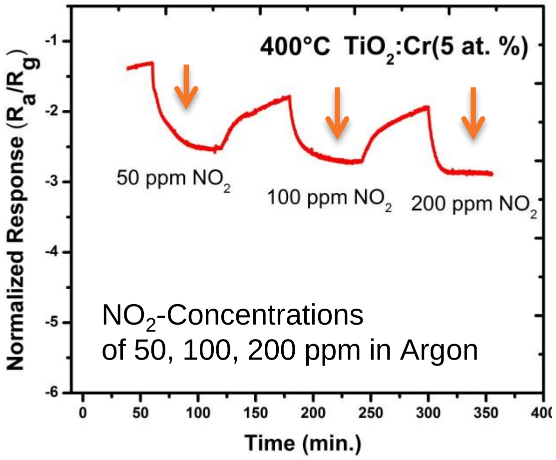
- NO_2-response of sputtered TiO_2 is present but very irregular at temperatures of 400°C to 600°C

NO_2-Sensor with undoped TiO_2 layer sputtered on IDE has <u>no sensing ability</u> at temperatures <u>below 400°C</u>

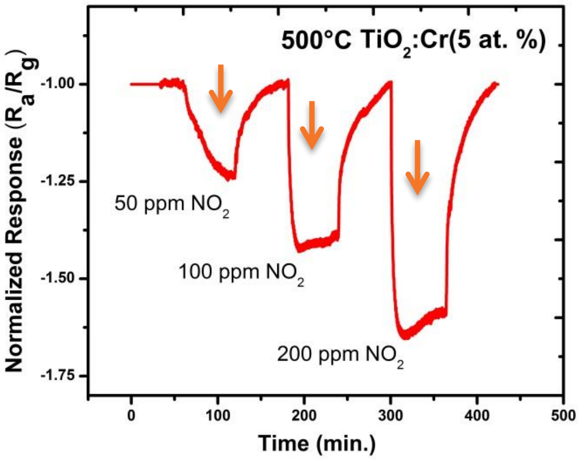
- shows <u>poor response</u> at temperatures above <u>400°C</u>
- better response with low sensitivity at 600°C

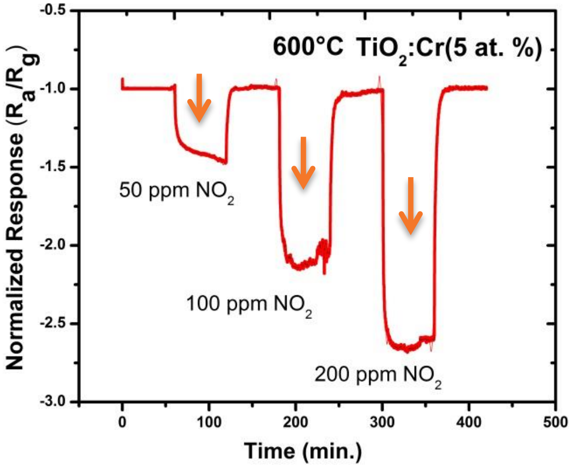
- TiO_2 layer thickness is 1.7 µm

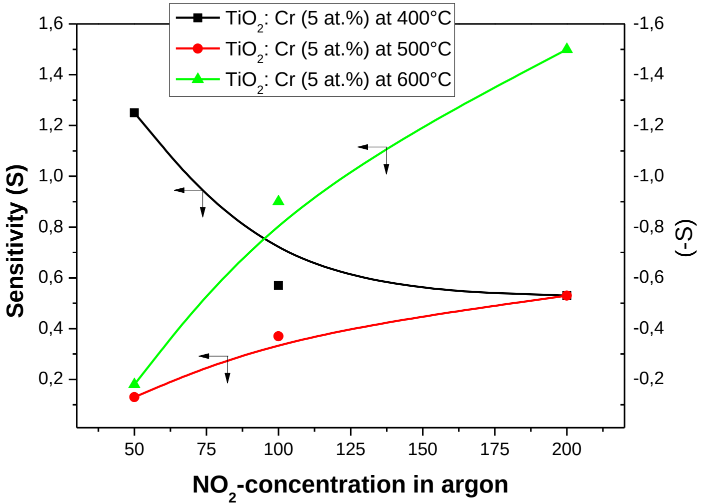
NO_2-response of TiO_2:Cr-layer sputtered on IDE



