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

COST Action TD1105

WGs & MC Meeting at SOFIA (BG), 16-18 December 2015

New Sensing Technologies for Indoor Air Quality Monitoring: Trends and Challenges

Action Start date: 01/07/2012 - Action End date: 30/04/2016 - Year 4: 1 July 2015 - 30 April 2016

HIGH SENSITIVITY AND LOW OPERATION TEMPERATURE SENSORS USING Pt/CHROMIUM-TiO_2/Pt-SANDWICH LAYERS

Bilge Saruhan-Brings
WG 1 Member
German Aerospace Center, Institute of Materials Research, Cologne/ Germany
Bilge.saruhan@dlr.de

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

ESF provides the COST Office through a European Commission contract

Scientific context and objectives

PROBLEM

- Robust detection of nitrogen oxides under the common conception of NOx ($NO+NO_2$) is highly demanding
  - NO and NO_2 results in sensor signals in the opposite direction to each other
  - At temperatures above 500 °C, thermodynamic equilibrium is on the NO-side
  - Semiconducting oxides such as TiO_2 are good candidate materials for NO_2 sensing however, higher operating temperatures are required (> 400 °C)

Scientific context and objectives

REQUIREMENT

- Sensor systems that are capable of NO_2 sensing at temperatures << 400 °C
- For that necessary optimization needs:
    - **Change in the electrical transport mechanism:**

  - Sensing material can be nano-structured and/or
  - Crystal chemistry can be changed by doping

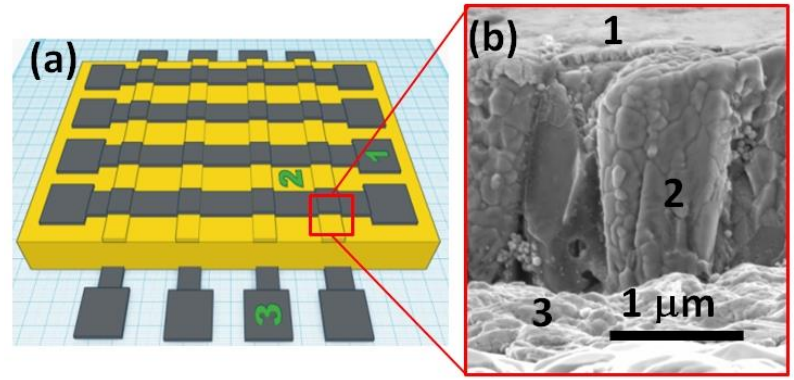
    - **Change in the electrical signal output through metallic electrodes:**

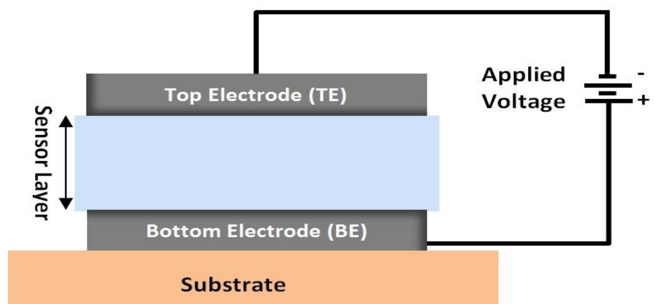
  - Sensor configuration can be altered

Current research activities

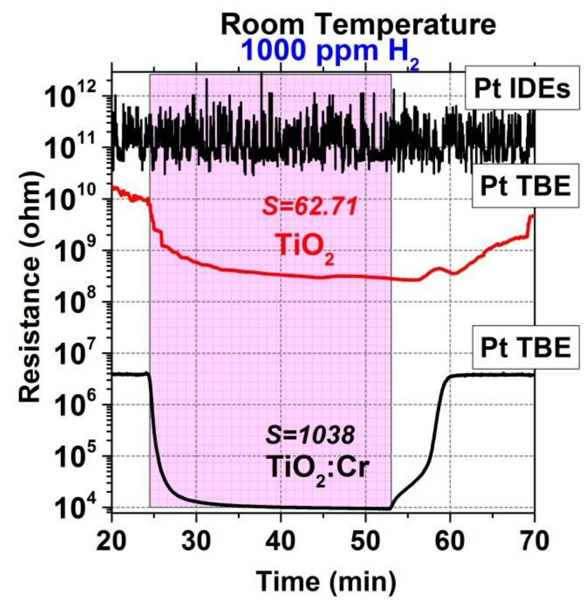
- **SOLUTION**

Interdigitale Electrodes (IDE)



