

# MCL

## Energy Autonomous Environmental Sensors

*Anton Köck*

*Group Leader “Sensor Solutions”*

GreEnergy Workshop

31/05/2022 – 01/06/2022



## MCL at a glance - History

- ❑ Founded 1999 MCL is one of the leading competence centres in material science in Austria with ~ 160 employees. The COMET K2 Centre for „Integrated Research in Materials, Processing and Product Engineering“ focuses on the full materials value chain in applications.
- ❑ In March 2012 the research area „Materials for Microelectronics“ was established:
  - ❑ Nanosensors and multi-sensor systems
  - ❑ CMOS integration of nanotechnology based sensor components
  - ❑ 3D-System Integration, Packaging and Reliability
  - ❑ Materials characterization from nano- to microscale.

*A. Köck, M. Deluca, F. Sosada-Ludwikowska, L. Egger*  
**Materials Center Leoben Forschung GmbH, Austria**

*M. Sagmeister, K. Rohrer, E. Wachmann*  
**ams AG, Austria (ams OSRAM)**

*J. Niehaus, S. Becker, Ö. Tokmak, H. Schlicke*

**Center for Applied Nanotechnology CAN, Fraunhofer Institute for Applied  
Polymer Research Germany**

*A. Blümel, K. Popovic, M. Tscherner*  
**Joanneum Research, Austria**

*S. Steinhauer, V. Zwiller*

**KTH Royal Institute of Technology, Quantum Nano Photonics, Sweden**

*M. Sowwan, V. Singh*

**Okinawa Institute of Science & Technology, Graduate University,  
Okinawa, Japan**

## *Outline*

1. Motivation
2. Gas Sensor Devices
3. Smart System Integration
4. Chemical Sensors @ MCL
5. Multi-Gas Sensor Device
6. The FOXES Project
7. Summary & Outlook

# 1. Motivation



- ❑ ~90% of time is spent indoors; outdoor pollutants also found indoors, additional indoor pollutant sources add to disease burden
- ❑ > 400.000 premature deaths in EU27+UK every year (EEA); COVID-19 and influenza add further mortality

# Air Quality Monitoring

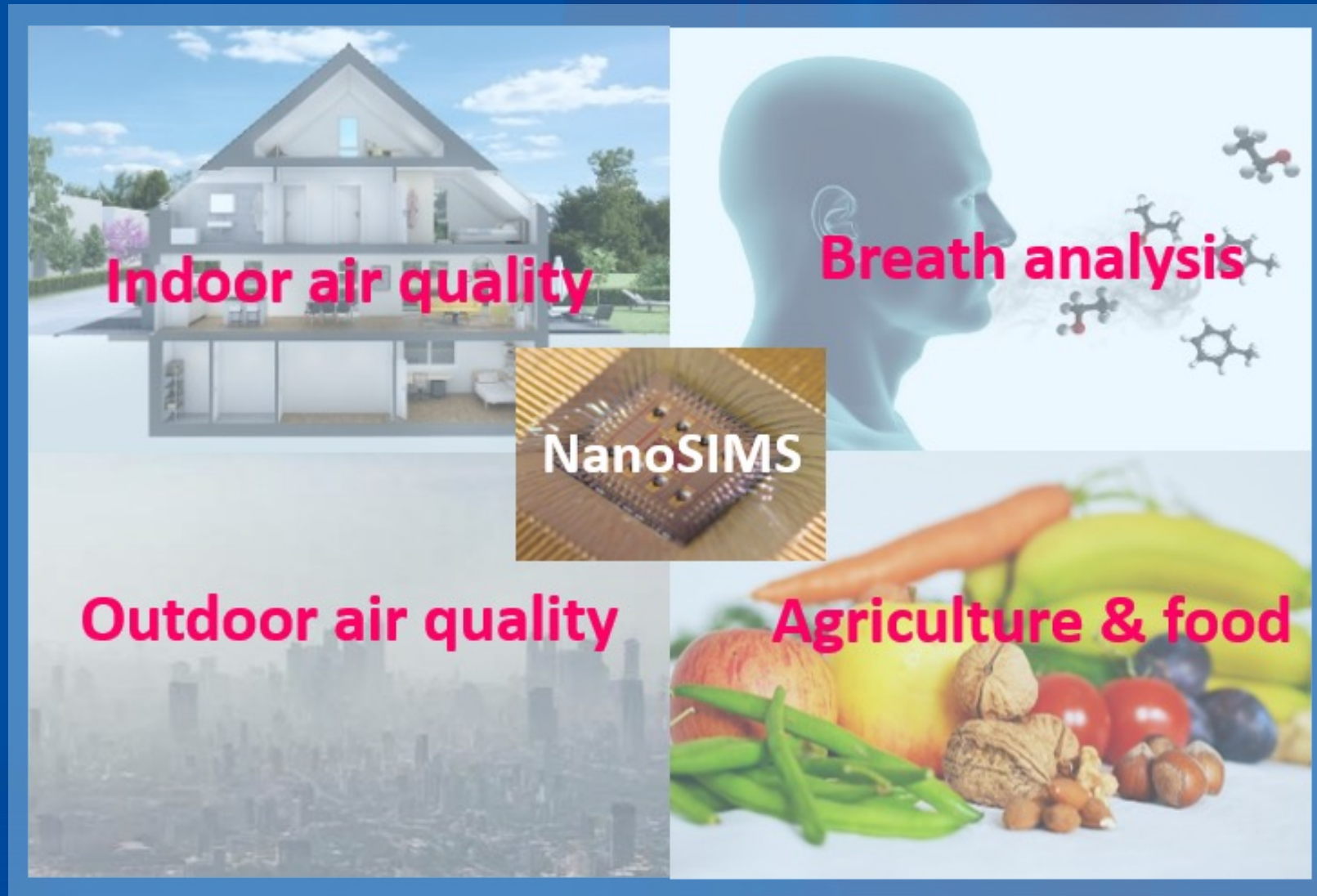


Indoors  
CO, CO<sub>2</sub>, VOCs, PM



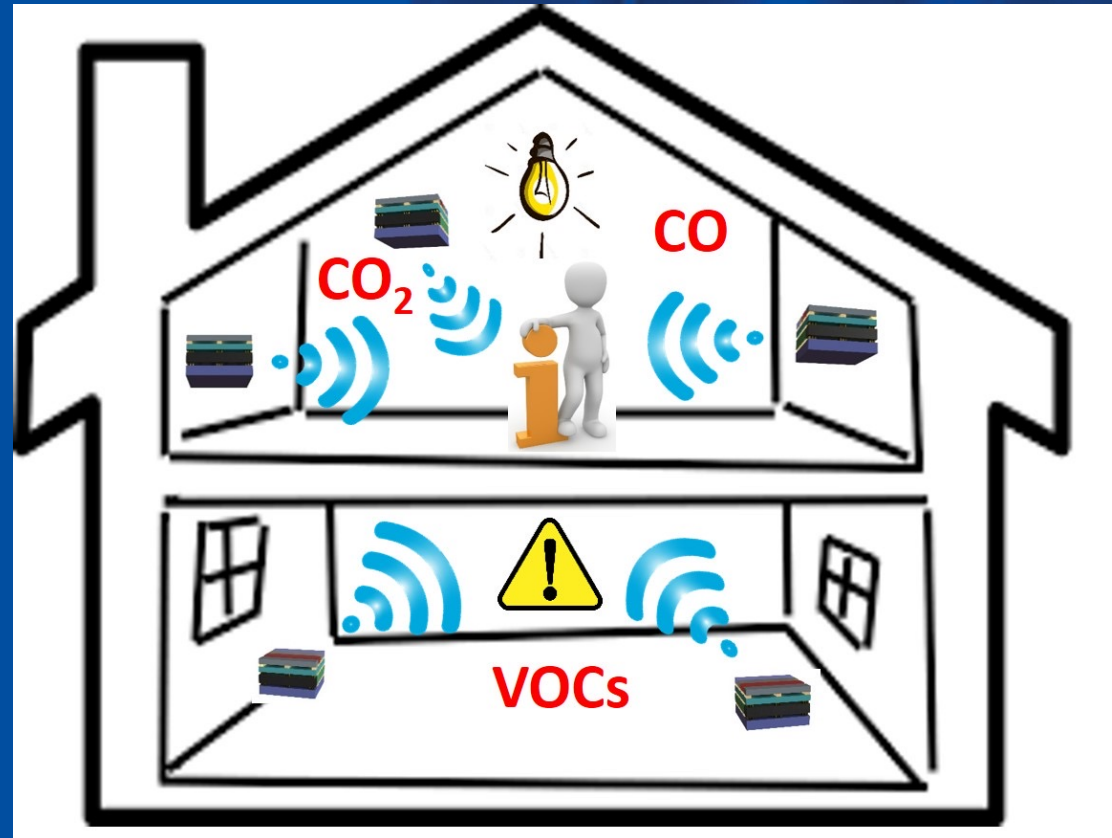
Outdoors  
NO<sub>2</sub>, O<sub>3</sub>, CO, PM<sub>10</sub>, PM<sub>2.5</sub>, UFPs

# Air Quality Monitoring



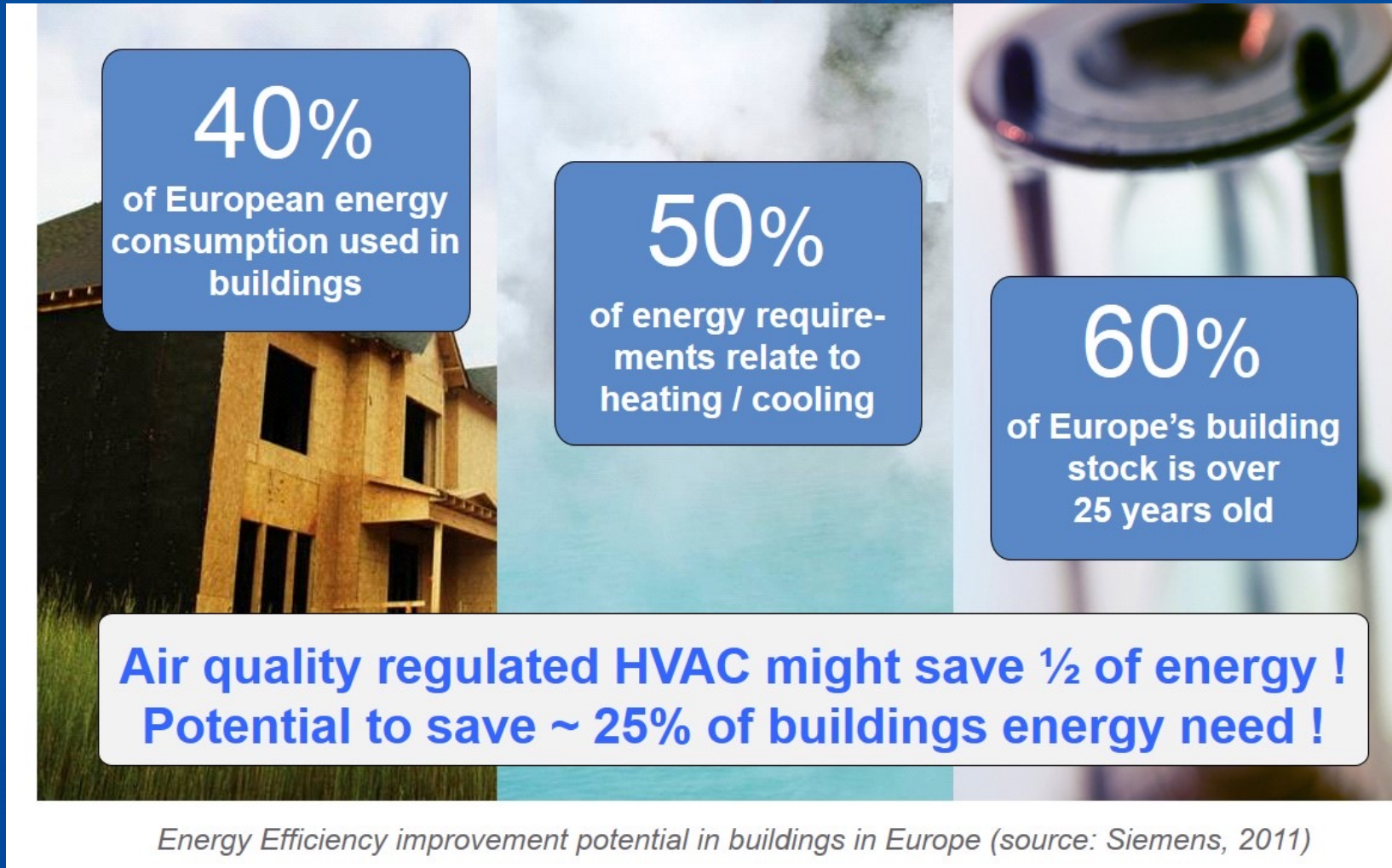
- ❑ Consumer Electronics: Individual monitoring of environmental conditions, for detection of potentially harmful situations, and for alerting people with health predisposition of upcoming afflicting environmental conditions ( $O_3$ ,  $NO_2$ , ...).
- ❑ Indoor environmental monitoring: Private homes, office buildings, hospitals or vehicle/airplane cabins.
- ❑ Outdoor environmental monitoring: Setting up sensor networks for area-wide monitoring of air pollutants ( $SO_2$ ,  $NO_2$ ,  $CO$ ,  $CO_2$ ,  $O_3$  etc.) and greenhouse gas emissions.
- ❑ Smart medicine & smart health: Breath analysis for monitoring patients with chronical illness (e.g. diabetes) and screening of upcoming diseases (e.g lung infections).
- ❑ Agriculture and Food: Monitoring gaseous conditions in green houses, monitoring freshness of fruits and taking preventive actions when conditions potentially endanger crops.

- ❑ Indoor Air Quality (IAQ) Monitoring everywhere - in all rooms !
- ❑ Smart Homes, Smart Living,...
- ❑ Outdoor Air Quality Monitoring – pollution mapping,...

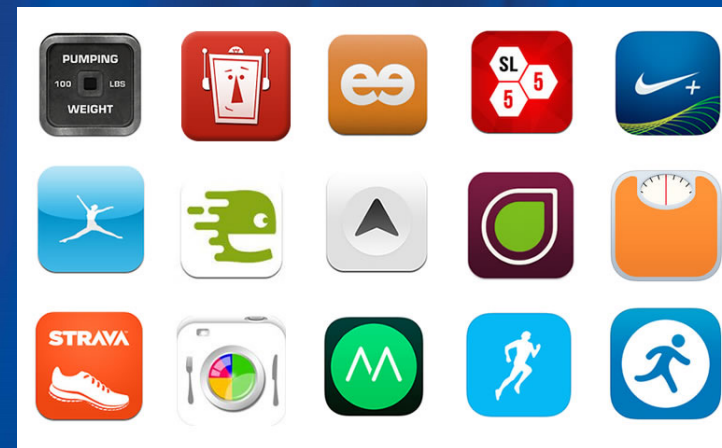


## IoT Sensor Networks for indoor and outdoor air quality monitoring

- ❑ Air Quality Monitoring for Heating, Ventilation, Air Conditioning (HVAC)
- ❑ Smart Building Management: VOCs, CO<sub>2</sub>,...



- ❑ New life style applications require chemical sensors in smart phones, smart watches,...
- ❑ Example: breath analyzes, individual monitoring of environmental conditions,...



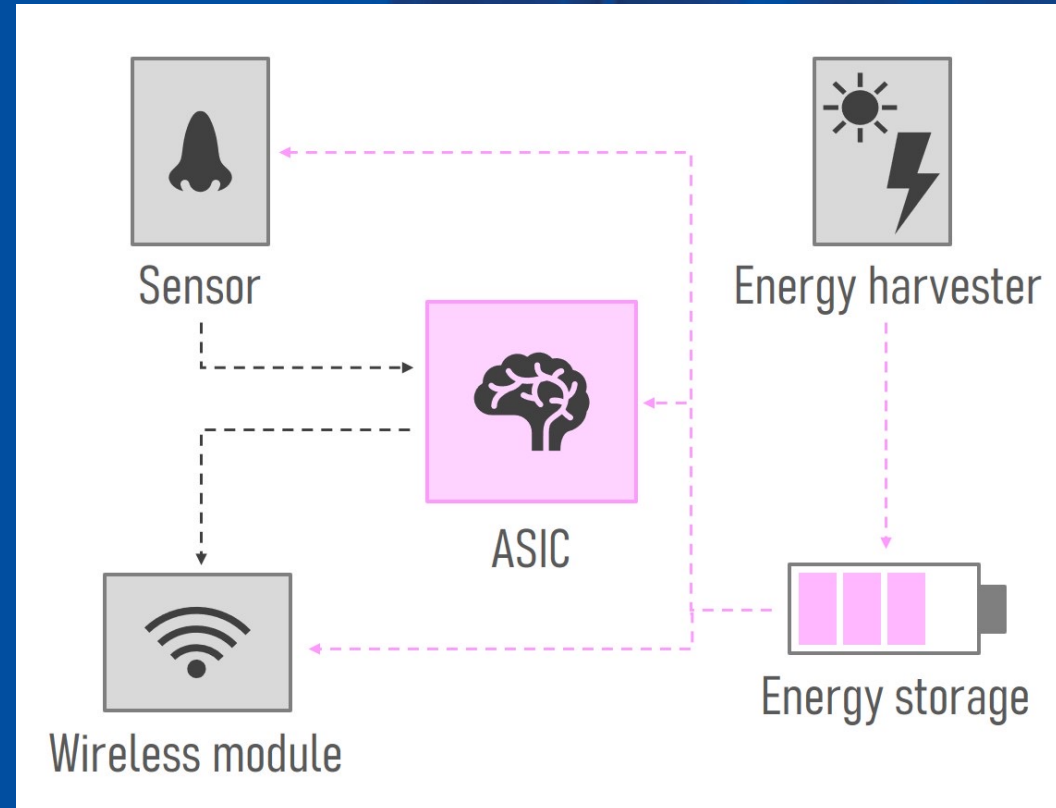
- ❑ New life style applications require chemical sensors in smart phones, smart watches,...
- ❑ Example: breath analyzes (smart medicine: diabetes, upcoming diseases...)



CMOS- & Smart System Integration are a MUST for consumer electronic applications !