NO_2-Concentrations of 50, 100, 200 ppm in Argon





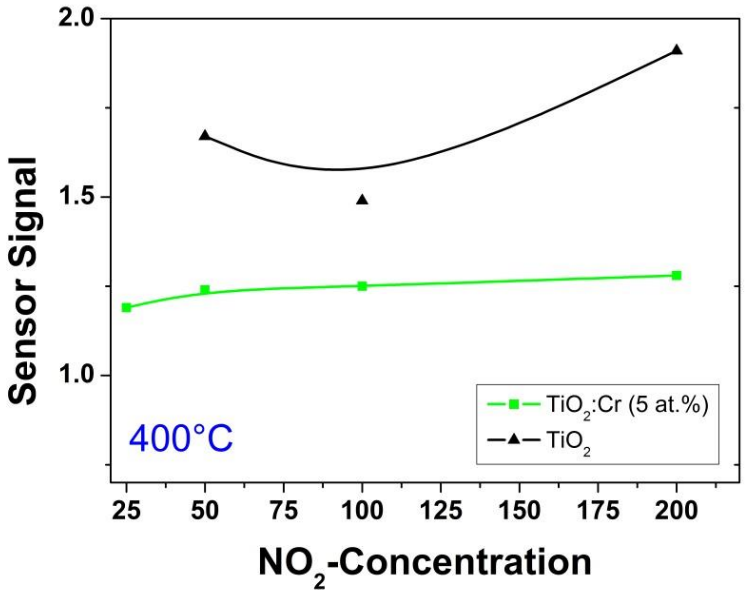


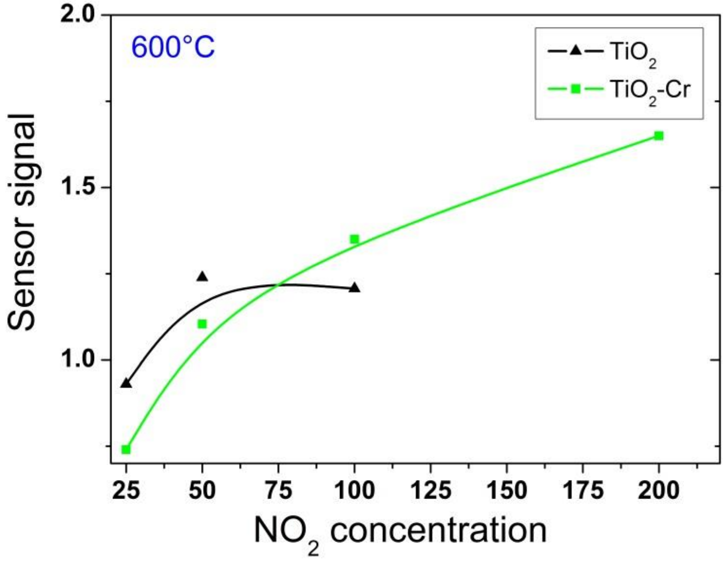
- NO_2-response is improved by doping sputtered TiO_2 with 5 at.% Cr (TiO_2:Cr) at temperatures above 400°C
- Sensor response has low resolution with concentration at 400°C