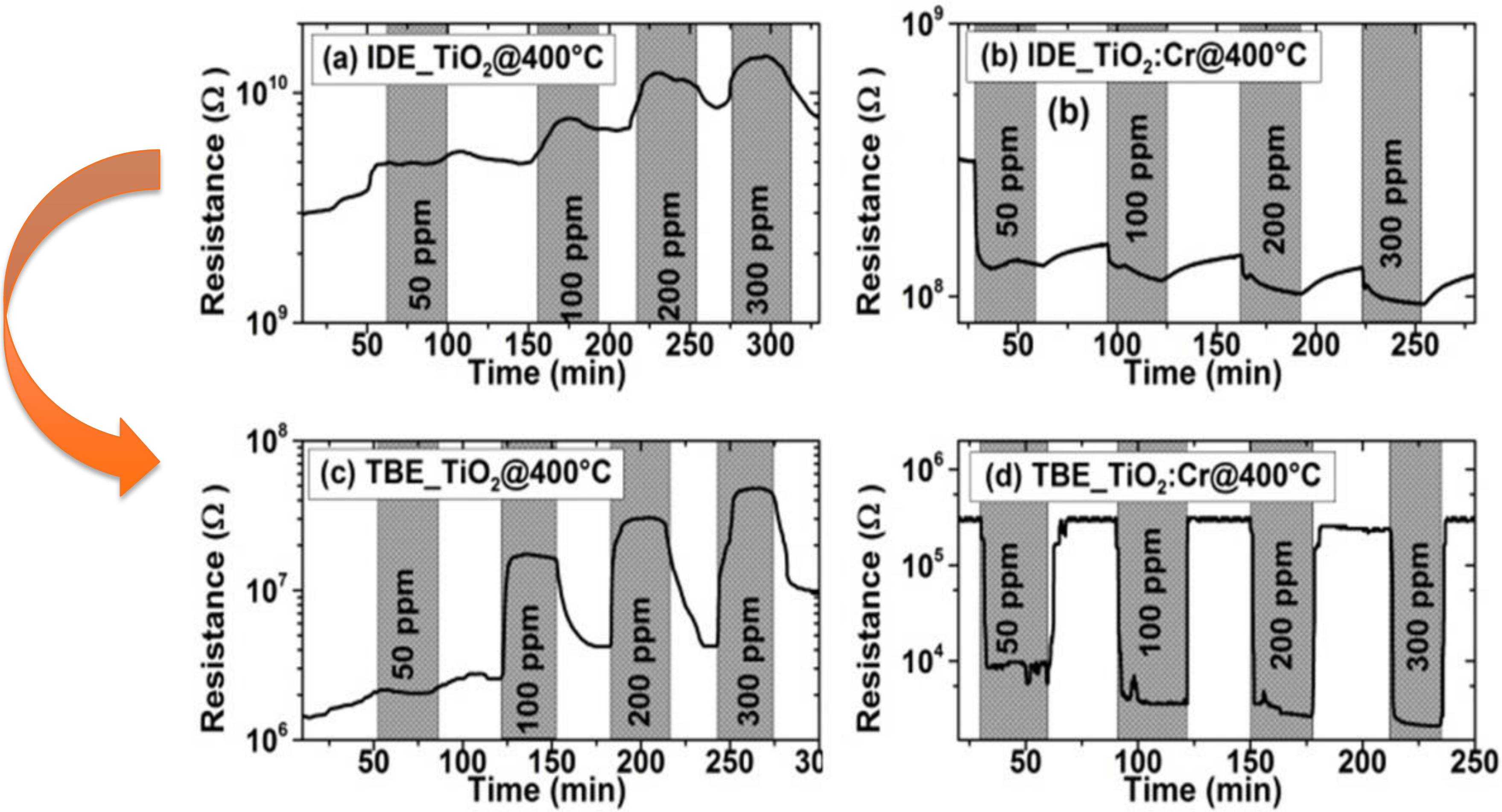


Top-Bottom Electrodes (TBE)