- Small footprint
- Low power consumption
- Multi-sensing capability

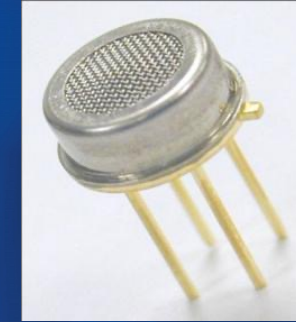
# Vision: Energy Autonomous Sensor Systems



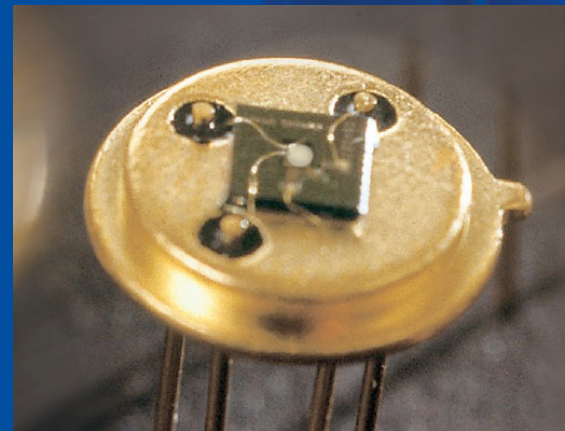
# IoT Sensor Networks for indoor and outdoor air quality monitoring

## 2. Gas Sensor Devices

- ❑ Rather conventional devices
- ❑ Cross selectivities
- ❑ High power consumption
- ❑ Mostly for professional use only

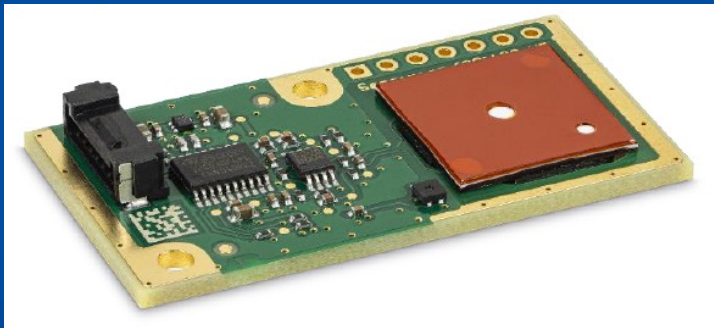


**CO-B4 Carbon Monoxide Sensor**  
4-Electrode



- ❑ Rather conventional devices
- ❑ Cross selectivities
- ❑ High power consumption
- ❑ Mostly for professional use only

**SENSIRION**



## Data Sheet SFA30

Formaldehyde Sensor Module for HVAC and Indoor Air Quality Applications

## Datasheet Sensirion SCD30 Sensor Module

CO<sub>2</sub>, humidity, and temperature sensor



**SENSIRION**

## BME680

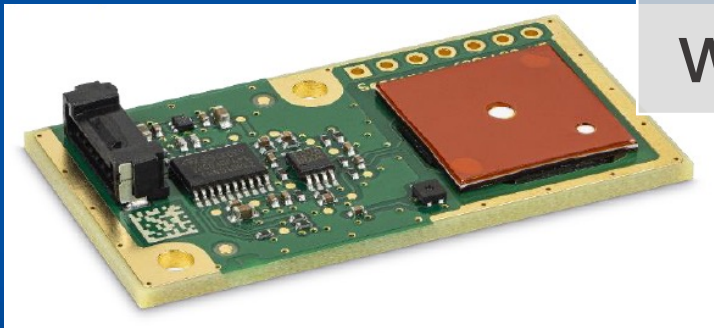
Low power gas, pressure, temperature & humidity sensor



 **BOSCH**

- ❑ Rather conventional devices
- ❑ Cross selectivities
- ❑ High power consumption
- ❑ Mostly for professional use only

**SENSIRION**



## Data Sheet SFA30

Formaldehyde Sensor Module for HVAC and Indoor Air Quality Applications

## Datasheet Sensirion SCD30 Sensor Module

CO<sub>2</sub>, humidity, and temperature sensor



**SENSIRION**

Most of today's gas sensors are not smart devices – no integration with CMOS technology!

BME680  
Low power gas, pressure, temperature & humidity sensor

Low power gas, pressure, temperature & humidity sensor



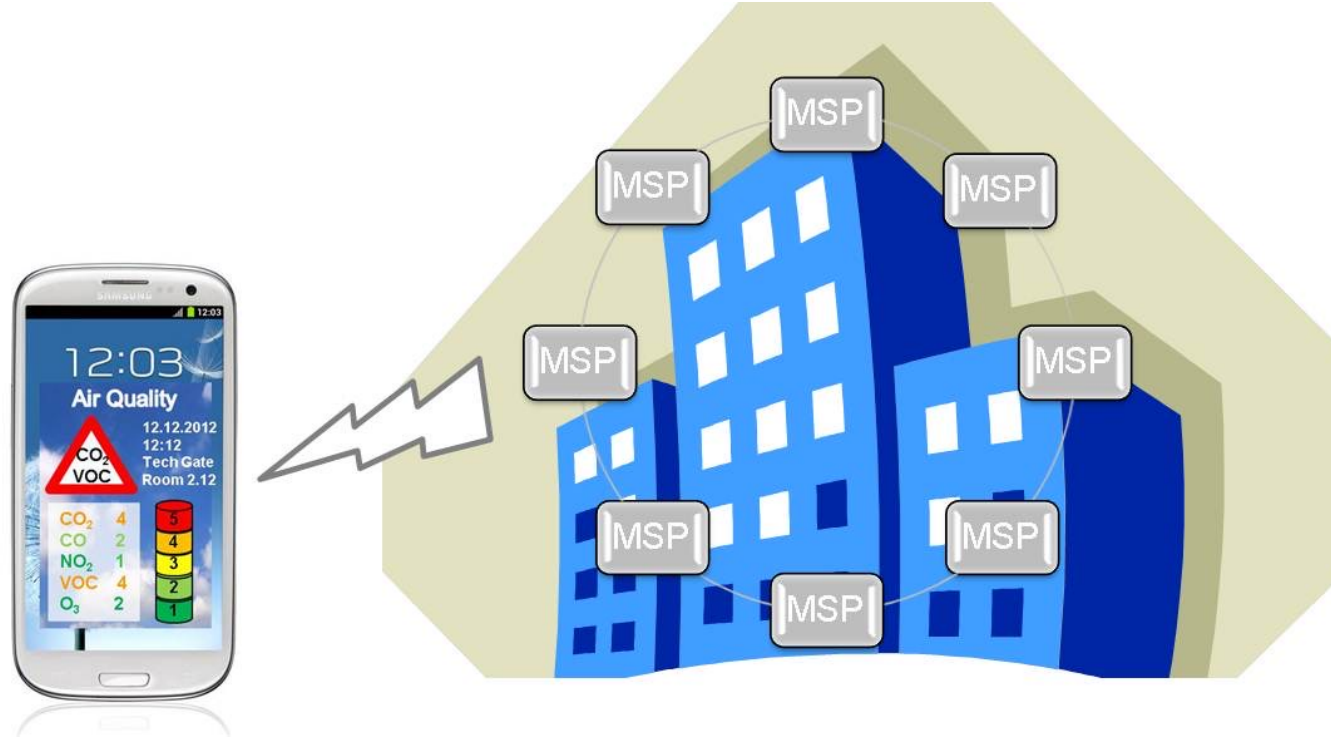
 **BOSCH**

# No Multi-Gas Sensor Devices !

|                            | MATEAS Device    | Bosch BME 680      | Sensirion SFA30 | Sensirion SGP41  | Alphasense         | Figaro TGS8100 |
|----------------------------|------------------|--------------------|-----------------|------------------|--------------------|----------------|
| <b>Detection principle</b> | conductometric   | conductometric     | conductometric  | conductometric   | electrolyte        | conductometric |
| Size [mm x mm x mm]        | < 4 x 4 x 2      | 3 x 3 x 1          | 17 x 17 x 1,5   | 2,4 x 2,4 x 0,85 | 32,3 x 32,3 x 16,5 | 3,2 x 2,5 x 1  |
| Power consumption[mW]      | < 0.5            | 11.9               | 10              | 10               | not specified      | 15             |
| Response time [sec]        | < 5              | not specified      | 120             | 120              | 30                 | not specified  |
| <b>Target gas</b>          |                  |                    |                 |                  |                    |                |
| "Air contaminants"         |                  | no                 | no              | no               | no                 | 0 - 30 ppm     |
| VOCs / Ethanol             | 100 ppb - 60 ppm | only quality index | no              | 500 - 10000 ppb  | no                 | no             |
| Nitrogen oxide             | 1 ppb - 10 ppm   | no                 | no              | 50 - 600 ppb     | no                 | no             |
| Formaldehyde               | 10 ppb - 1 ppm   | no                 | 0 - 1000 ppb    | no               | no                 | no             |
| Carbon monoxide            | 1 ppm - 1000 ppm | no                 | no              | no               | 100 ppb - 10 ppm   | no             |
| Benzene                    | 0 - 15 ppb       | no                 | no              | no               | no                 | no             |
| Toluene                    | 50 ppb - 50 ppm  | no                 | no              | no               | no                 | no             |
| Ammonic                    | 1 ppm - 500 ppm  | no                 | no              | no               | no                 | no             |
| Ozone                      | 1 ppb - 1000 ppb | no                 | no              | no               | no                 | no             |
| Sulfur dioxide             | 1 ppb - 1000 ppb | no                 | no              | no               | no                 | no             |
| Hydrogen sulfide           | 50 ppb - 50 ppm  | no                 | no              | no               | no                 | no             |

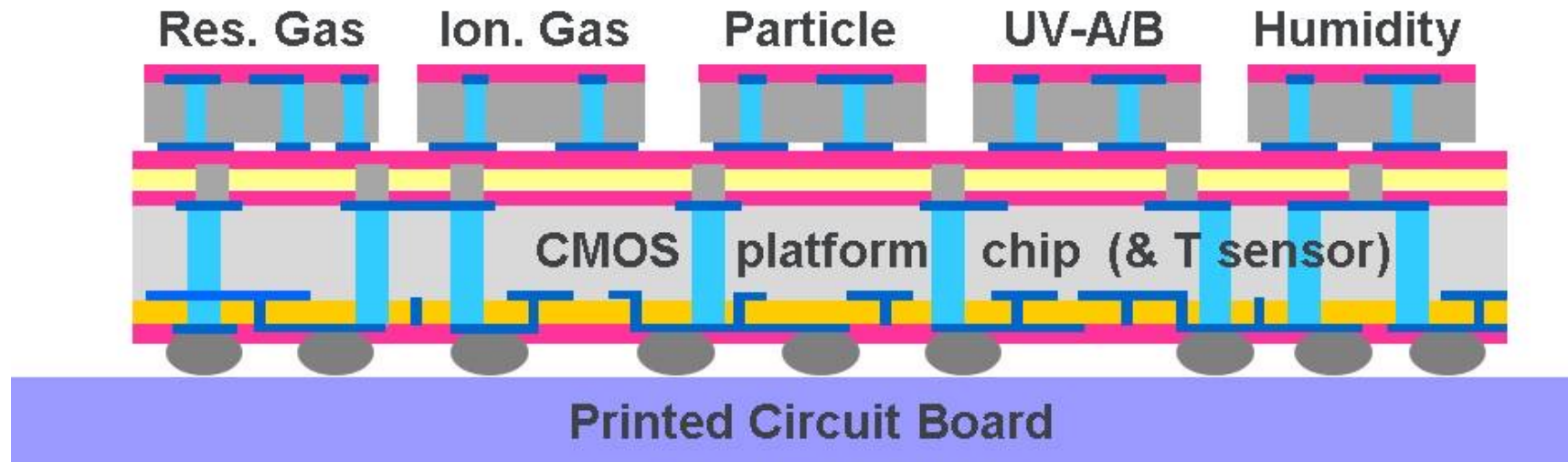
### 3. Smart System Integration

## The MSP-Project - Multi Sensor Platform for Smart Building Management

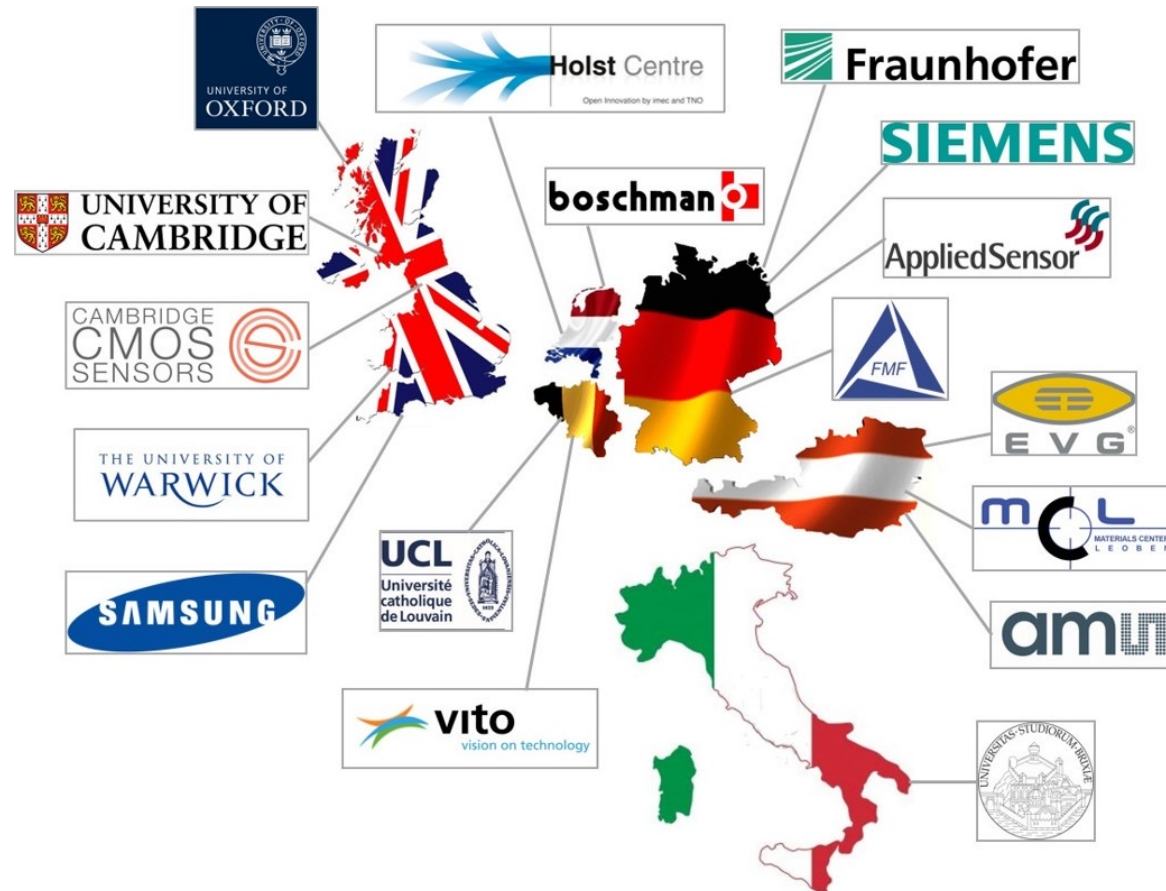


FP7-Project – Grant Agreement No. 611887

- Development of smart 3D-integrated multi-sensor systems enabling indoor and outdoor environmental monitoring !

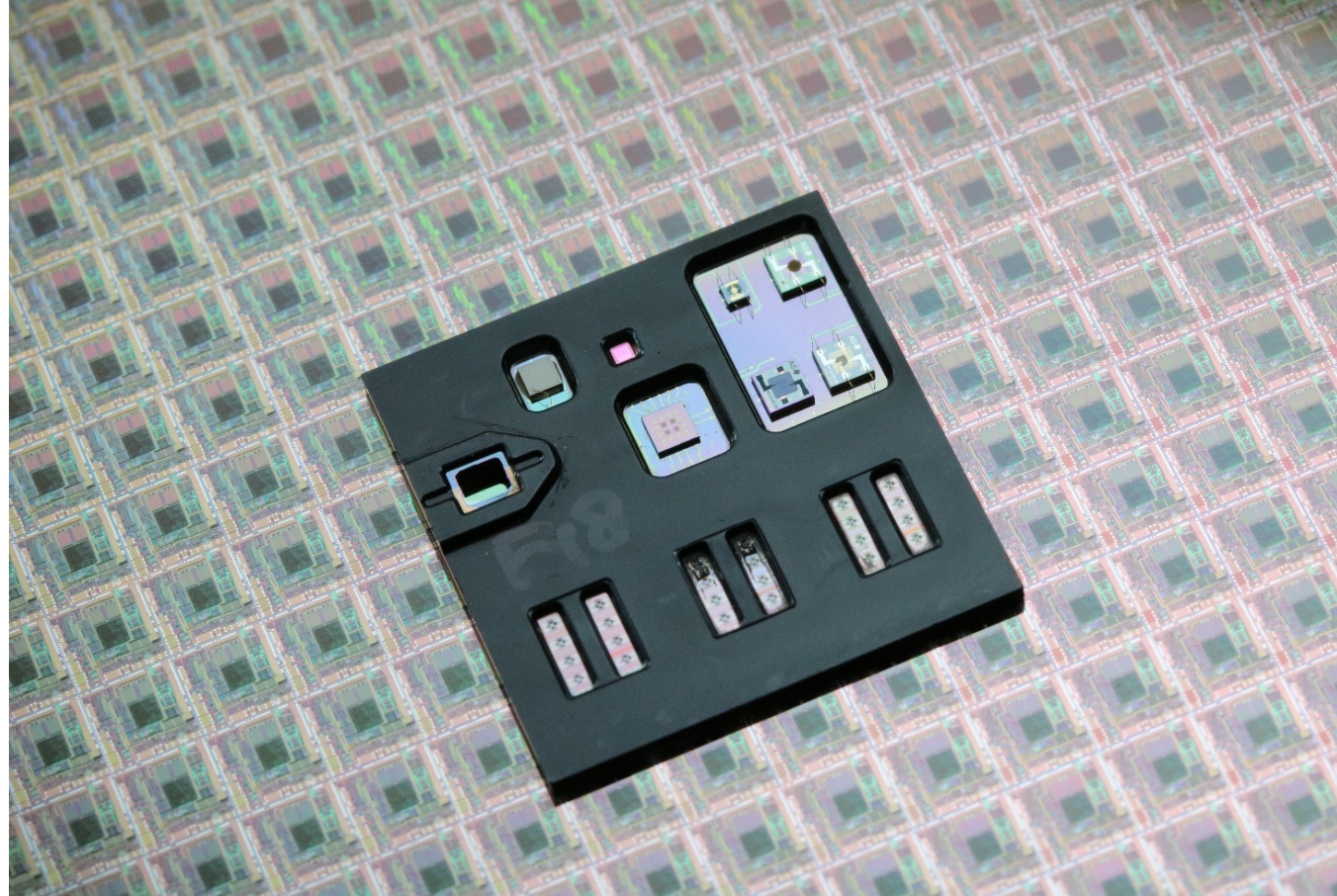


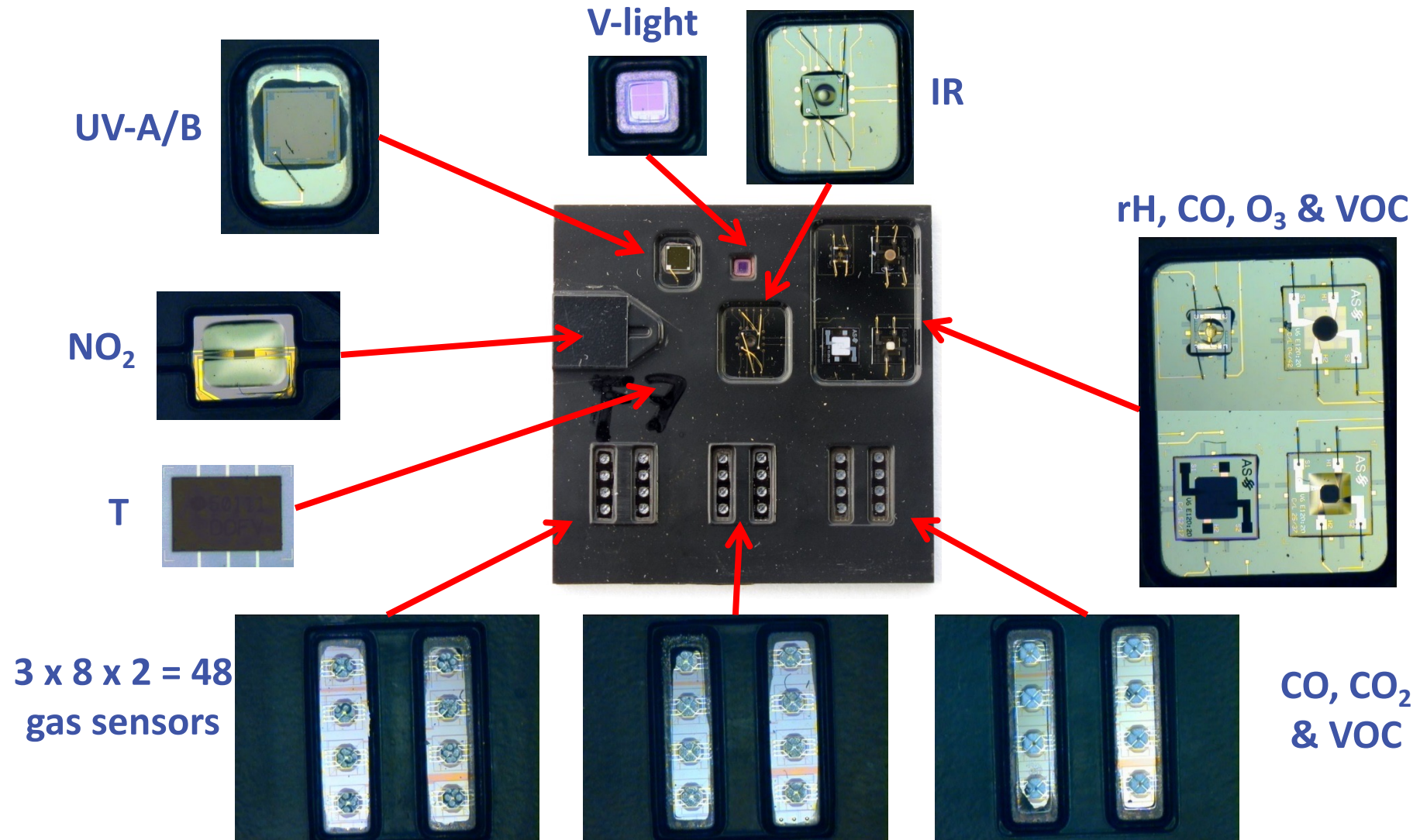
- 17 partners from 6 countries – 1/9/2013 – 30/4/2017
- 18.5 M€ budget and ~ 1300 Person Months effort