➡ Best sensor response is achieved above 500°C

- TiO_2 layer thickness is 1.5 µm

Sputtered TiO_2 vs. Sputtered TiO_2:Cr on IDE

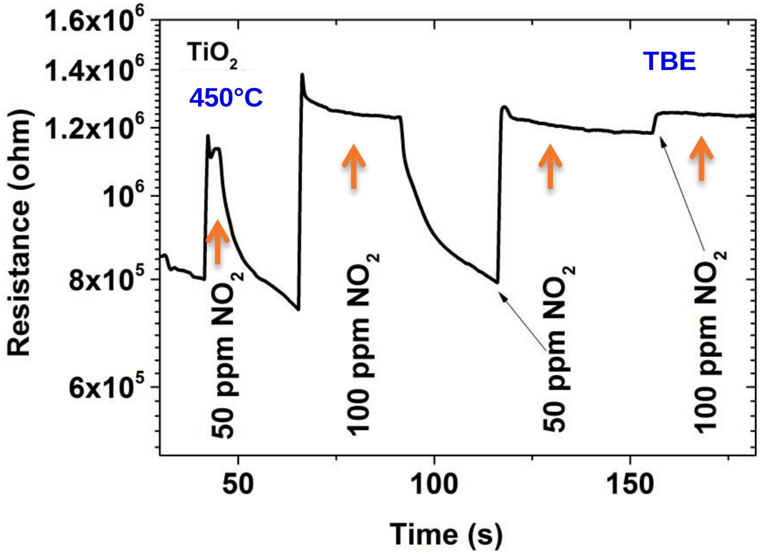


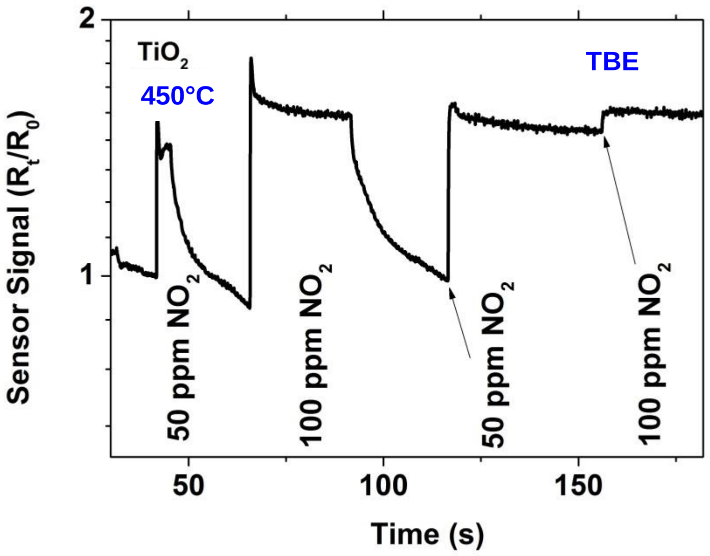


- At 400°C: NO_2-sensitivity of sputtered TiO_2:Cr-layer appears lower than sputtered TiO_2,
- However sensor response of undoped TiO_2 at 400°C is very irregular and indicates poisioning on high concentration of gas exposure
- Above 500°C: NO_2-sensitivity of sputtered TiO_2:Cr-layer increases steadily and yields a reasonably well sensor response

➡ Sensor with TiO_2:Cr layer sputtered on IDE can be used above 500°C

NO_2-response of TiO_2 sputtered between TBE



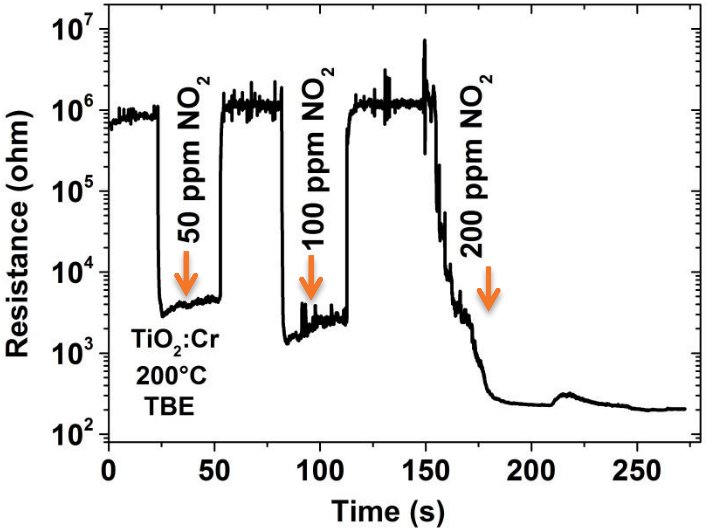


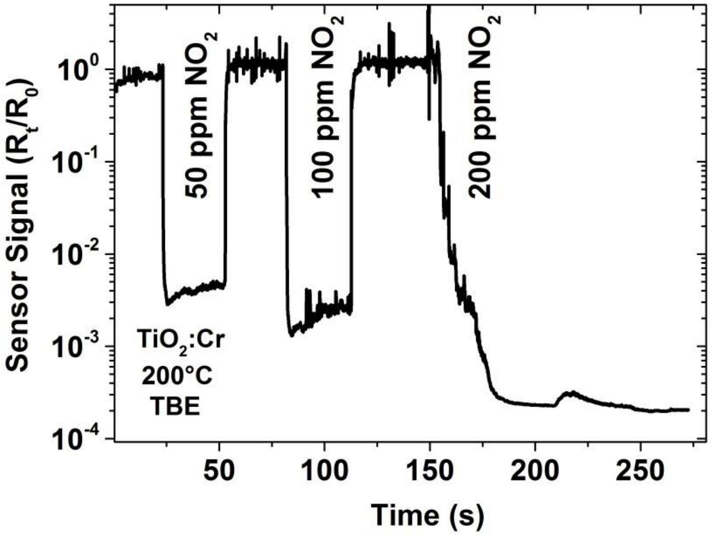
➡ NO_2-response of TiO_2 layer sputtered between TBE is improved but there is still slow recovery at 450°C