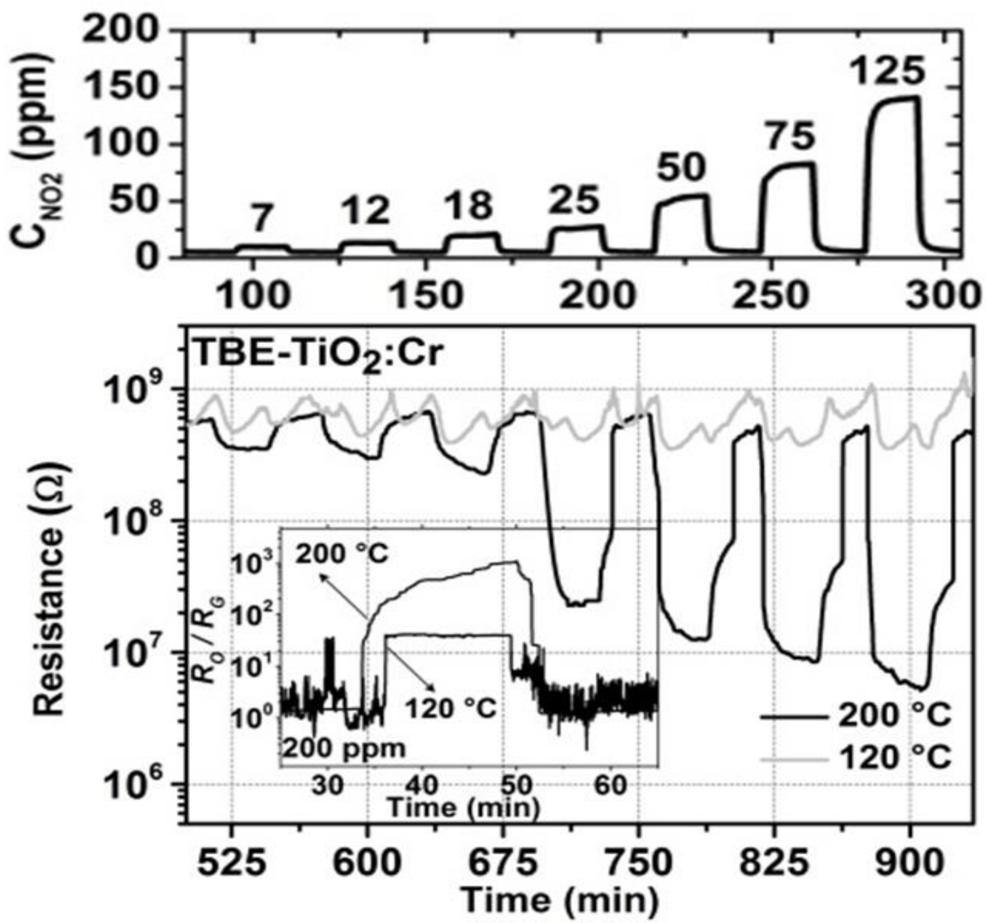
Current research activities

- **IDE vs. TBE with the same sensing material at 400°C**



Current research activities

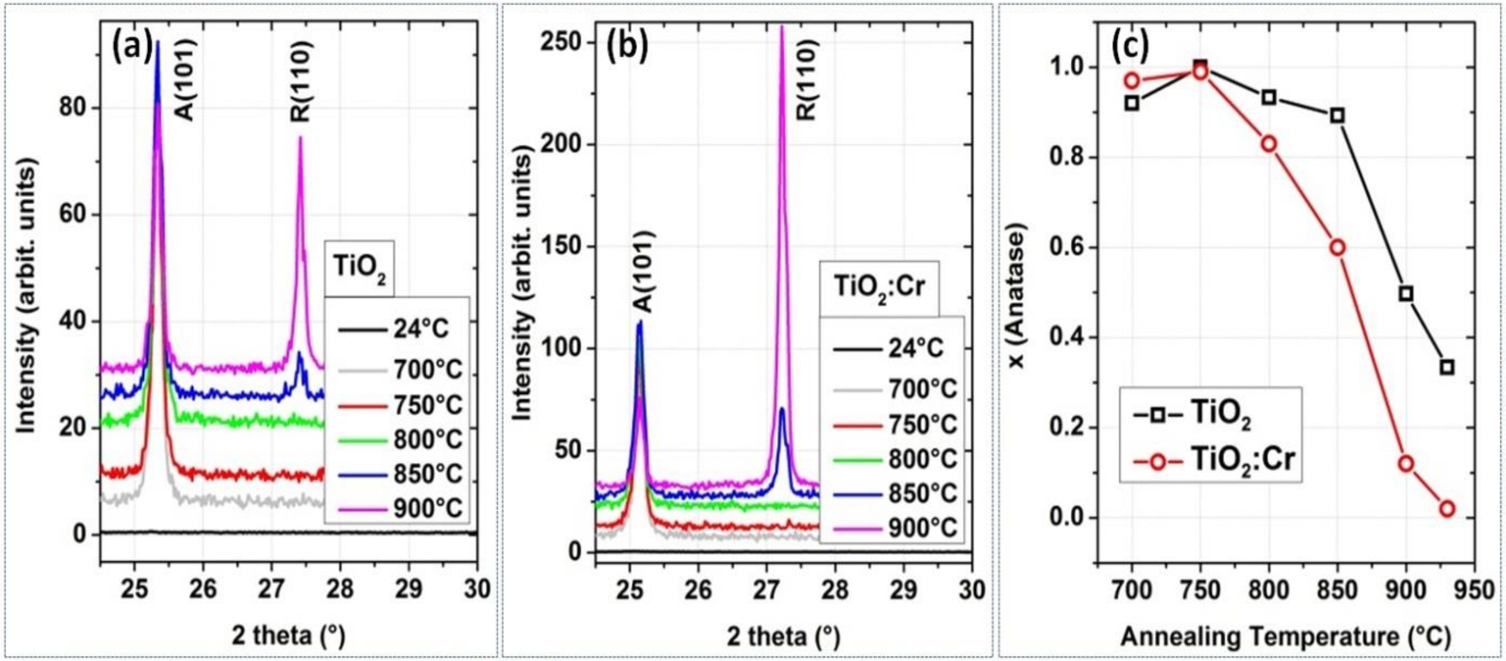
- **Dynamic response of TiO_2:Cr sensing layer towards NO_2 with TBE configuration at 120 °C and 200 °C**