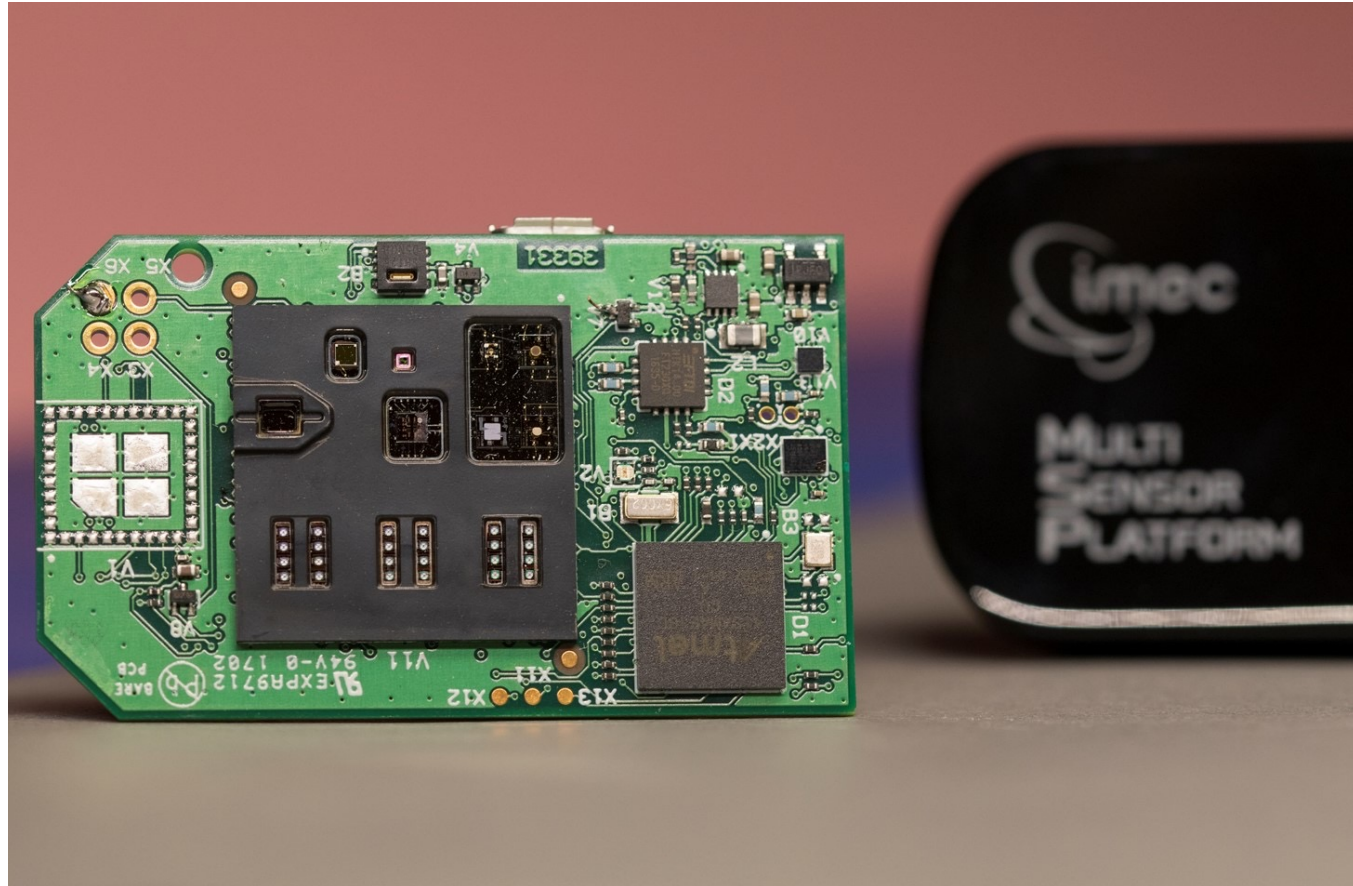
- 3D-integrated Multi-Sensor System !
- Worldwide unique Smart System - 57 Sensors!

Energy harvesting:  
piezoelectric +  
photovoltaics





## MSP WEARABLE DEVICE



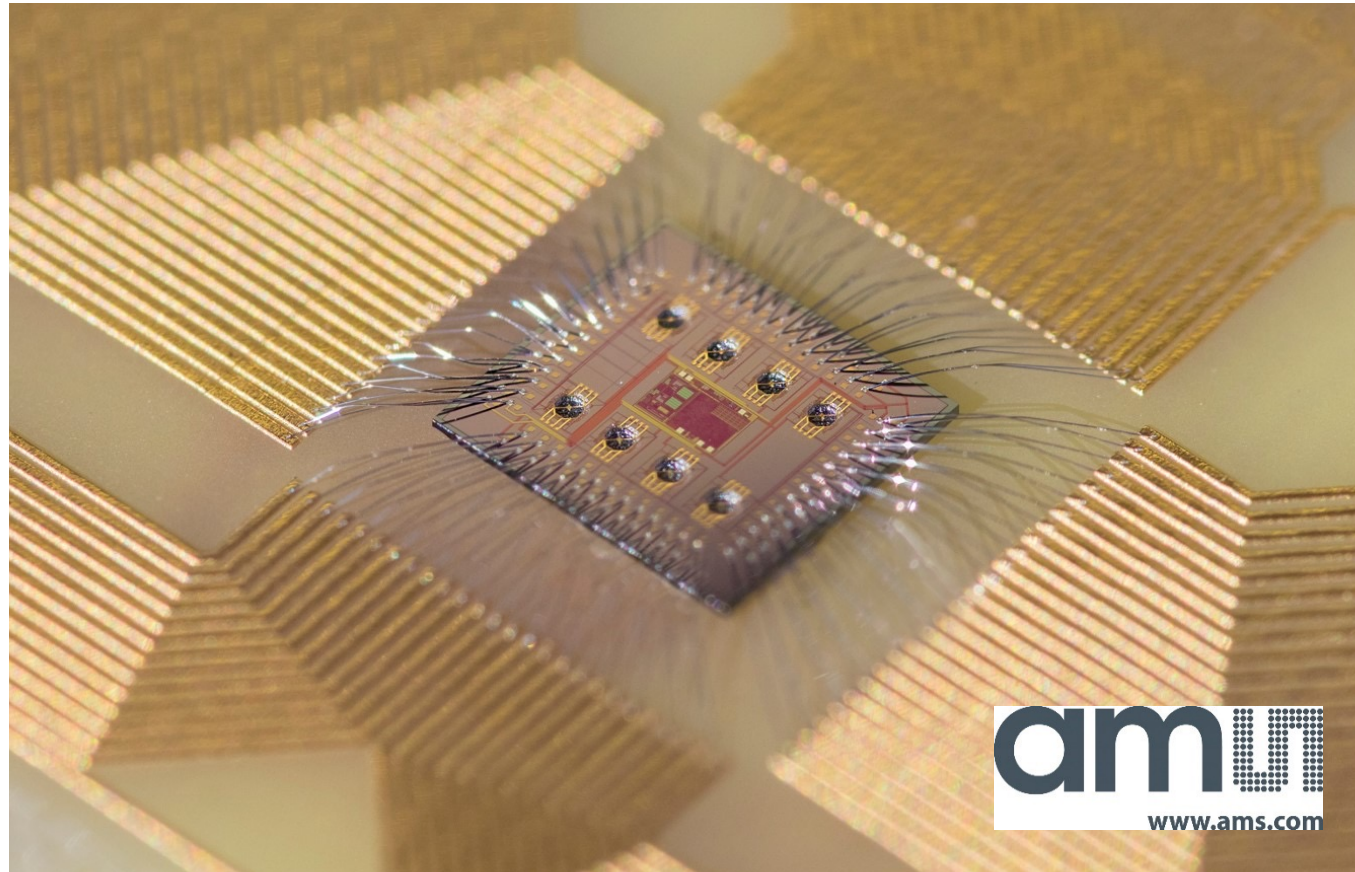
## MSP WEARABLE DEVICE



## MSP WEARABLE DEVICE



- Worldwide unique CMOS based micro-hotplate chip
- 8 micro-hotplates for 16 gas sensors



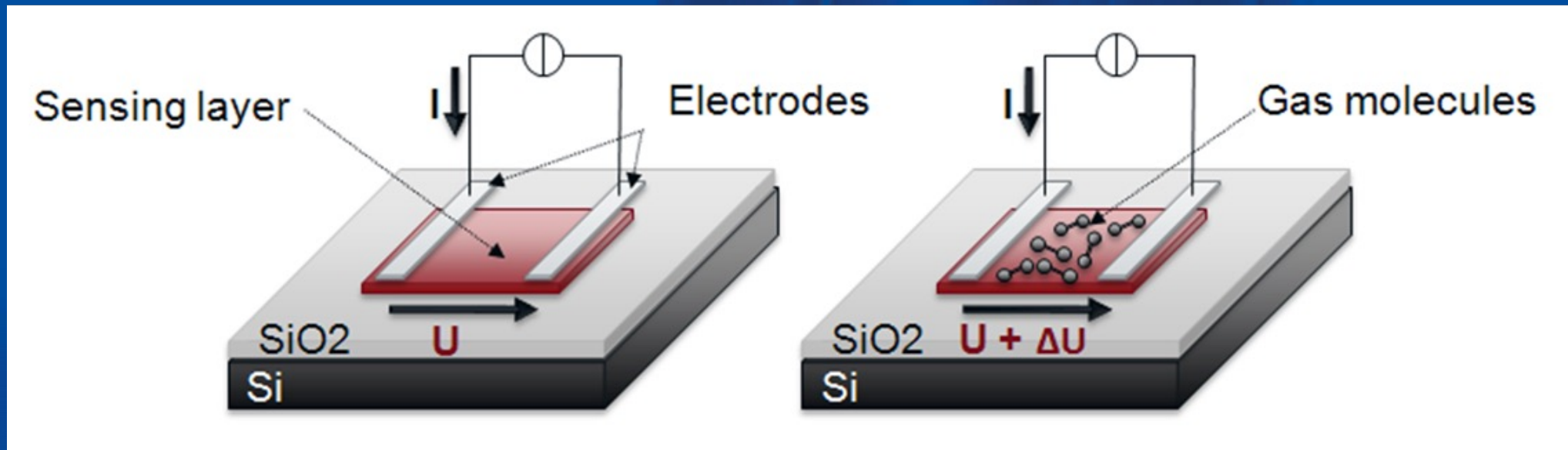
## 4. Chemical Sensors @ MCL

### □ Ultrathin MOx films, nanowires, and nanoparticles

- $\text{SnO}_2$ -,  $\text{ZnO}$ -,  $\text{CuO}$ -films
- $\text{SnO}_2$ -,  $\text{CuO}$ -,  $\text{ZnO}$ -NWs
- $\text{WO}_3$ -NWs

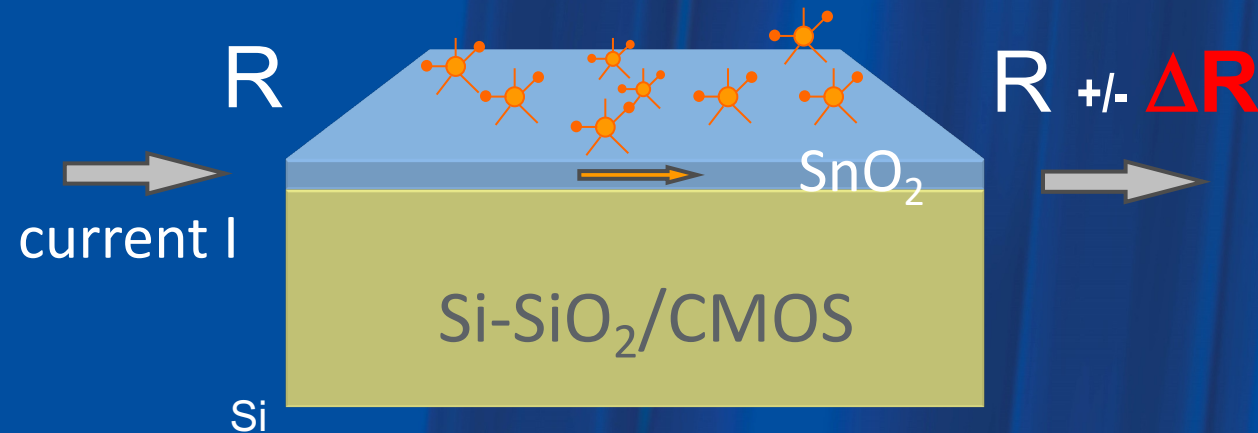
- Au, Pt, Pd
- AuPd, PdPt,...
- PdRuAg,...

- CO,  $\text{CO}_2$ , VOCs, HCmix
- $\text{H}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{O}_3$  and  $\text{NO}_2$
- In dry & humid air



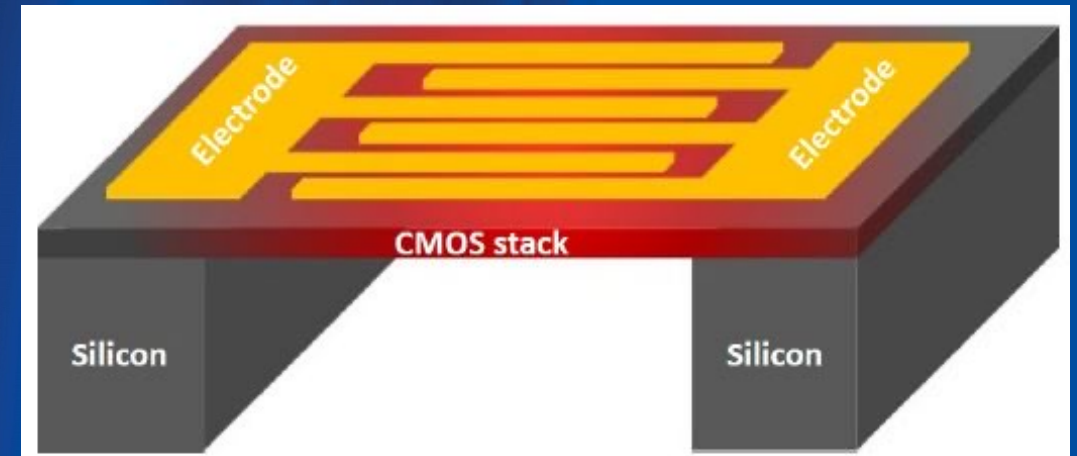
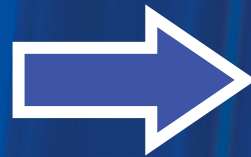
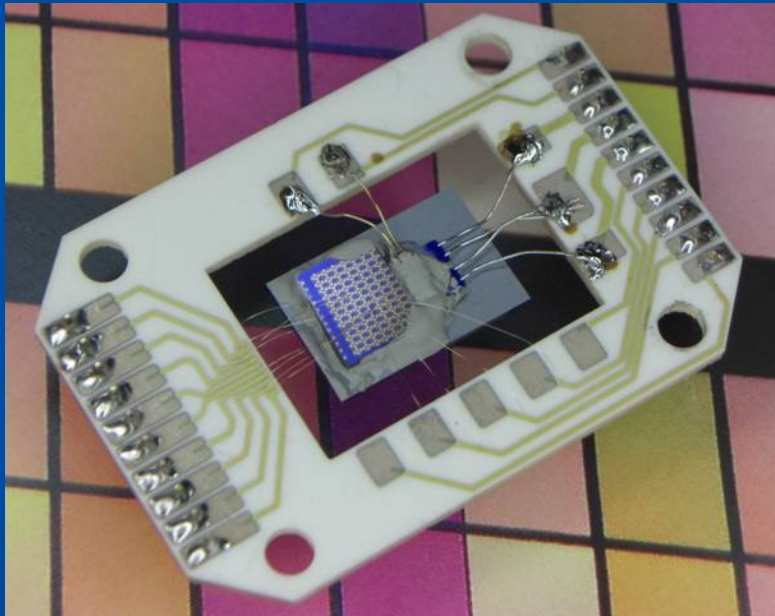
## Sensor principle

- ❑ Reducing gas:  $\text{CO} + \text{O}^- \longrightarrow \text{CO}_2 + \text{e}^-$
- ❑ Oxidizing gas:  $\text{NO}_2 + \text{e}^- \longrightarrow \text{NO}_2^-$
- ❑ Change of resistivity  $R \longrightarrow$  Sensor device !