- At temperature below 400°C, NO_2-Sensor with undoped TiO_2 layer sputtered between TBE has also no reasonable sensing ability
- Sensor behavior at temperatures above 450°C are under investigation

- TiO_2 layer thickness is 2.1 µm

NO_2-response of TiO_2: 2.2 at.% Cr-layer sputtered between TBE



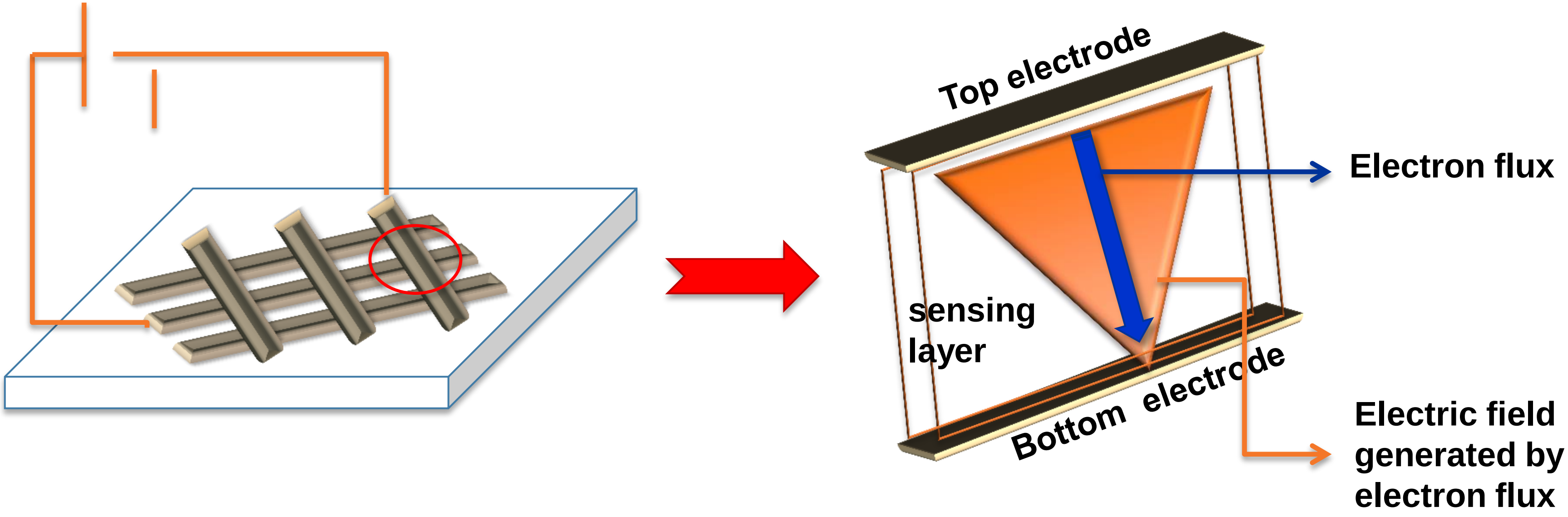


➡ NO_2-response of TiO_2 with 2.2 at.% Cr (TiO_2:Cr) sputtered between TBE yields good sensor response with high sensitivity at temperatures as low as 200°C

- The sensitivity for 50 ppm NO_2 is a factor of $5X10^2$ higher than that achieved with same sensor material on IDE
- The baseline-resistance decreases on exposure to NO_2-concentrations above 200 ppm.
- The investigation to understand the cause of this and similar phenomena is under way.