The inset shows enlarged normalized dynamic response of the same sensor towards 200 ppm NO_2 at 120 °C and 200 °C

Current research activities

- **Phase sequences by <u>TiO_2</u> (left) and <u>TiO_2:Cr</u> (right) layers during in-situ HT-XRD**



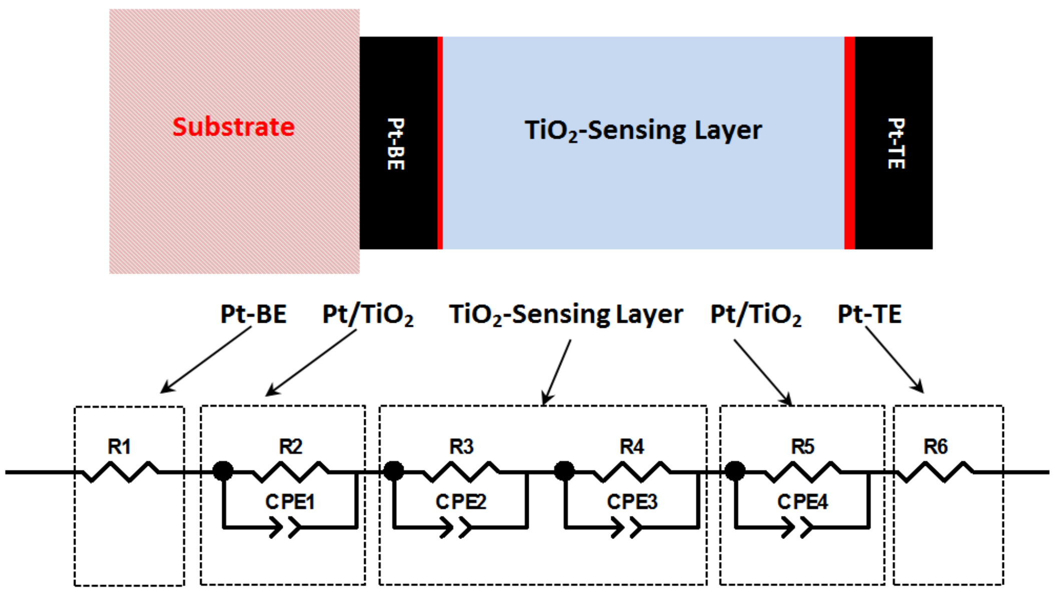
XRD of ex-situ heat-treated (800 °C for 3 h) coatings exhibit:

- undoped TiO_2 layers consist of both anatase (64%) and rutile phases (36%)
- while TiO_2:Cr layers contains only rutile phase.

Current research activities

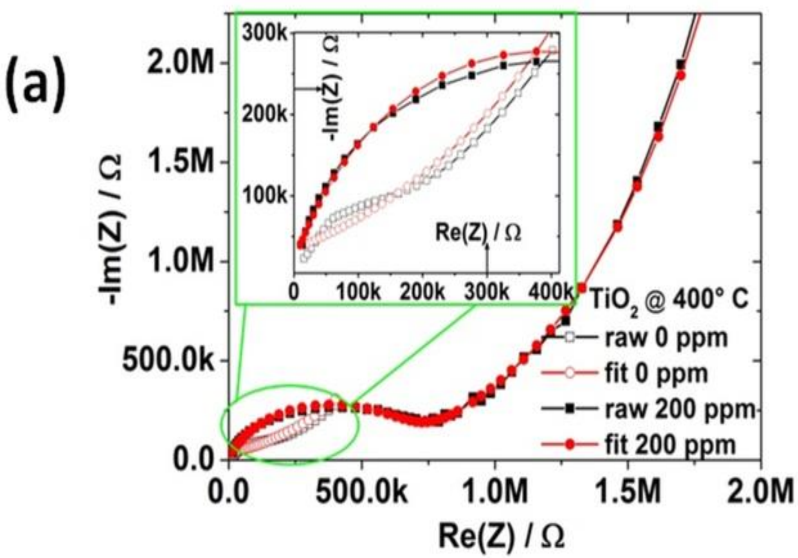
Impedance Measurements and Equivalent Circuit Modelling

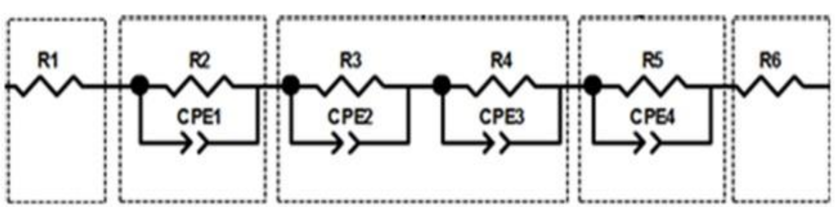
- **Sensing towards NO_2 with Pt-TBE configuration and sandwich TiO_2 layer**