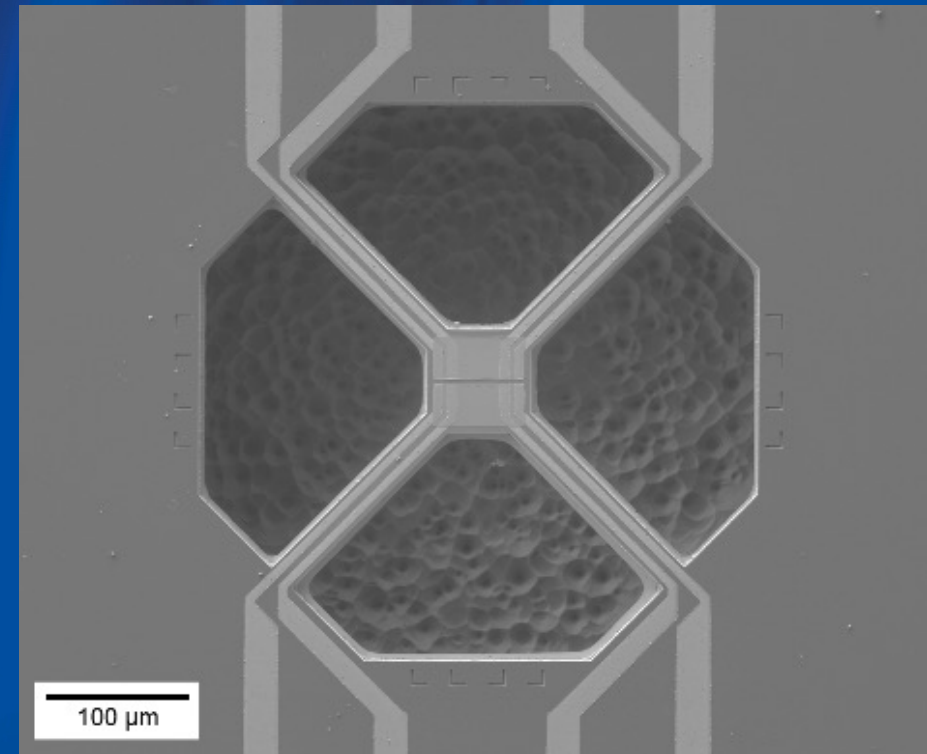
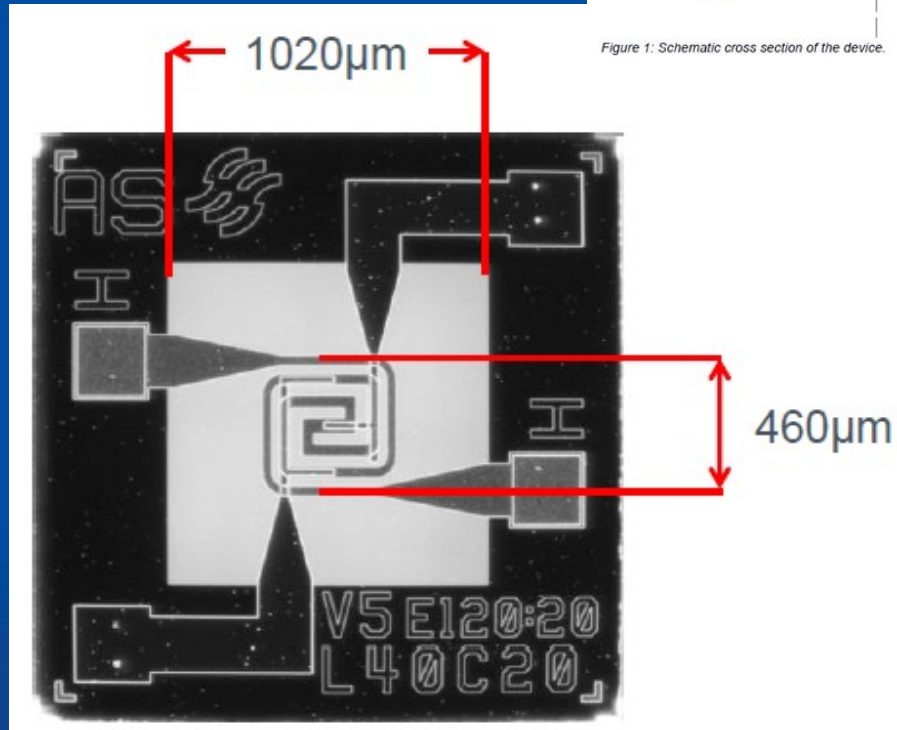
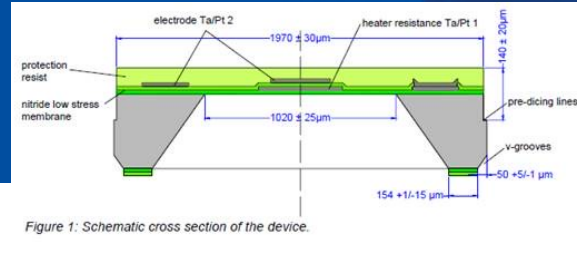


Very thin films - nanosensor – big effect  $\Delta R$  !

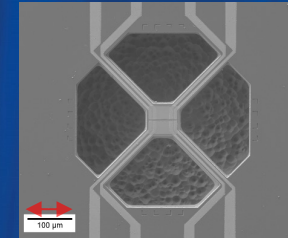
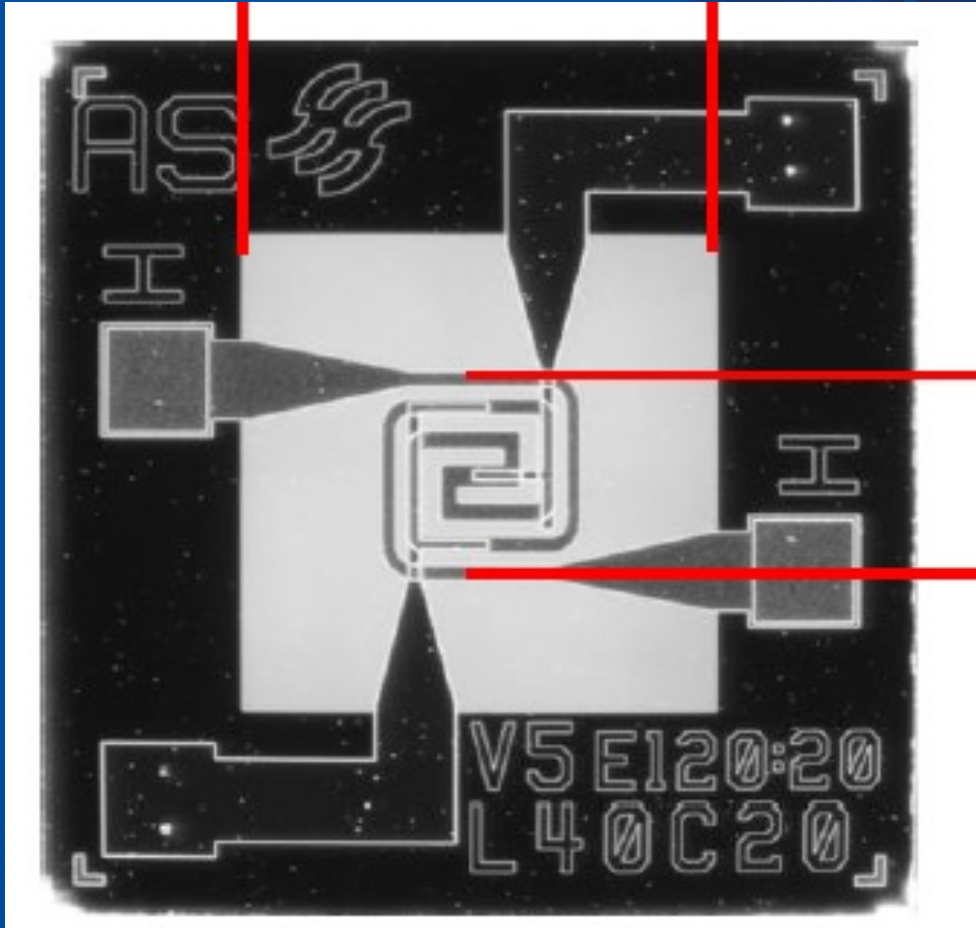
- ❑ MOx film sensors require heating up to 400°C and more !
- ❑ Macroscopic setup (power > 100 mW) for heating the sensor structures
- ❑ Integration on CMOS-based micro-hotplate ( $\mu$ hp) devices to minimize power consumption



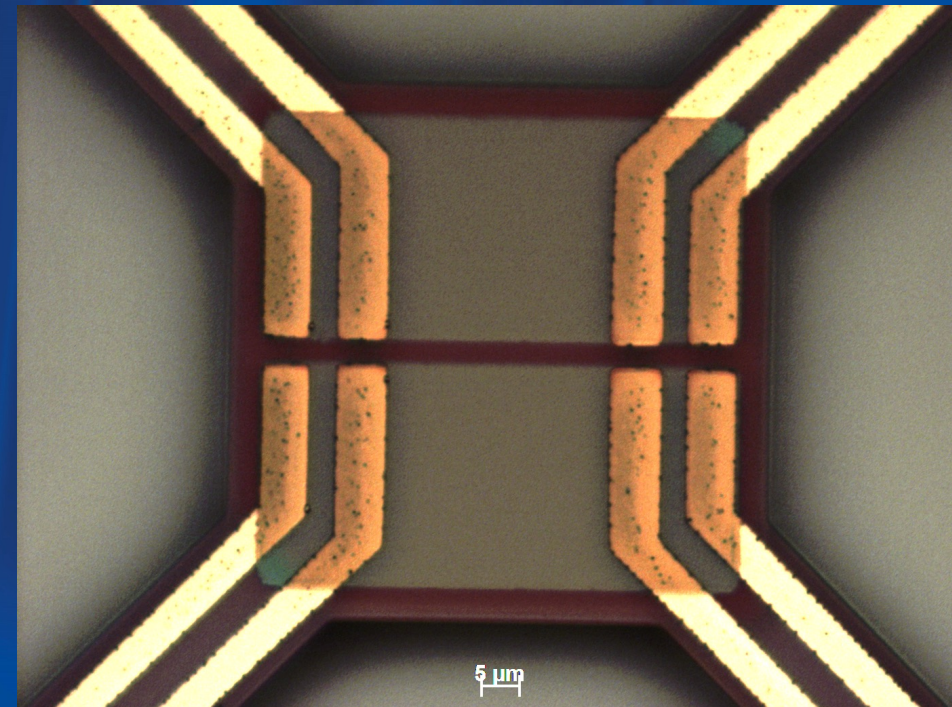
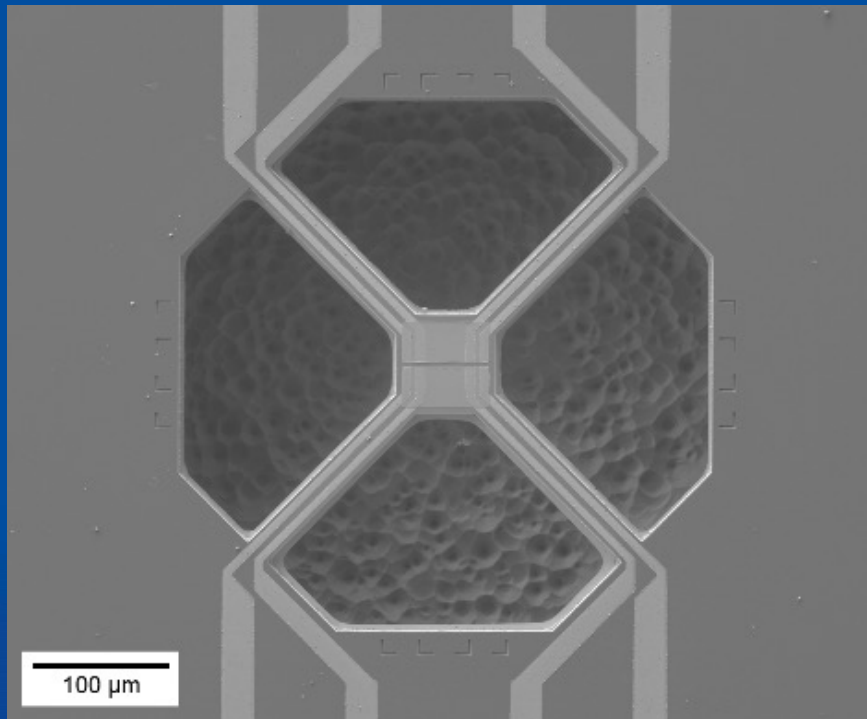
- ❑ Gen 1: SiN-based microhotplate
- ❑ Gen 2: CMOS-integrated micro-hotplate devices



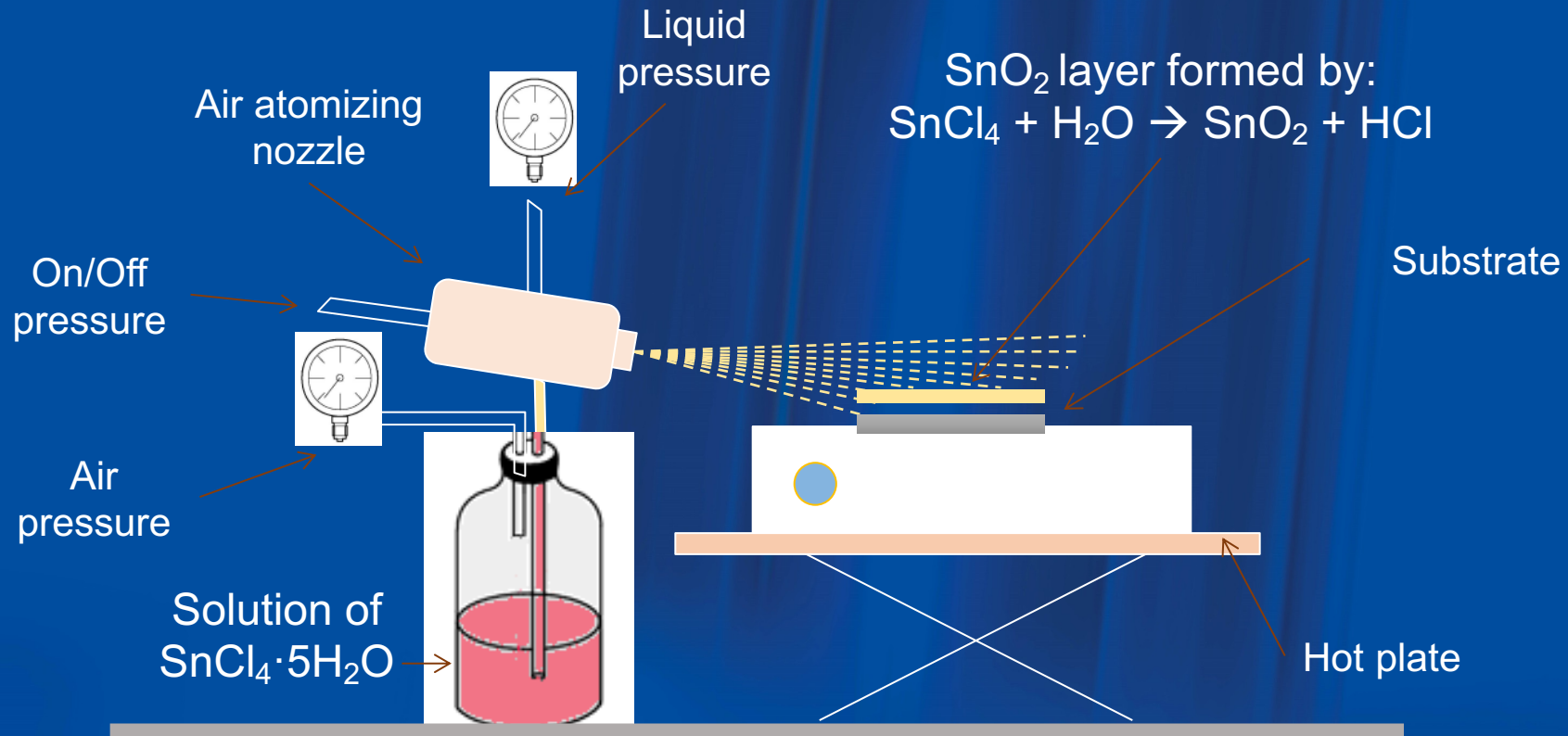
- Gen1:  $1020 \times 1020 \times 0,8 \text{ } \mu\text{m} = 832.320 \text{ } \mu\text{m}^3$
- Gen2:  $80 \times 80 \times 8 \text{ } \mu\text{m} = 51.200 \text{ } \mu\text{m}^3$



- ❑ Development of CMOS-integrated micro-hotplate devices for heating up to 400°C !
- ❑ Complex manufacturing chain (post-processing of nanomaterials on CMOS etc.) !



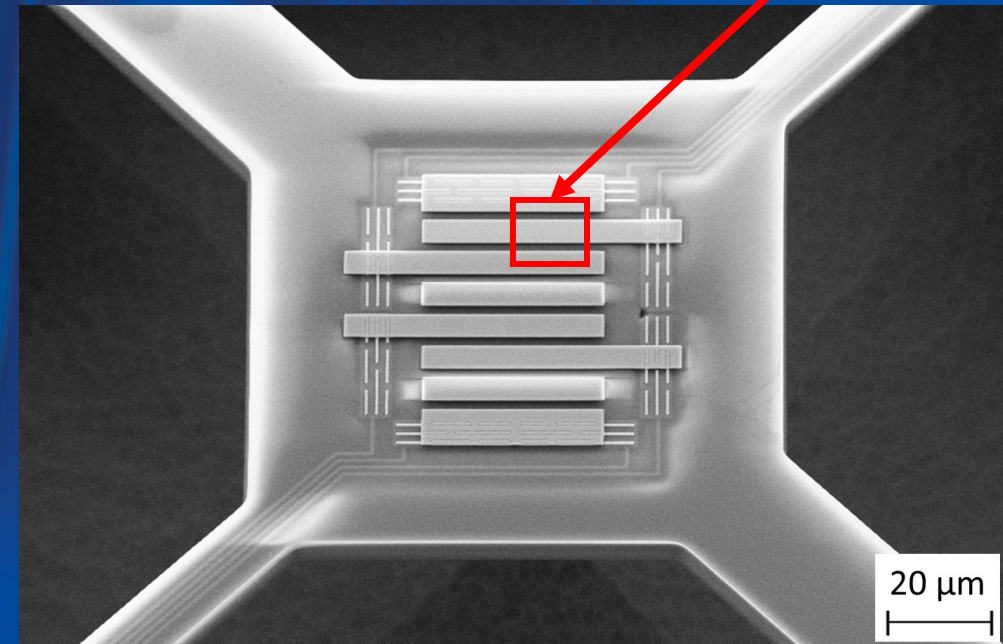
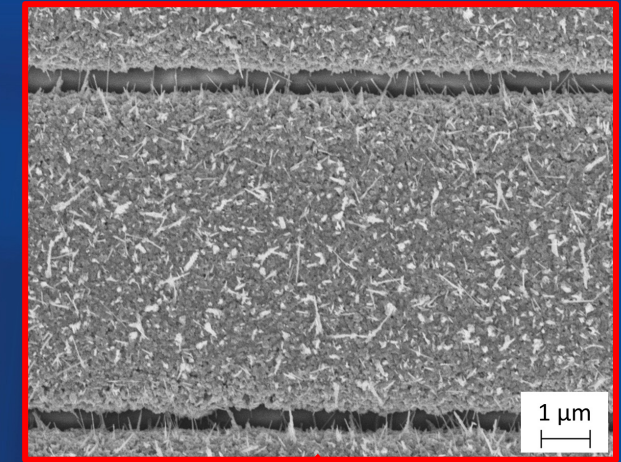
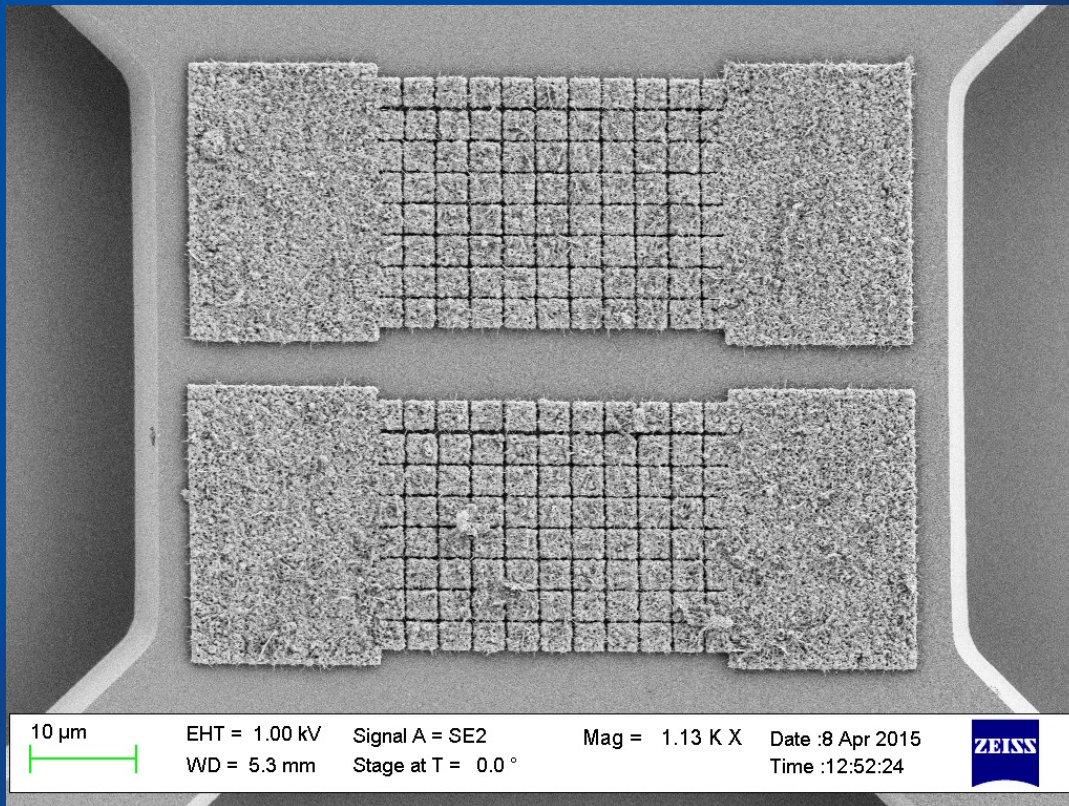
- ❑  $\text{SnO}_2$ -thin film deposition by spray pyrolysis
- ❑ Nanocrystalline  $\text{SnO}_2$ -film ~ 50 nm thickness
- ❑ Photolithography and etching