- TiO_2 layer thickness is 1.8 µm

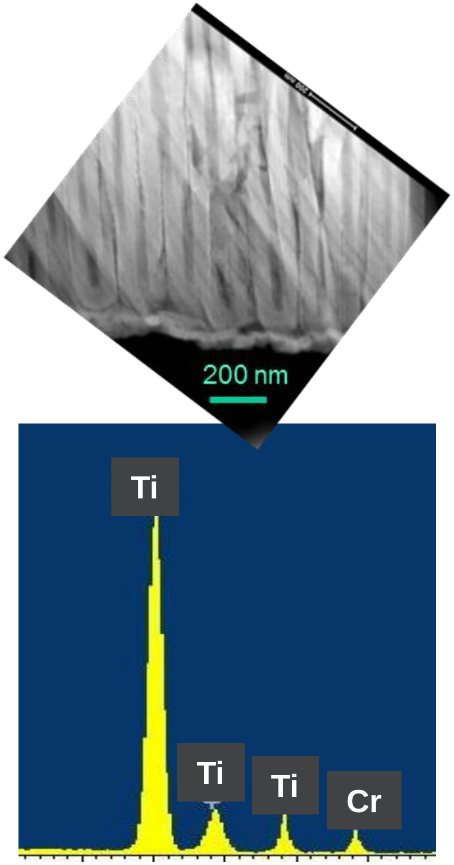
Principle of TBE „Resistive Switching“

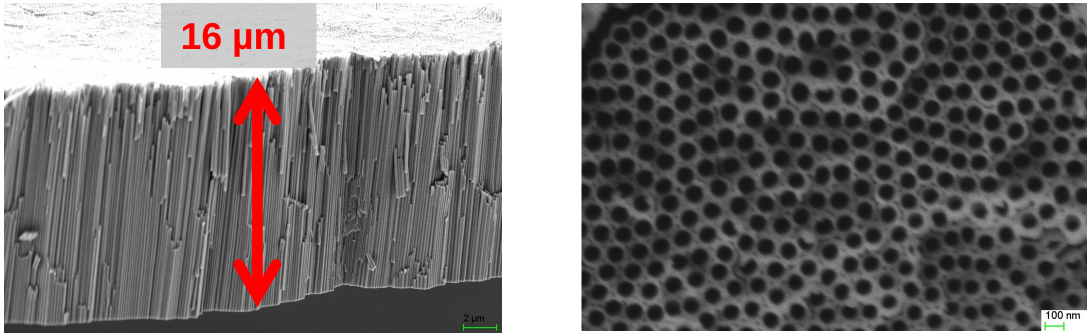


- On change of the charge loading direction, the polarity gains importance and plays great role in sensing
- Electron flux is influenced by
    - polarity,
    - electrode material and dimensions and
    - semiconductor layer thickness.

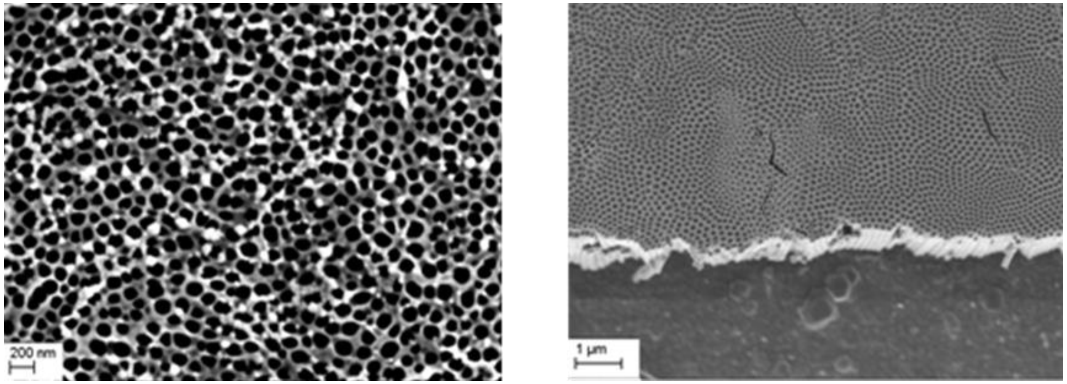
Microstructure of Nano-Tubular TiO_2:Cr (2.4 at.%)