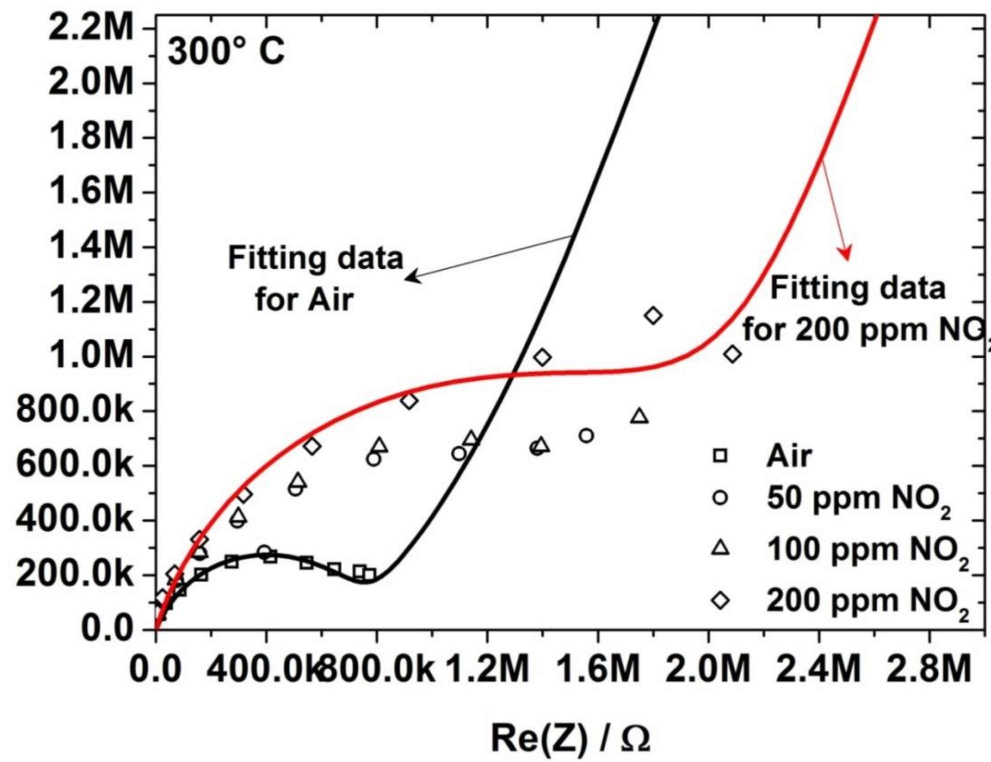


Current research activities

- **Impedance Measurements and Equivalent Circuit Fitting towards NO_2 with TiO_2 and TBE sensor configuration at 400 °C**

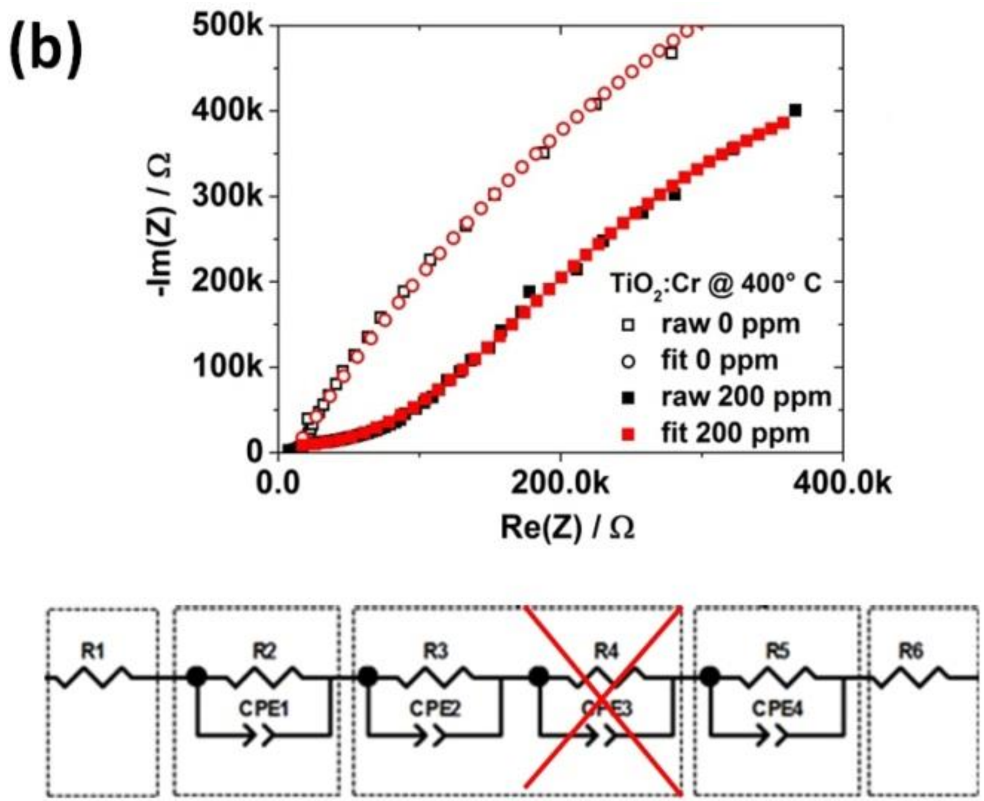






Current research activities

- **Impedance Measurements and Equivalent Circuit Fitting towards NO_2 with TiO_2:Cr and TBE configuration at 400 °C**