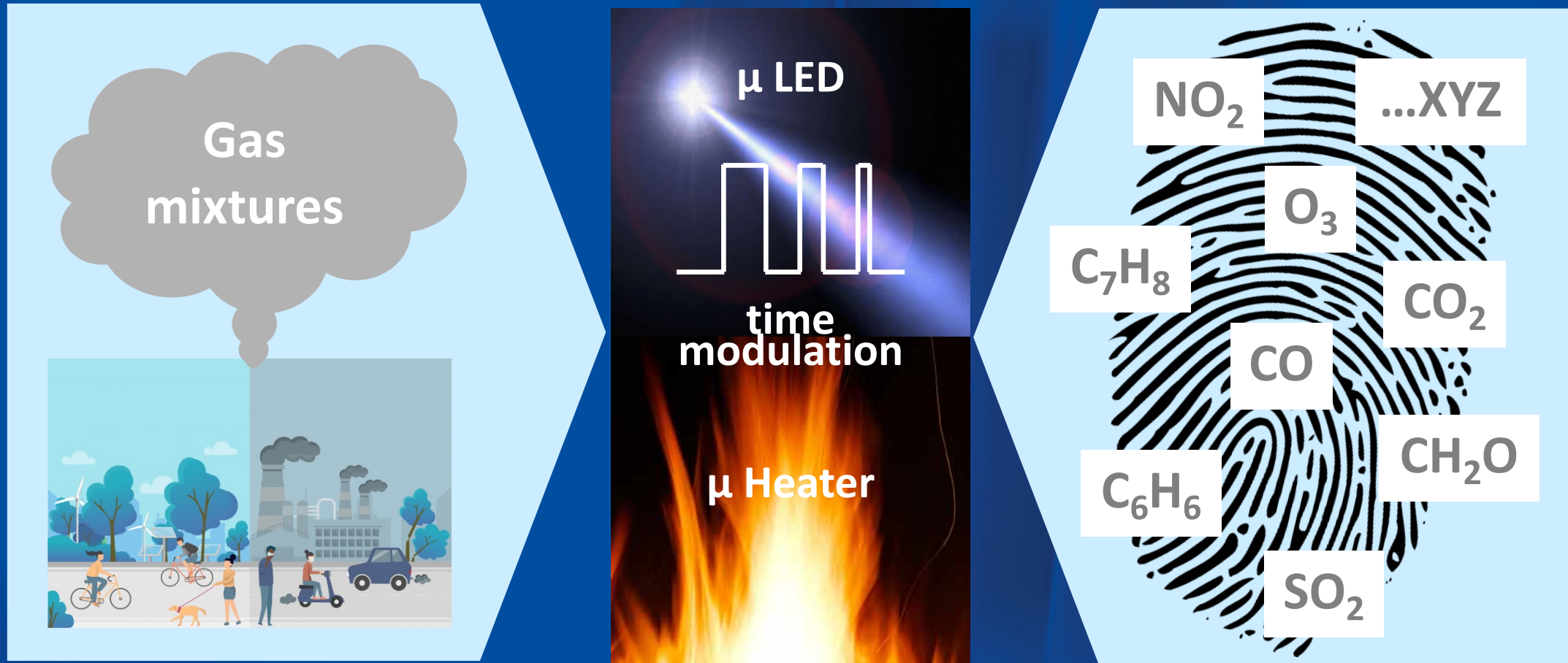
- ❑ Spray pyrolysis tool @MCL for MOx thin film deposition
- ❑ Up to 200 mm wafer size



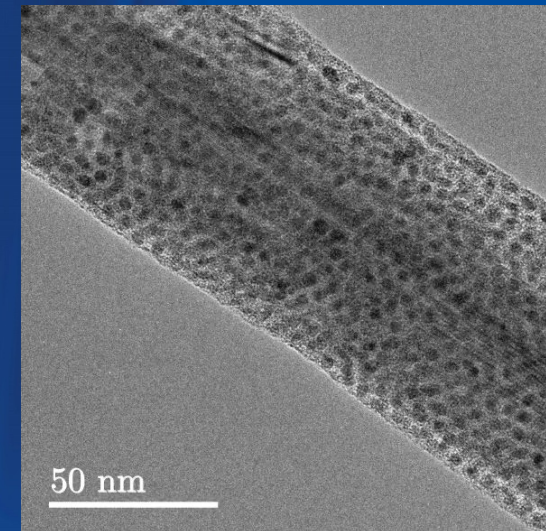
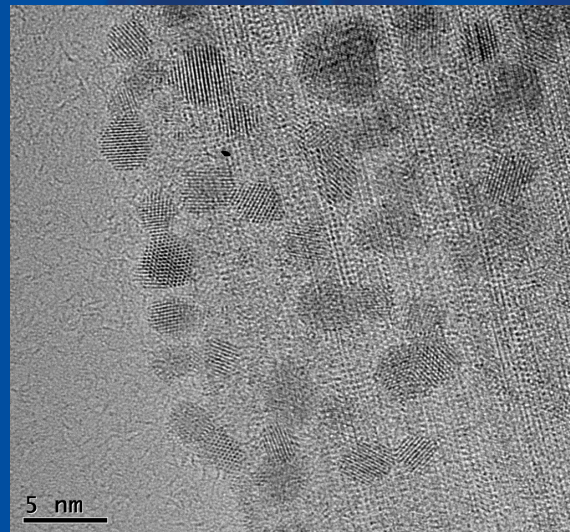
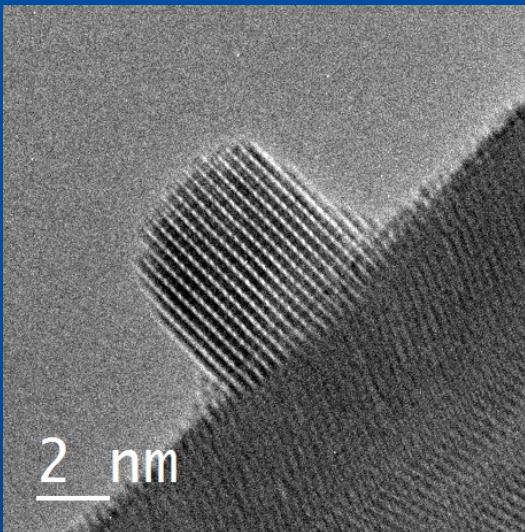
- ❑ Local synthesis of ZnO- and CuO-NWs on  $\mu$ hp
- ❑ Evaporation of metal films & thermal oxidation



## 5. Multi-Gas Sensor Device



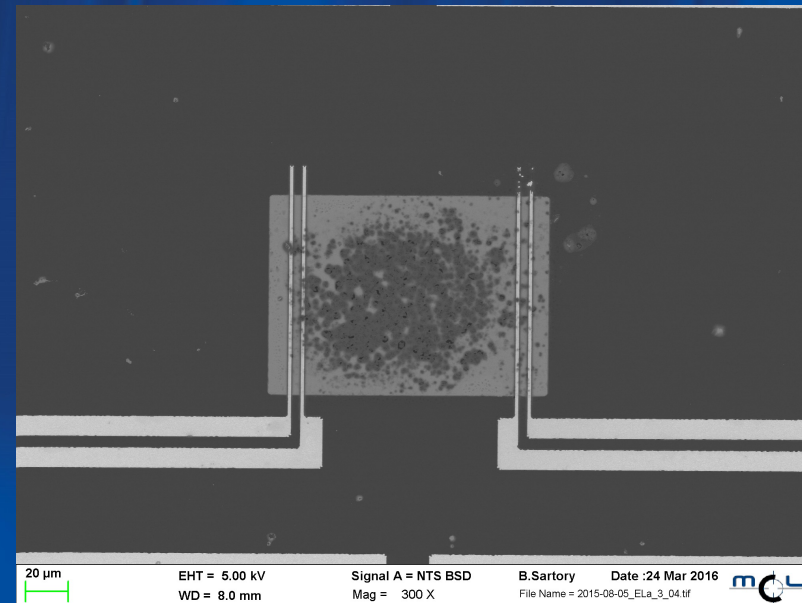
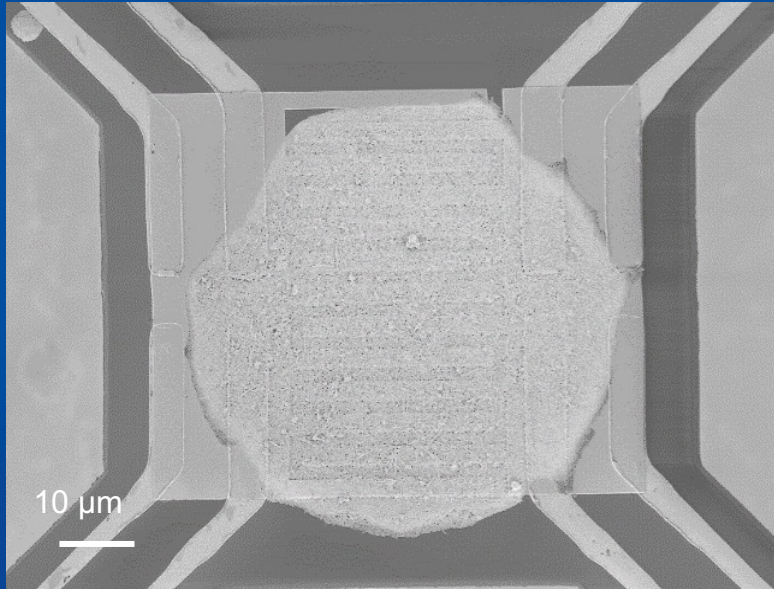
- ❑ Use of multi-functional NPs
- ❑ Mono-, bi, & trimetallic: Au, Pt, Pd, Ag, Ru, AuPd, NiPt, PdRuAg...
- ❑ NPs increase the response to specific target gas !
- ❑ NPs suppress cross sensitivities to humidity !



- ❑ „Organic approach“: Flow synthesis of (bi)metallic NPs und Ink-Jetting on CMOS devices

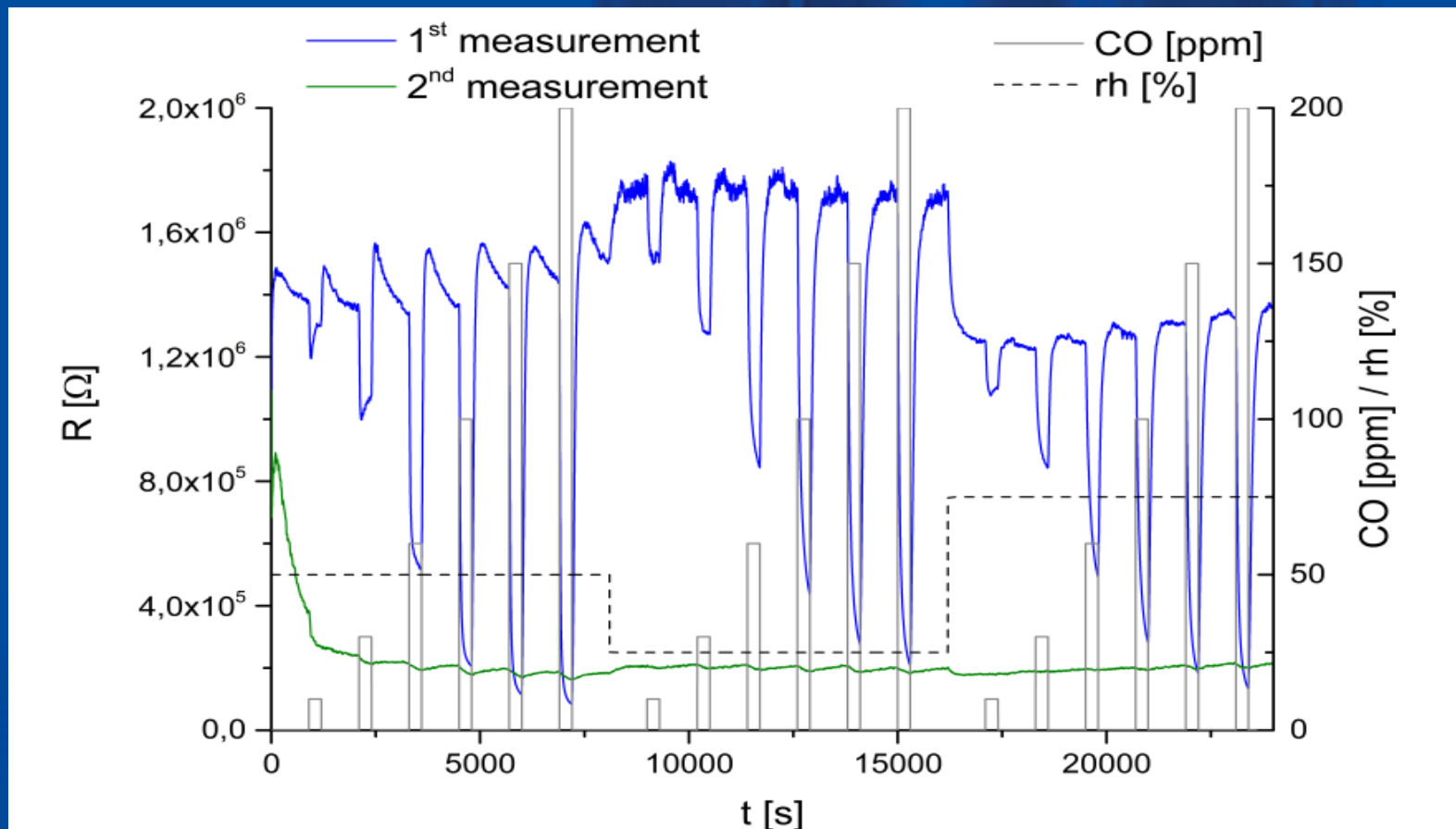


- ❑ „Anorganic approach“: Sputter deposition of (mono/bi/tri)-metallic NPs



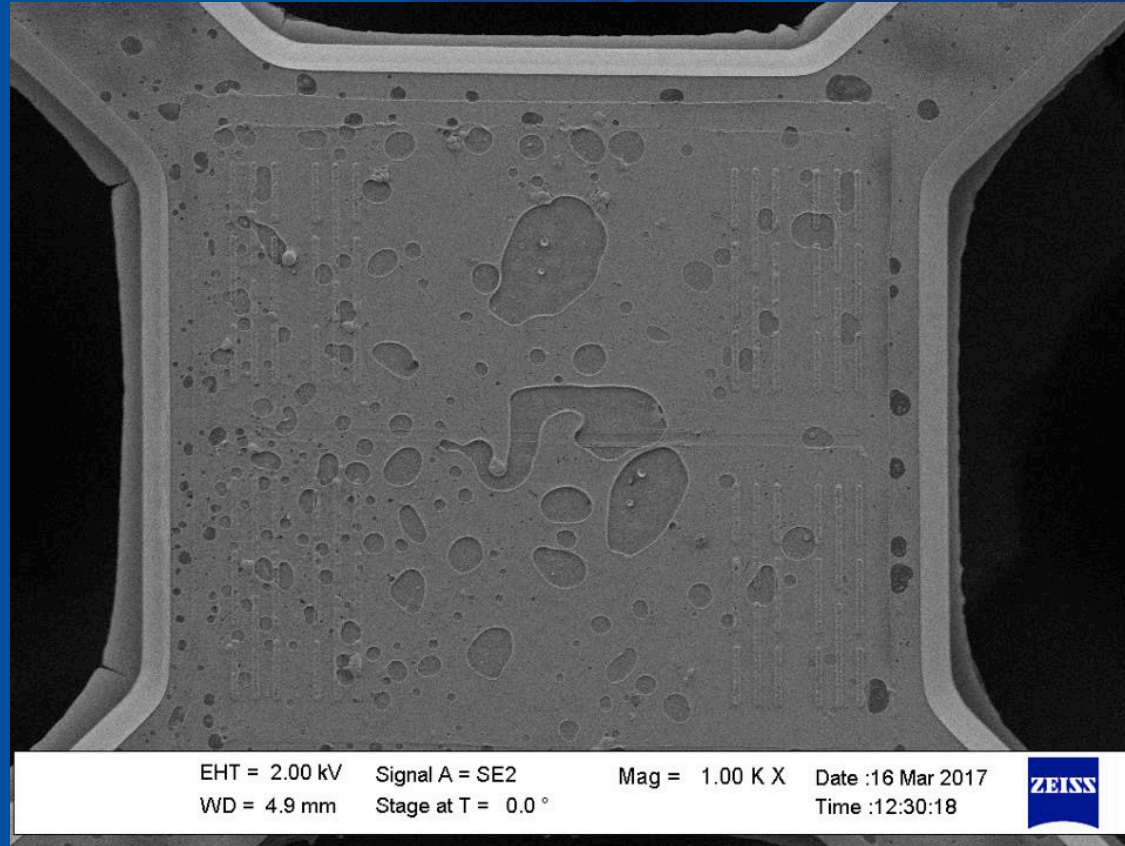
## Example 1:

- Response of SnO<sub>2</sub>-thin film + NiPt-NPs to CO
- Exposed to 10, 30, 60, 100, 150 and 200 ppm at different humidity levels



## Example 1:

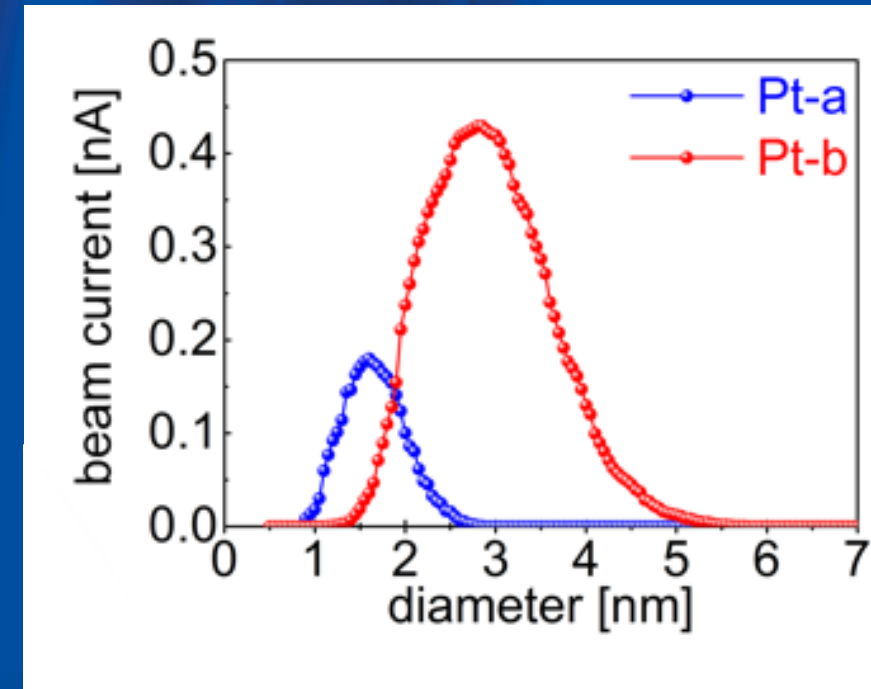
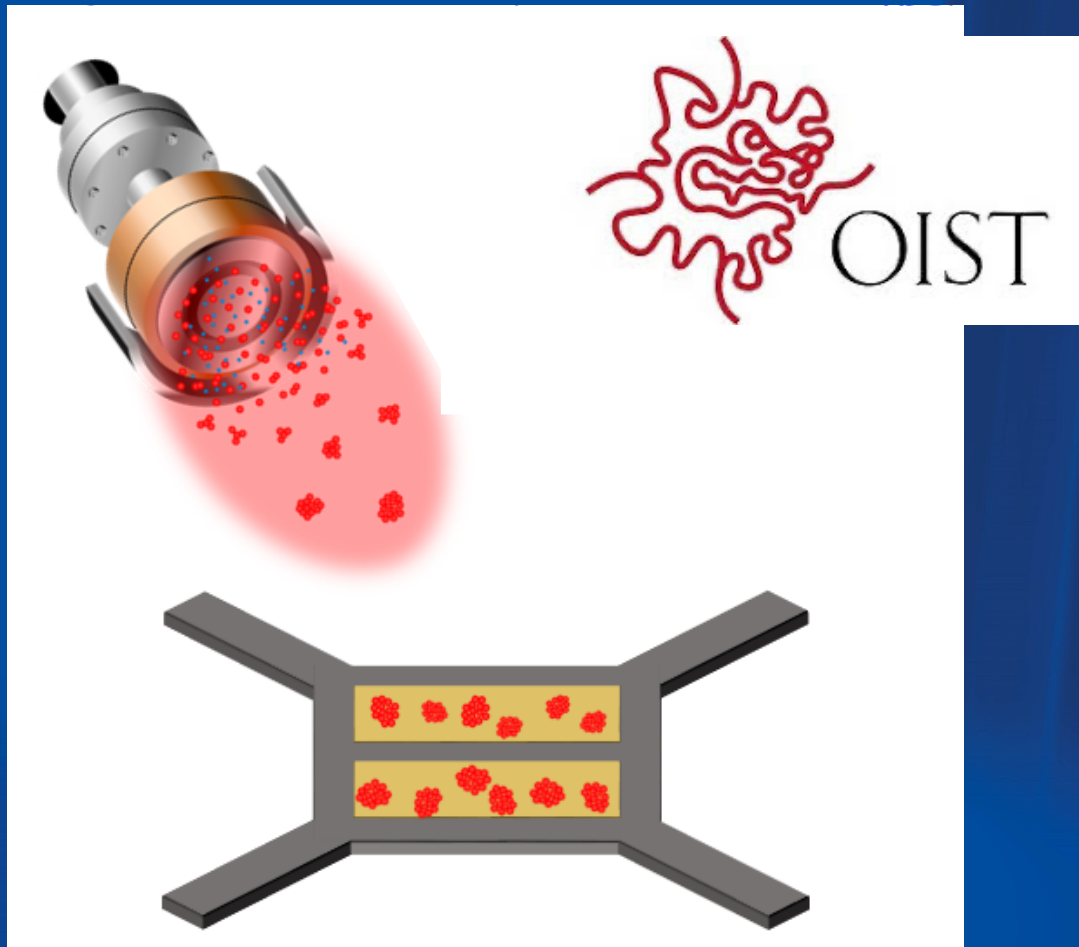
- ❑ Sensor „died“ at temperatures  $> 300^{\circ}\text{C}$  !
- ❑ Obviously the NiPt NPs melted and formed a metal alloy film covering the  $\text{SnO}_2$  layer !



can

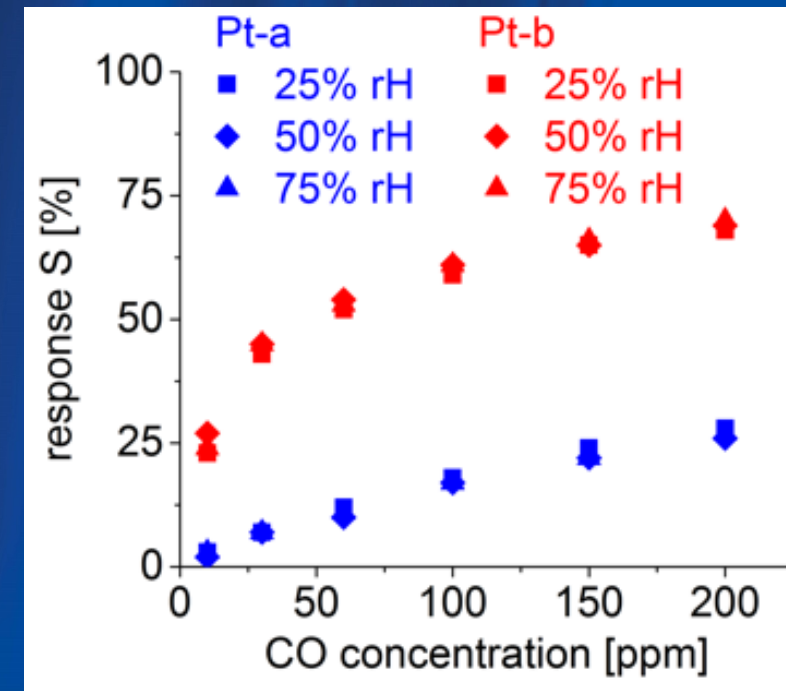
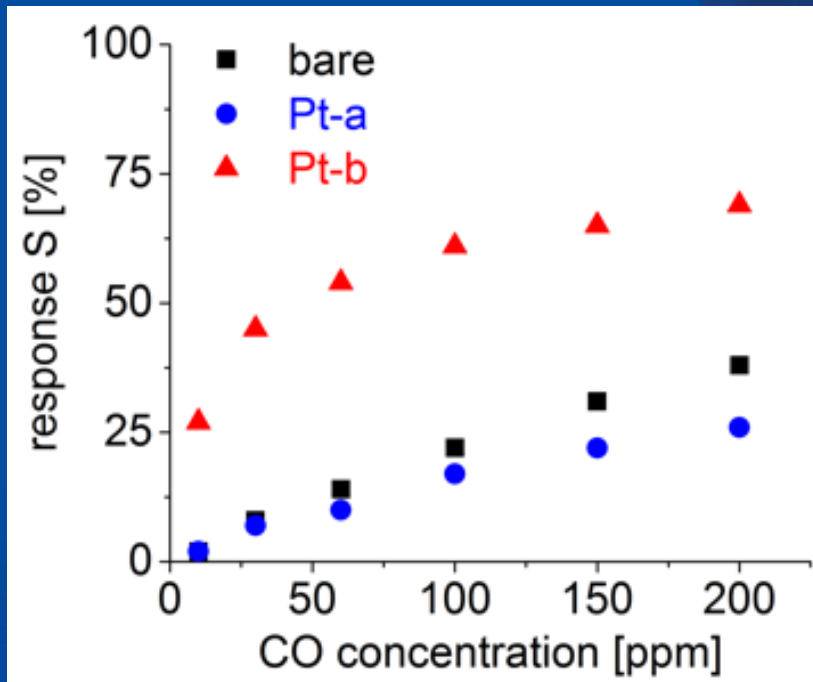
## Example 2:

- Sputter deposition of Pt-NPs with different diameters



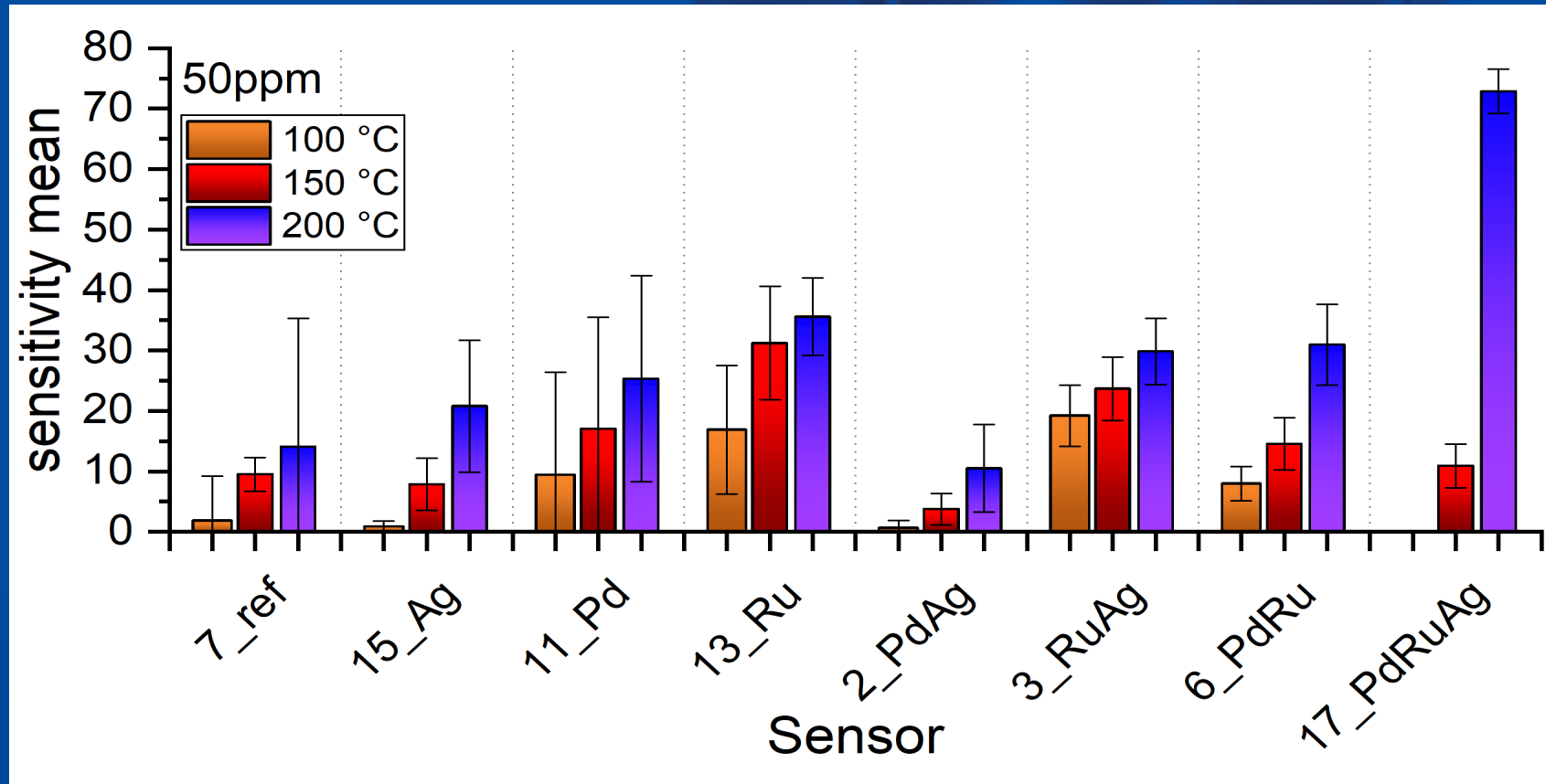
## Example 2:

- $\text{SnO}_2$  thin film + Pt-NPs with different diameters
- Exposed to 10, 30, 60, 100, 150 and 200 ppm CO
- $T = 375^\circ\text{C}$

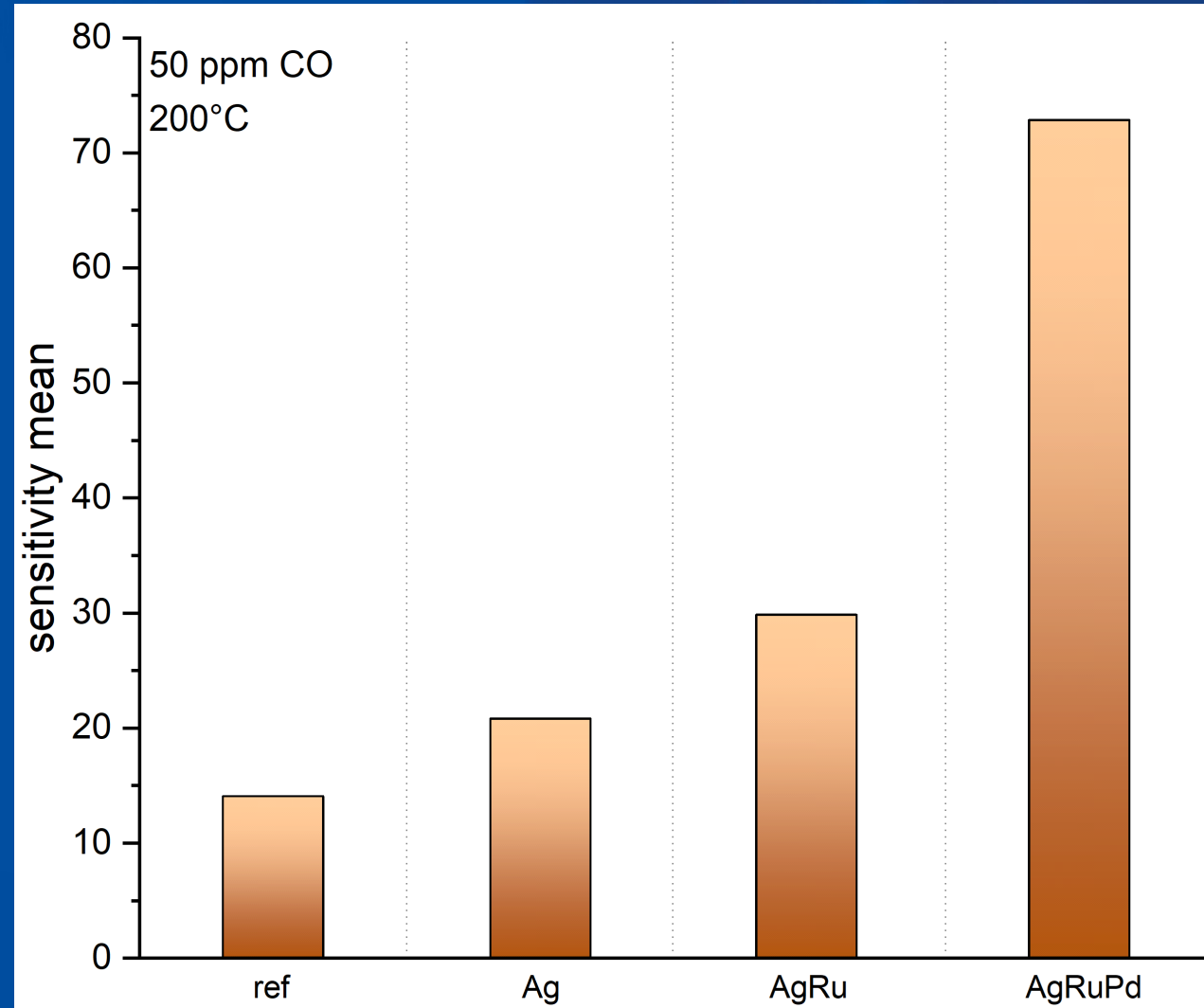


## Example 3:

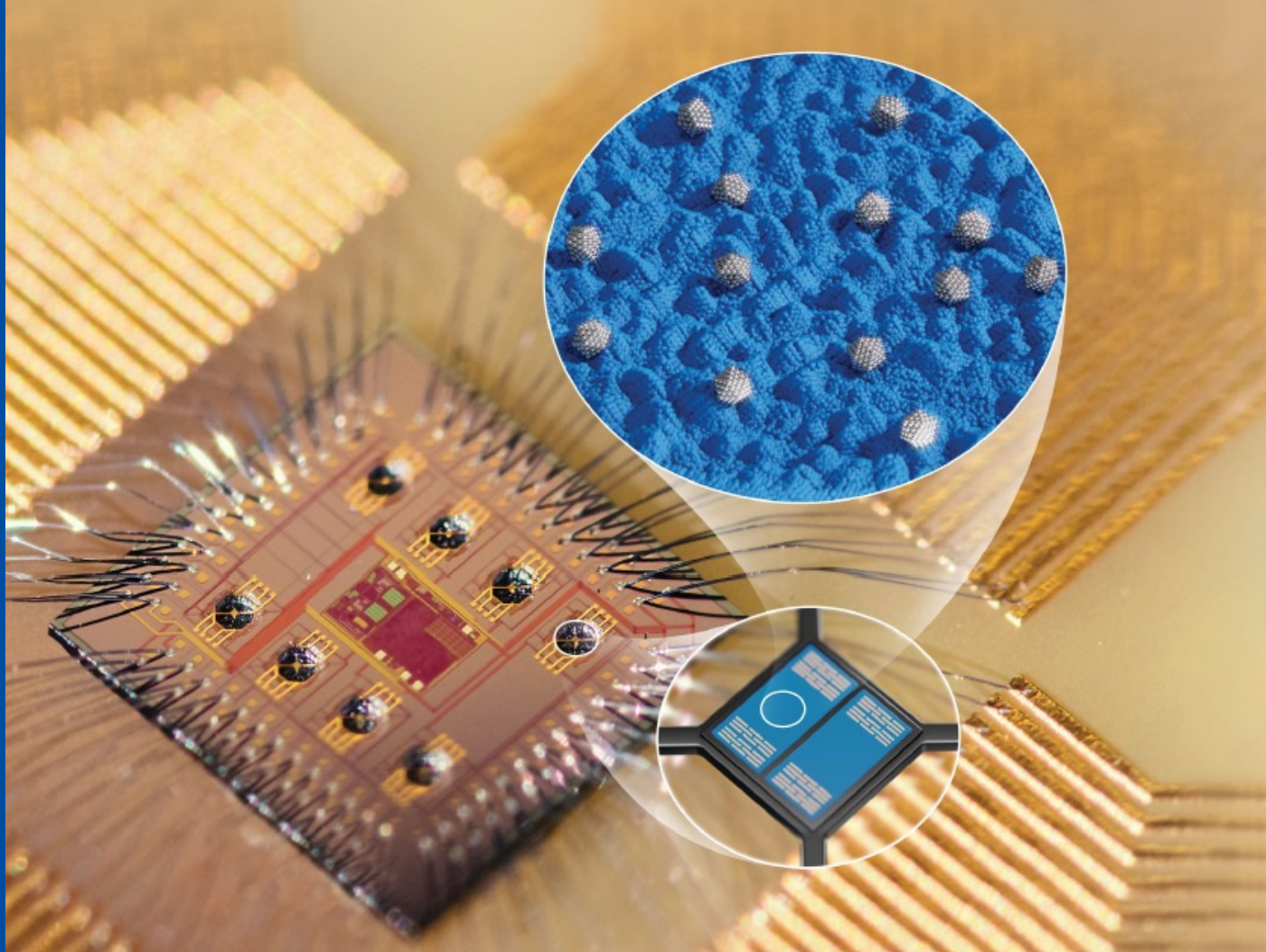
- $\text{SnO}_2$  thin film + mono-, bi-, & trimetallic NPs (Ag, Pd, Ru)
- Exposed to 50 ppm CO (50% rH)