TiO_2-NT soaked in $Cr(NO_3)_3$-sol for 5h and annealed at 450°C and 700°C



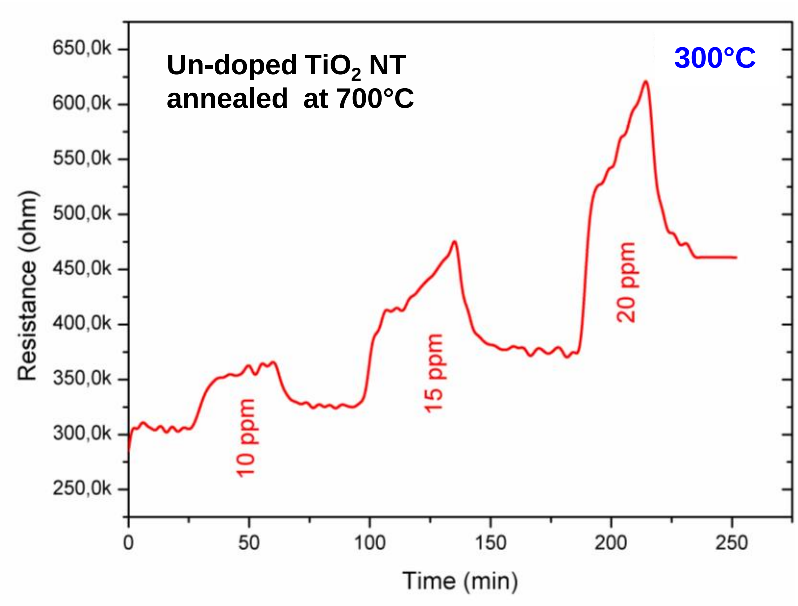


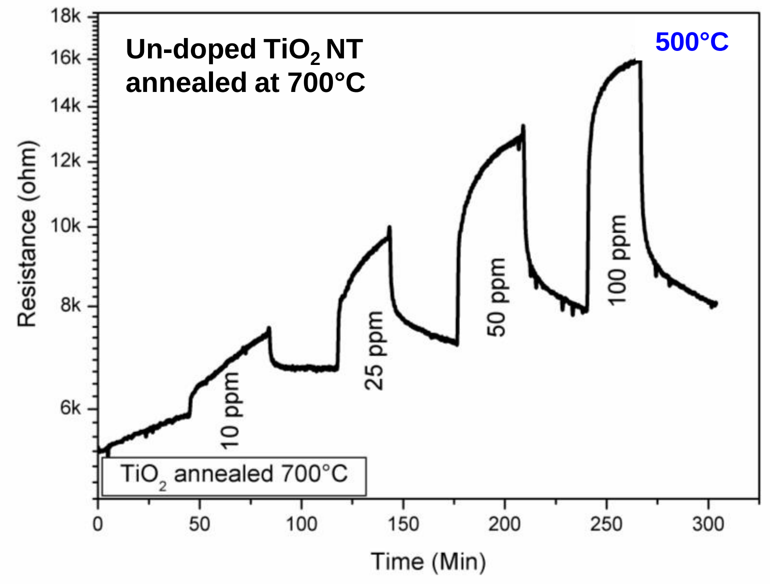
Undoped nano-tubular TiO_2 after annealing at 700°C