The advantageous sensor behavior is due to the Cr-doping introduced oxygen vacancies and holes

Not because of the different phase constituents (i.e. main phase anatase as in TiO_2:Cr vs. rutile in undoped TiO_2)

Current research activities

- **Sensing behavior towards NO_2 with TiO_2:Cr and TBE sensor configuration**

In the case of Cr-doping, as NO_2 interacts with the sensor layer:

- hole formation below conduction band results in large changes in true capacitance values ($C_{V0,0ppm} << C_{V0,200ppm}$)

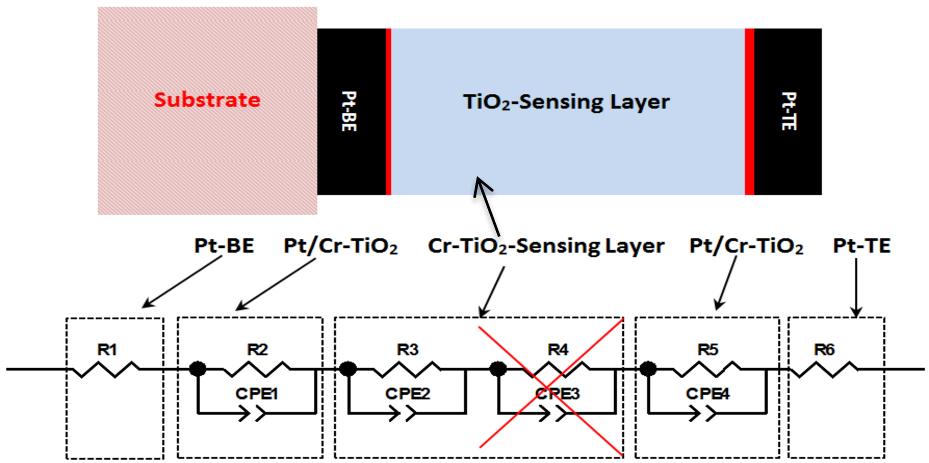
This is because

- the inverse layer becomes thinner as NO_2 gas approaches to the surface
- occurrence of huge decrease in true capacitance value, C_{V0} (six orders of magnitude) as NO_2 diffuses through it

Sample/C_{NO2}	$C_{TE/SL}$ (F)	$C_{BE/SL}$ (F)	C_{V0} (F)	C_{gb} (F)
TBE-TiO_2/0-ppm	5.80×10^{-8}	7.90×10^{-11}	1.08×10^{-7}	1.87×10^{-4}
TBE-TiO_2/200-ppm	1.19×10^{-4}	2.81×10^{-7}	1.05×10^{-10}	3.72×10^{-4}
TBE-TiO_2:Cr/0-ppm	9.94×10^{-4}	2.10×10^{-5}	**3.46×10^{-5}**	×
TBE-TiO_2:Cr /200-ppm	5.56×10^{-4}	1.77×10^{-3}	**2.72×10^{-11}**	×

Current research activities

- **Sensing behavior towards NO_2 with TiO_2:Cr and TBE sensor configuration**
  - Dopant introduced oxygen vacancies and hole formation results in faster electronic diffusion through grains than diffusion at grain boundaries
  - Lower resistance in TiO_2:Cr samples is an indication for that
  - The grain boundary contribution (C_{gb}) seems to play minor/no role, because, the equivalent circuit model requires no second Cole element



Summary

Sensing mechanism with TBE configuration is attributed to various sensor parts

- NO_2 surface reaction at Pt-TE
- Diffusion through sensing layer (SL)
- Pt-TE and SL interface.