## Example 3:

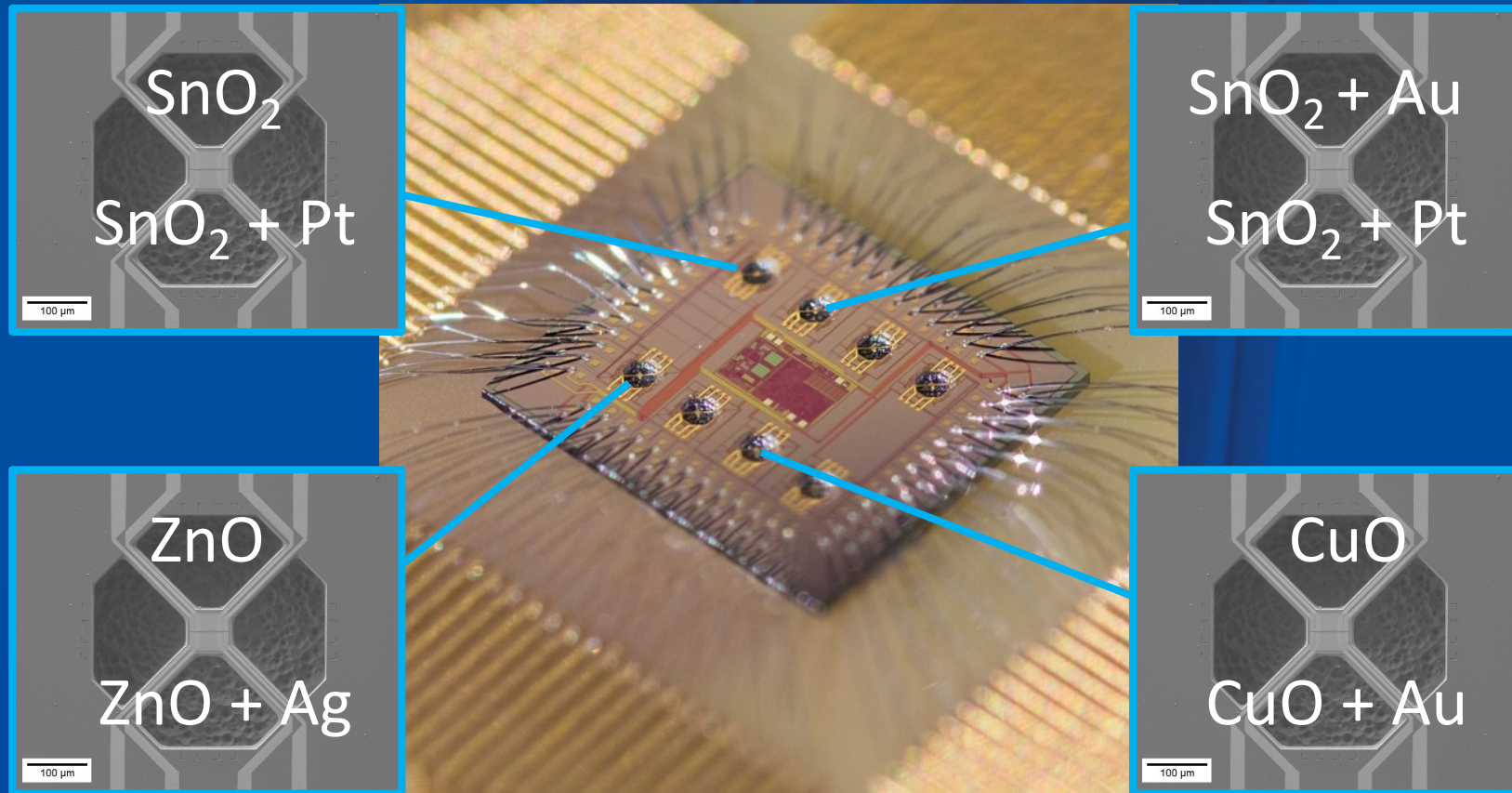


## Next steps towards multi-gas sensor device



Next steps towards multi-gas sensor device

- ❑ Integration of different MOx on CMOS
- ❑ Functionalization with NPs



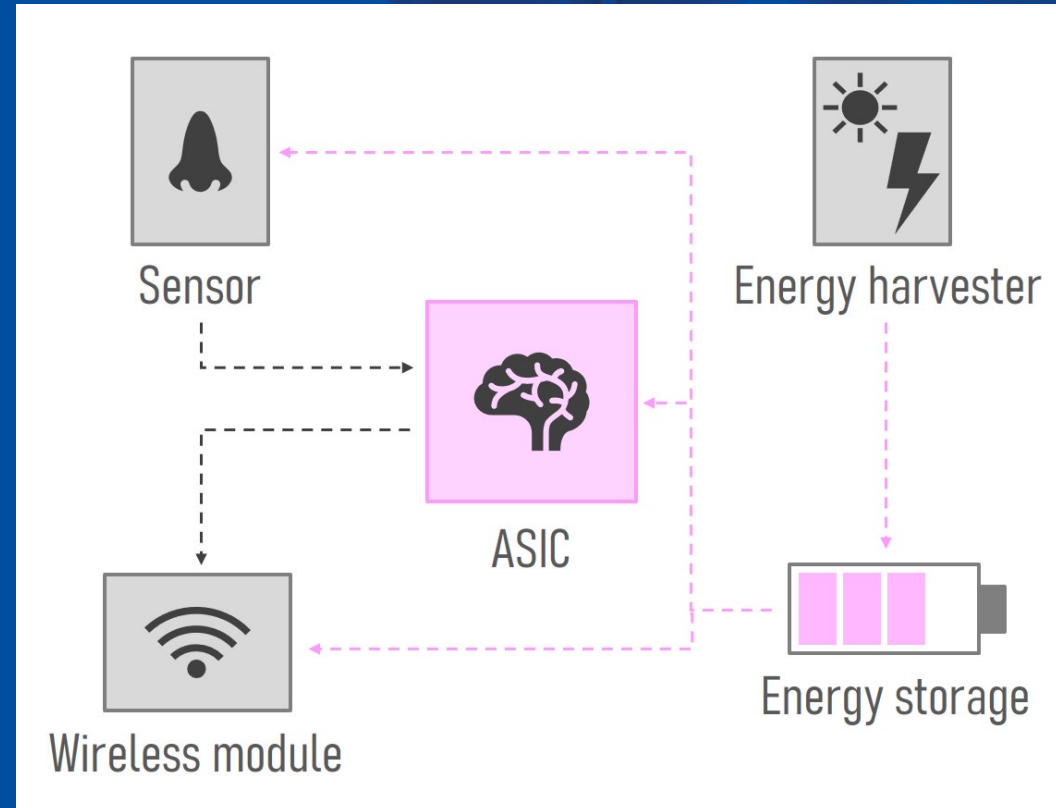
## Intermediate Summary

- ❑ Successful realization as CMOS-integrated devices !
- ❑ Multifunctional NPs are key for optimization of chemical sensor devices !
- ❑ Many open questions - How does NP size/shape influence the response ?  
Chemical reaction in case of NP-combinations or alloys etc. ?
- ❑ Reasonable approach towards integrated multi-gas sensor device !

## BUT:

- ❑ Power consumption ~ 15 mW (400°C) per sensor in DC operation !
- ❑ How to realize an **energy autonomous** multi-sensor system ?

# Vision: Energy Autonomous Sensor Systems



# IoT Sensor Networks for indoor and outdoor air quality monitoring

## Power budget – rough estimation

- ❑ Power consumption  $\sim 10$  mW ( $300^{\circ}\text{C}$ ) per sensor in DC operation !
- ❑  $8 \times 10$  mW  $\sim 100$  mW (DC)

## Photovoltaic energy harvesting

- ❑ Solar constant  $1361$  W/m<sup>2</sup>
- ❑  $200$  W/m<sup>2</sup>  $\sim 5$  cm<sup>2</sup> solar cell area for  $100$  mW (24 hours)
- ❑ (4h/day & night)  $\times 6 \sim 30$  cm<sup>2</sup> solar cell (plus energy storage) to supply  $4 \times 4$  mm<sup>2</sup> sized sensor chip (Smart System? IoT?)
- ❑ + Circuitry + AI-based data evaluation + data transmission...

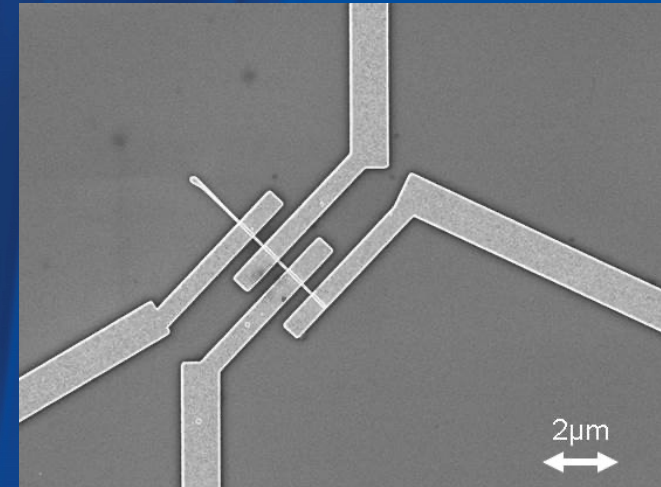
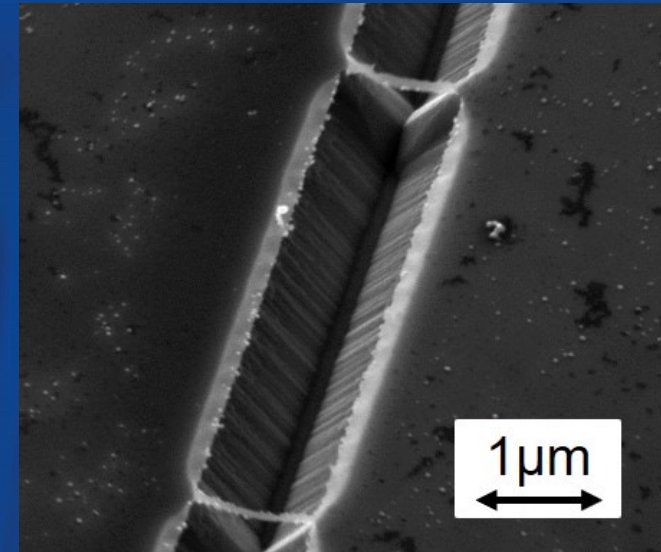
**Energy harvesting & energy storage is a huge challenge!**

## Ultra-low-power chemical sensor arrays

$\ll 1\text{mW}$

Various approaches:

- ☐ Switching between the sensor array (10 mW)
- ☐ AC-operation - 1:10 (1 mW)
- ☐ Radical scaling of micro-heater devices
- ☐ Self heating of single nanowires
- ☐ Employment of time domain (AC operation)
- ☐ Combination of thermal & optical excitation



# MCL

## 6. The FOXES Project

H2020-EIC-FETPROACT-2019 GA 951774

# FOXES

Fully Oxide-Based Zero-Emission and Portable Energy Supply

[www.foxes-project.eu](http://www.foxes-project.eu)



This document contains information that is treated as confidential and proprietary by the FOXES Consortium. Neither this document nor the information contained herein shall be used, duplicated or communicated by any means to any third party, in whole or in parts, except with prior written consent of the FOXES Consortium.



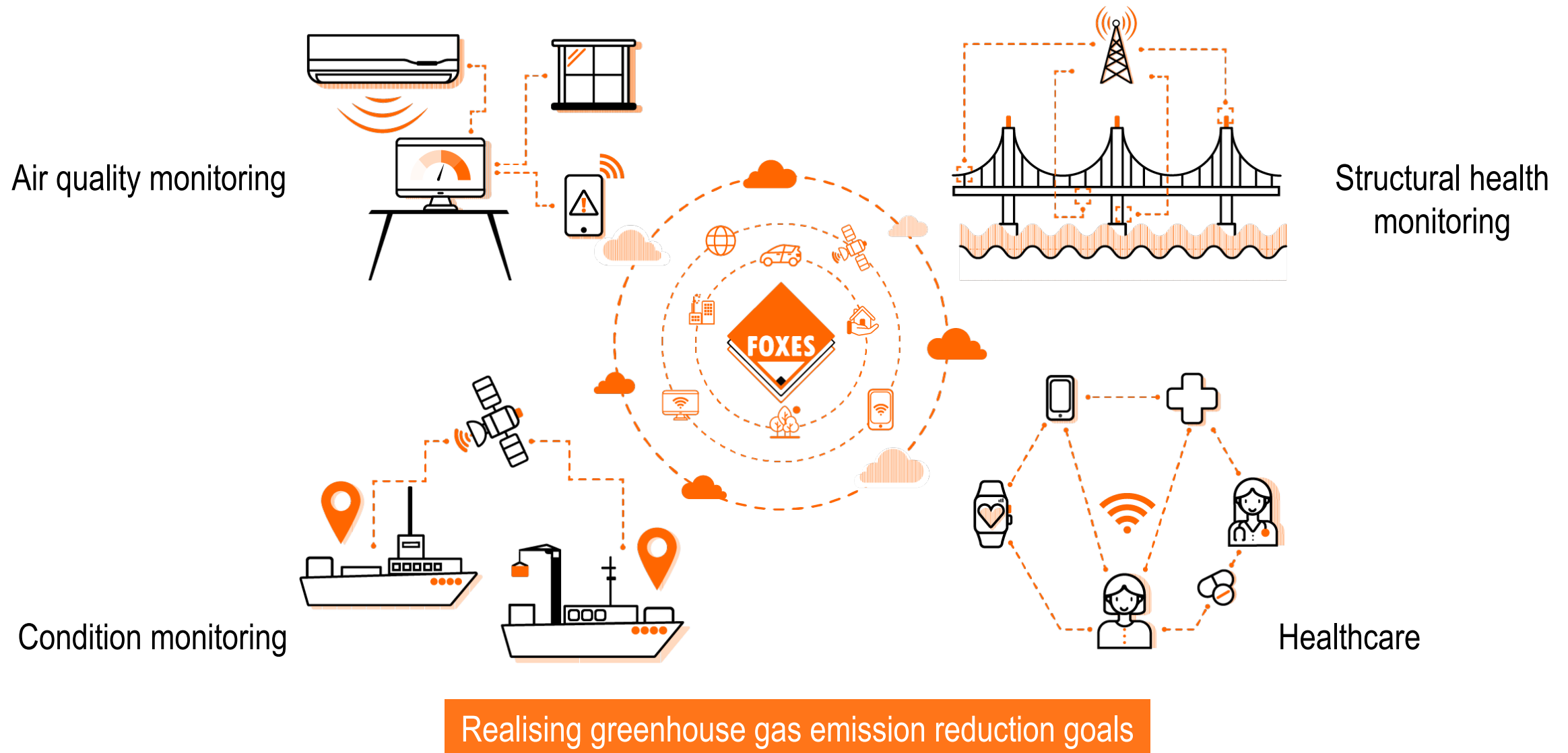
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 951774 (FOXES). This document reflects only the view of the author(s). The Agency is not responsible for any use that may be made of the information it contains.