Cr^{3+}-doped nano-tubular TiO_2 after annealing at 700°C

NO_2-sensitivity of TiO_2 -NTs with // Pt-electrodes

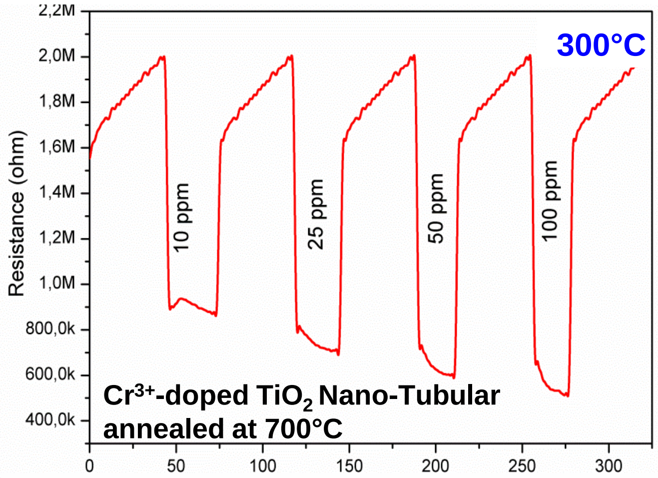


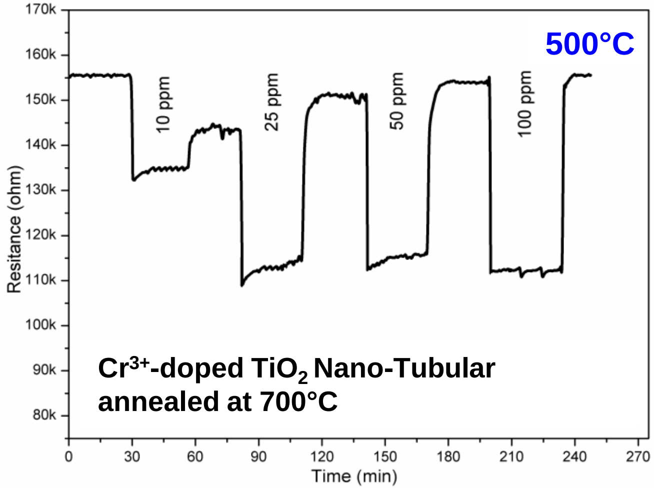


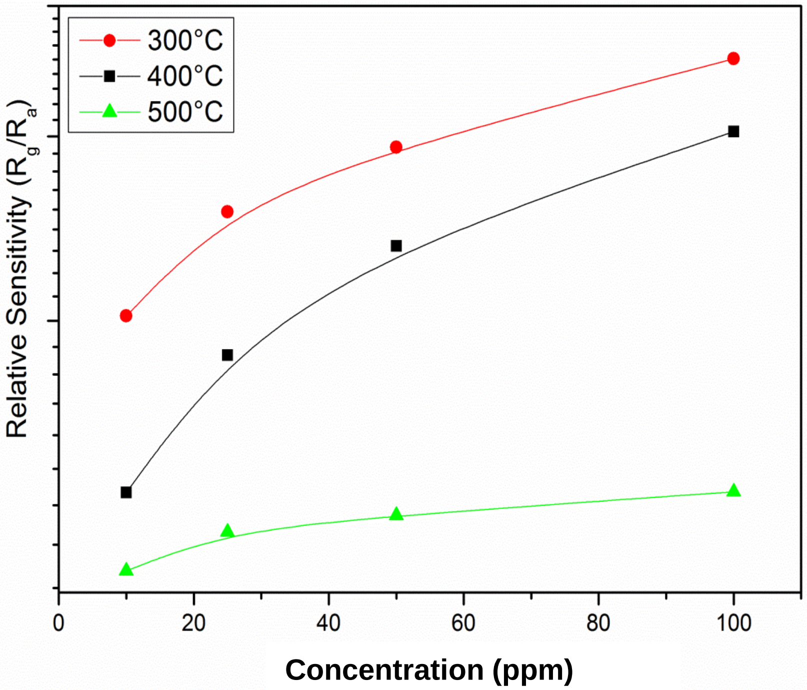
- TiO_2-NTs yields sensor response towards relatively lower NO_2 concentrations at temperatures between 300°C - 500°C
- Some drift is present

- TiO_2 NT-layer thickness is 12 µm

NO_2-sensitivity of TiO_2:Cr-NT with // Pt-electrodes







- NO_2-sensitivity of TiO_2:Cr NTs reduces with temperature and becomes low at 500°C
- Sensor response is more steady at 500°C, however the resolution with concentration is poor
- Optimum sensor response is achieved at 400°C

Conclusions

- TiO_2 yields n-type sensor response with all three sensor configuration and after nano-structuring
- Cr-doping of TiO_2 converts the sensor behavior from n-type to p-type
- Sputtering facilitates doping of semiconductor oxides with various contents and the manufacturing of good quality sensing layers suitable to lithography and MEMS-processing
- TBE sensor configuration enables NO_2 sensing at temperatures as low as 200°C with high sensitivity ($10X10^2$)
- Nano-structuring of TiO_2 yielding tubes (NTs) with 70 nm pore diameters and 10 nm wall thickness leads to better sensing response
- Wet-chemical Cr-doping of TiO_2 NTs improves the sensor response and enables NO_2 sensing at 300°-500°C

Suggested R&I Needs for future research

- Polarity effects
- Effects of electrode size and structure
- Catalytic effects of Pt on sensing
- Analysis the role of each sensor element by means of Impedance Equivalent Circuit Fitting
- Characterization of electronic state (work function, band gap structure)
- Understanding the reasons leading to sensor poisoning

valuable contributions of

- Dr. A. A. Haidry
- Dr. Y. Gönüllü
- Dr. E. Ciftyürek are acknowledged.

- Thank you very much for your attention..