Below Pt-TE: Increase in the Schottky Barrier strongly due to NO_2 gas reaction with Pt-surface

At SL

For n-type TiO_2 layer between TBE,

- depletion region increases nearby the surface resulting in small change in true capacitance, C_{V0}
- Grain boundary diffusion contributes

For p-type TiO_2:Cr in contrast

- sensing mechanism is predominantly controlled by inversion layer
- holes driven faster electronic diffusion through grains

Acknowledgement

My Co-workers

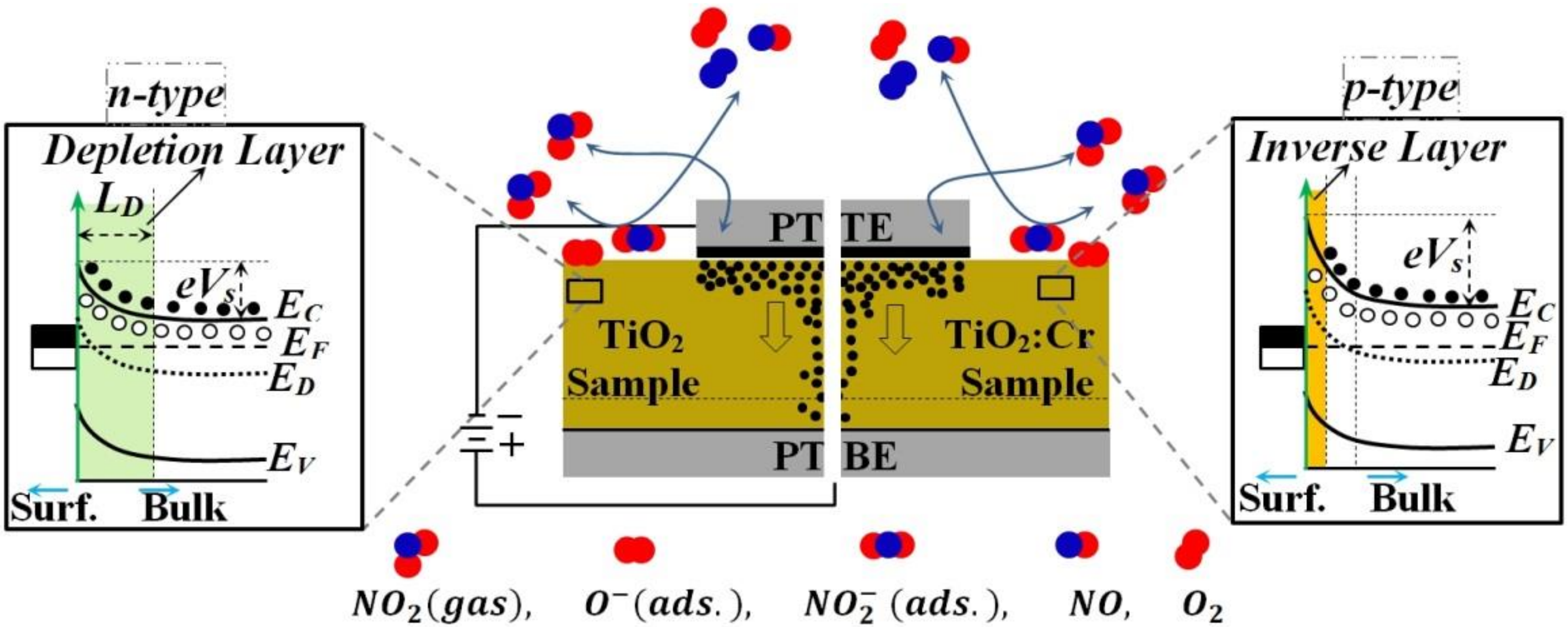
- Dr. Azhar Ali Haidry (for sensor development and measurement and equivalent circuit modelling)
- Cagdas Cetin (BSc.) (for equivalent circuit modelling)
- Dr. Klemens Kelm (for XRD analysis)

Dr. Michele Penza for invitation

Thank you for your attention

Current research activities

- **Typical sensing mechanism with undoped TiO_2 and TiO_2:Cr adsorbates in the case of TBE sensor configuration.**



<u>For n-type TiO_2 :</u> The conductivity is governed by the <u>depletion layer</u> where the Fermi level lies near the conduction level and the majority carriers are <u>electrons</u> (left).

<u>For p-type Cr-TiO_2:</u> The <u>inverse layer</u> is formed near the donor energy level where the Fermi level is situated and the majority carriers are <u>holes</u> (right).

Research Facilities available for the Partner (2/2)

SESAM – DLR-Köln