*Anton Köck (MCL)*

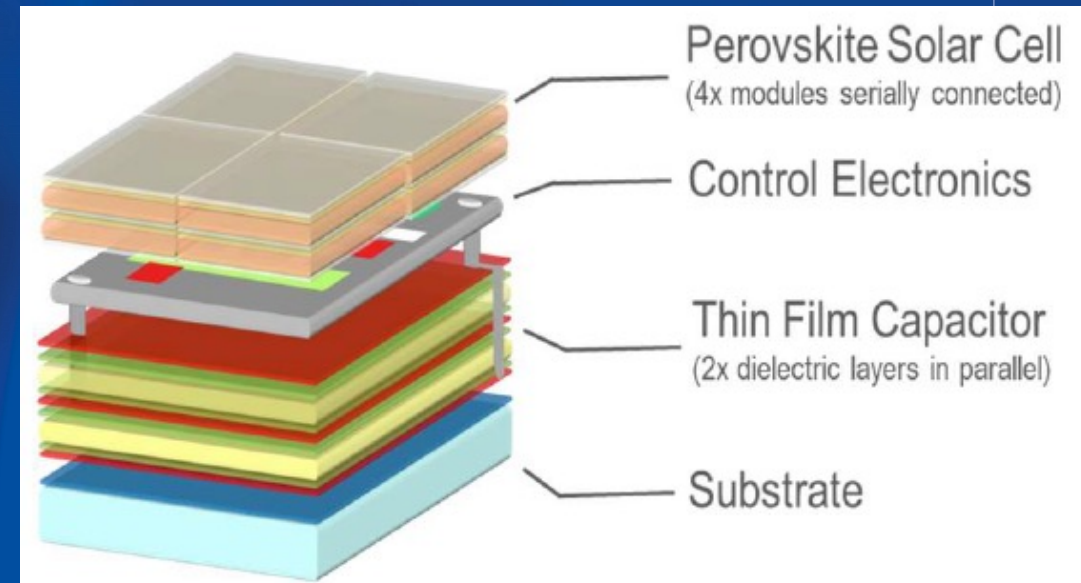


## FULLY OXIDE-BASED ZERO EMISSION AND PORTABLE ENERGY SUPPLY (FOXES)

| Participant No. | Participant organisation name                             | Country |
|-----------------|---|---------|
| 1 (Coordinator) | Materials Center Leoben Forschung GmbH (MCL)              | AT      |
| 2               | Bergische Universität Wuppertal (BUW)                     | DE      |
| 3               | AMO GmbH (AMO)  | DE      |
| 4               | Instituto de Desenvolvimento de Novas Tecnologias (UNOVA) | PT      |
| 5               | Universitat de Barcelona (UB)                             | ES      |

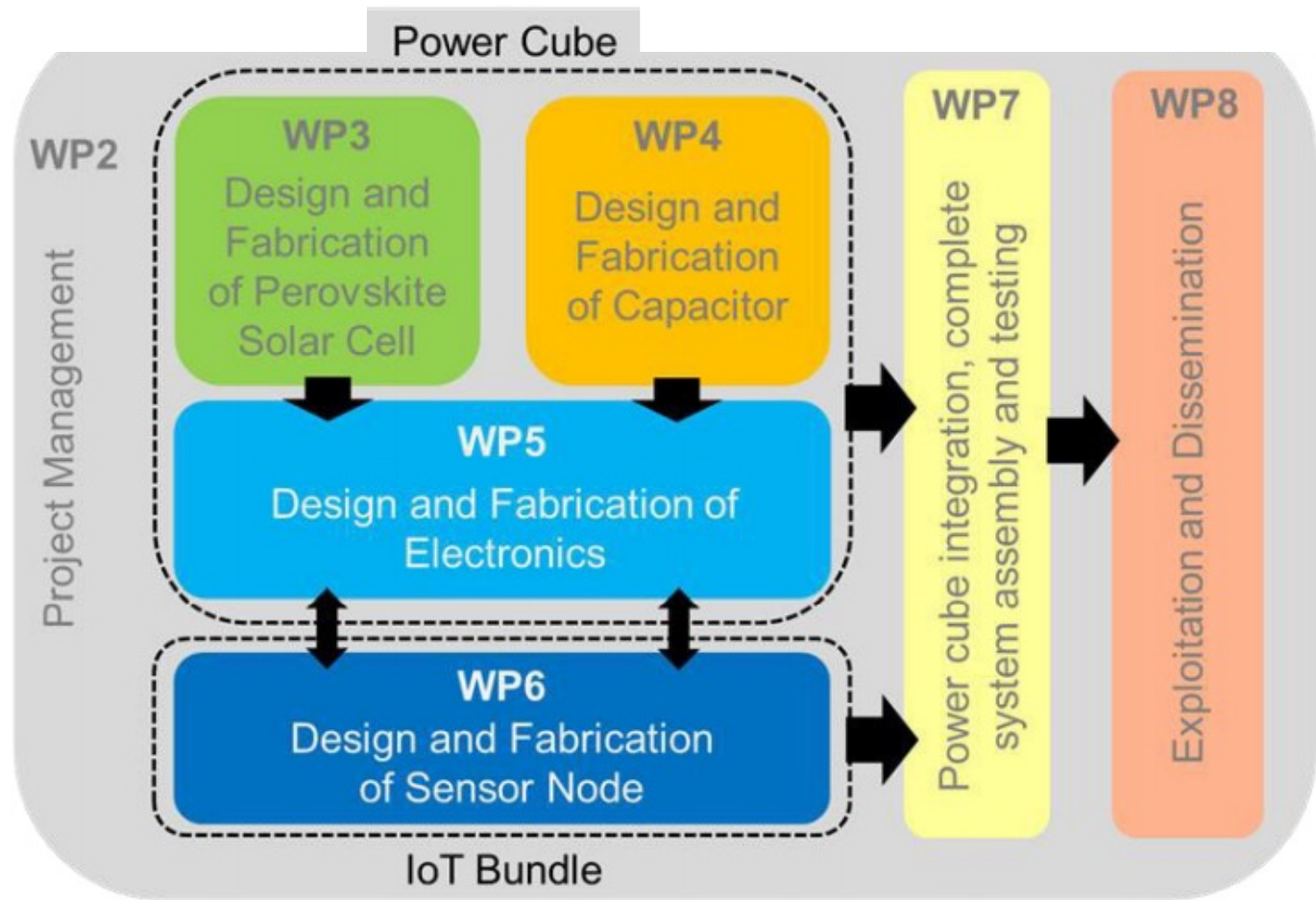


- ❑ Realization of a novel stand alone zero emission solid state power generating and storage system (Power Cube)
- ❑ Combination of photovoltaic energy harvester with a multilayer capacitor
- ❑ Oxide based 3D-integrated system exploiting eco-friendly materials – no negative impact for end-of life
- ❑ Energy supply and storage system for an air quality monitoring system
- ❑ Demonstration of capability for supplying autonomous IoT devices installed in remote locations - field test campaign in Barcelona urban area (2024)



**Figure 1.1:** The FOXES Power Cube is constituted by:

- Fully lead-free PSC with  $> 10\%$  efficiency (mini-module, voltage  $> 4V$ ).
- Lead-free perovskite multilayer TFC with high energy density ( $> 50 J/cm^3$ ).
- Metal-oxide based electronics (integrated circuits) coupled with graphene electrodes for the energy management circuit.



WP Leaders:

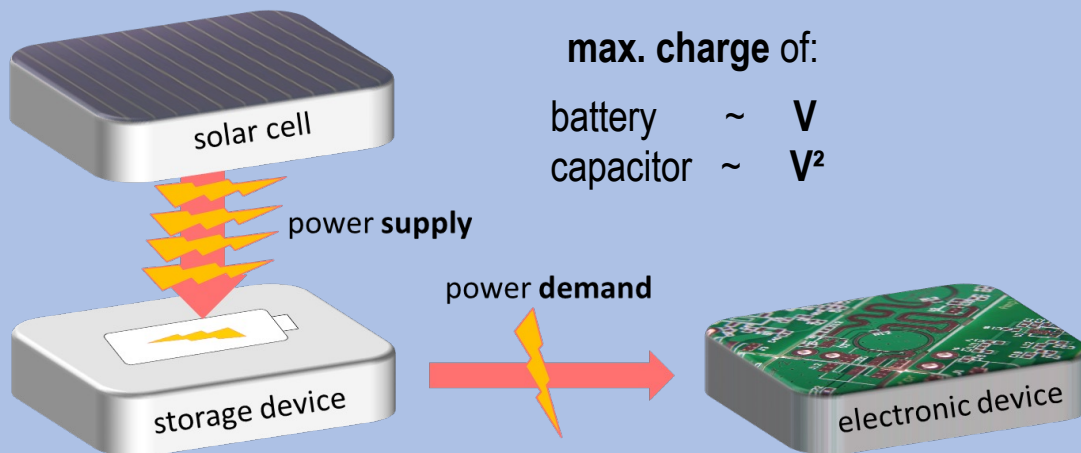
|  |  |  |  |
|--|--|--|--|
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |

BERGISCHE  
UNIVERSITÄT  
WUPPERTAL

## Pb-free Tandem Perovskite-Based Tandem Solar Cells with High Voltage for Microelectronics and Efficient Module Integration

### High operation voltage

- Efficient module integration = high geometric fill factor
- Increase chargeable energy of storage devices



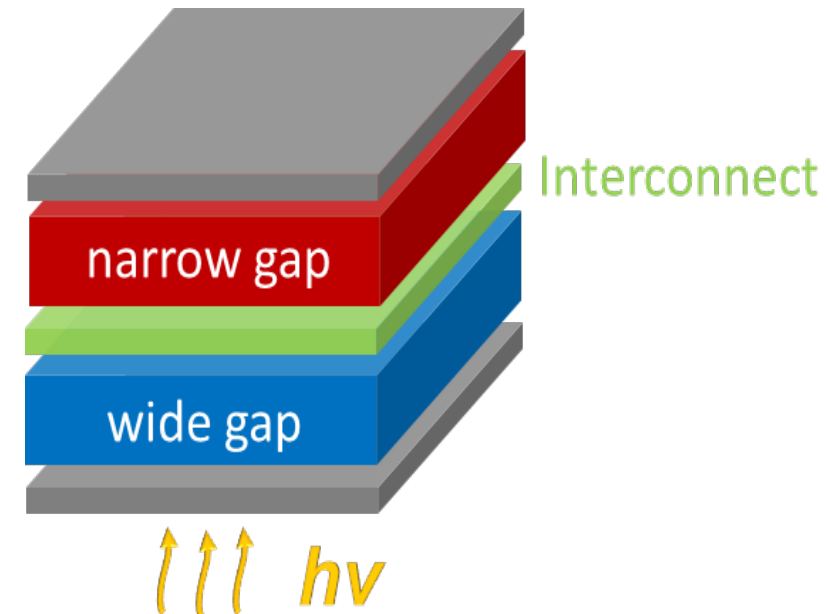
### Perovskite tandem cell



### Environmentally friendly

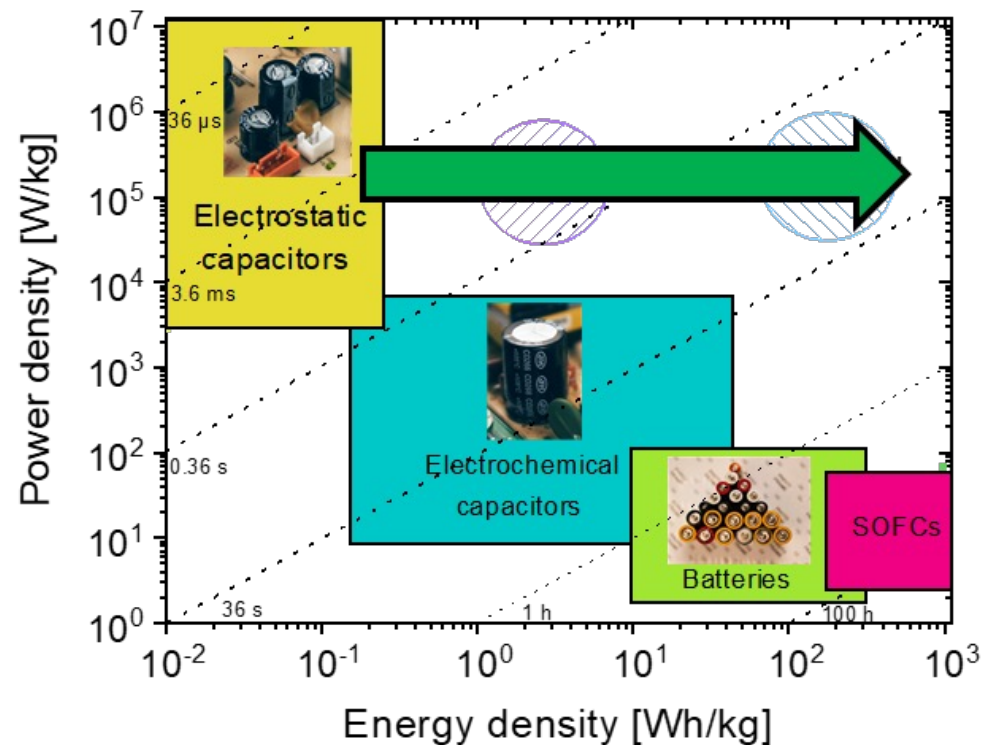
narrow gap cell  
(Sn-based or organic)

wide gap cell  
(Pb- and Sn-free)



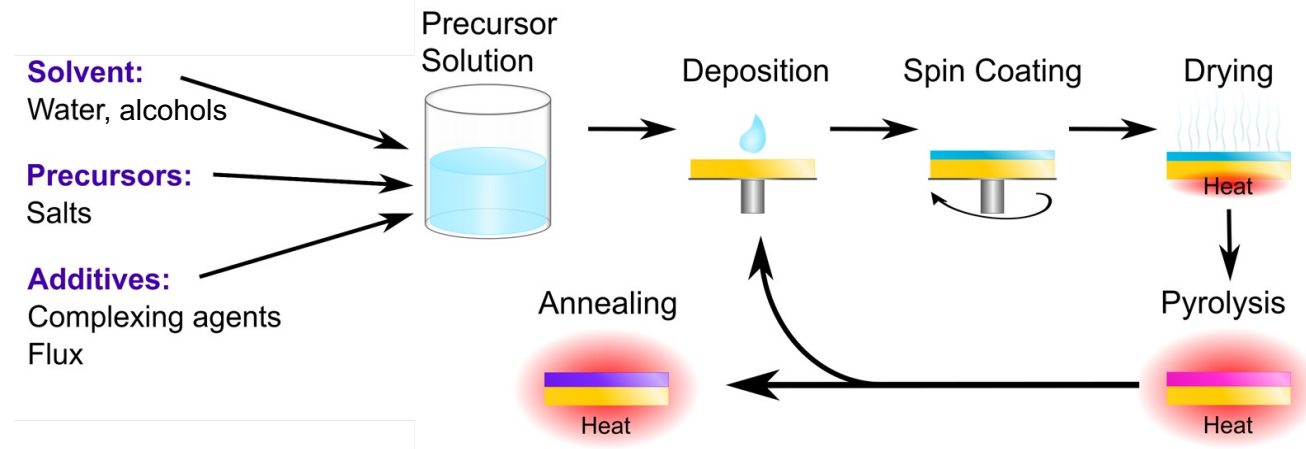
### Challenges:

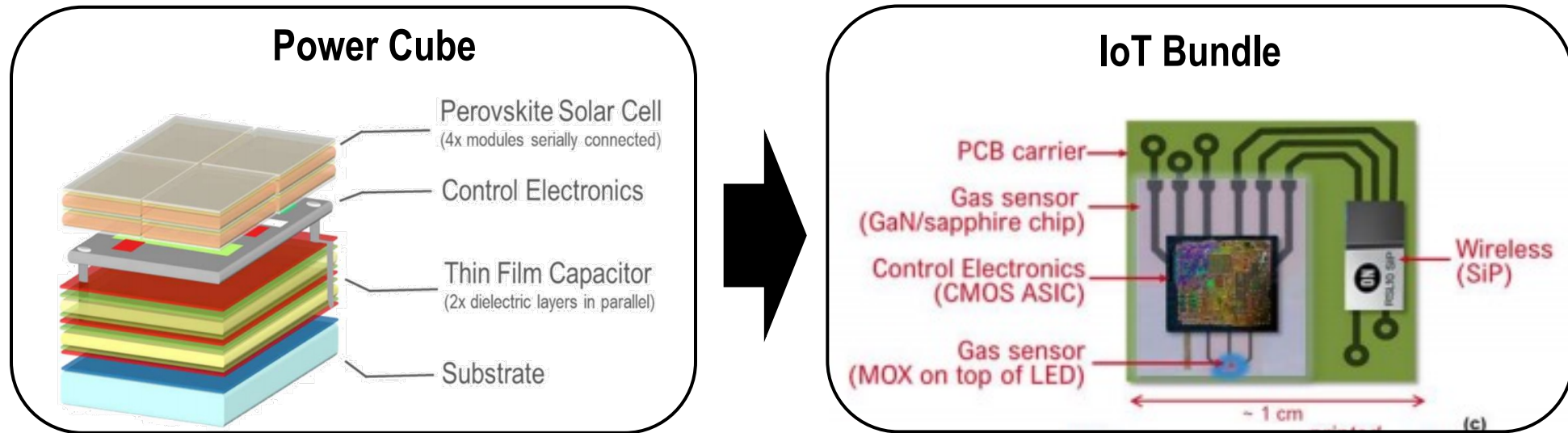
- Currently no energy storage system can provide at the same time high power density and energy density, with sufficient stability and environmental friendliness, and the potential to be integrated on flexible substrates



### FOXES Innovation:

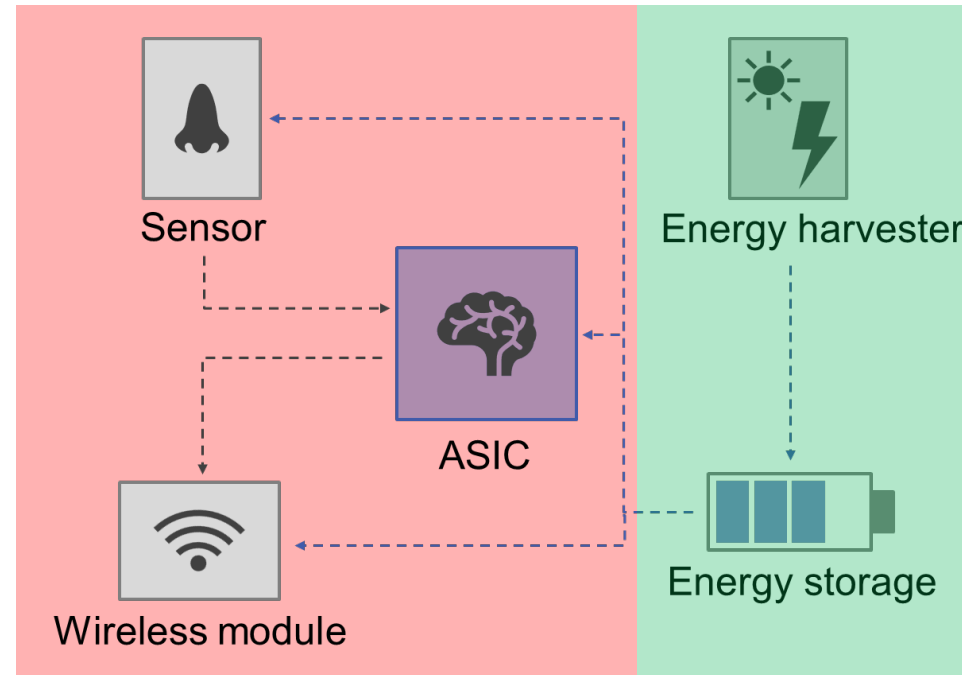
- Multilayer or stacked **thin film electrostatic capacitors** based on ceramic perovskites with **high energy density** and conductive metal oxide electrodes, produced using **nontoxic materials and methods**
- BaZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub>**
- LaNiO<sub>3</sub> electrodes.**





**Goal:** Realise an *integrated* Power Cube to power an IoT Bundle containing a gas sensor, and testing it!

- KPIs:**
- Pb- and Sn-free perovskite multi-junction solar cell with 4 V output (WP3)
  - Pb-free multilayer thin film capacitor with 0.6 mJ stored energy @4 V (WP4)
  - Energy management circuit with > 50% efficiency (WP5)
  - Sensor node sensitive to < 1 ppm NO<sub>2</sub>/O<sub>3</sub> and IoT Bundle power budget < 50 μW (WP6)



Ceramic ultracapacitors

### Power consumption/day

|               |                    |
|---------------|--------------------|
| per event     | <b>0.5 mJ</b>      |
| per 1 h sleep | <b>1.8 mJ</b>      |
| 4 x events/h  | <b>91.2 mJ/day</b> |

Gas sensor - 1 mW  
AC-operation (1:10) –  
86,4 J/day

### Energy harvesting/day

**260 mJ/12 h** illumination

### Energy storage

At least **45.6 mJ** energy storage capacity &  
ms charge/discharge capability

## 7. Summary & Outlook

- ❑ Successful realization as CMOS-integrated chemical sensor devices !
- ❑ Performance has to be optimized (cross sensitivities !)
- ❑ We need many more chemical sensor devices with high selectivity
- ❑ Integrated multi-gas sensor devices
- ❑ Power consumption of sensor devices has to be drastically decreased
- ❑ Environmental-friendly technologies for energy harvesting and energy storage (sensor networks everywhere)
- ❑ Efficient 3D-integration technologies required !
- ❑ Energy autonomous IoT sensor devices – still a big challenge !