Nanotechnology based intelligent multi-SENSor System with selective pre-concentration for Indoor air quality control

Using passive fluidics to improve chemical micro-nano-sensor systems – the SENSIndoor approach

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Motivation: VOCs - key for Indoor Air Quality

- Volatile Organic Compounds (VOCs) are highly relevant for IAQ
- Some are proven or suspected to be carcinogenic
- Resulting target concentrations are low ppb or even sub-ppb
  → **High sensitivity required**
- Benign VOCs (e.g. ethanol) can occur at much higher conc. (ppm)
  → **High selectivity required**
- Most relevant target VOCs according to European studies: formaldehyde, benzene, naphthalene

<table>
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<tr>
<th>Target gas</th>
<th>Guideline values</th>
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<tr>
<td></td>
<td>µg/m³</td>
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<tr>
<td>Formaldehyde [1]</td>
<td>100</td>
</tr>
<tr>
<td>Benzene [2]</td>
<td>5</td>
</tr>
<tr>
<td>Naphthalene [1]</td>
<td>10</td>
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</table>

[1]: WHO guidelines for indoor air quality (2010)
[2]: Umweltbundesamt Infoblatt Benzol (12/2010)
Note: *some national regulations target even lower concentration limits, e.g. France*
SENSIndoor has developed a pulsed laser deposition (PLD) process for gas sensors.

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Well suited deposition method for porous nanocrystalline layers of SnO\textsubscript{2} and WO\textsubscript{3} (for MOS sensors) and for dense layers with noble metal decoration (for Gas-FET sensors).

Noble metal doping with alternating deposition.

Suitable for wafer level deposition: process scale-up demonstrated.

Partners: Univ. of Oulu, Picodeon.


Pulsed laser deposition

SnO\textsubscript{2} „nanotrees“
SENS Indoor has developed new nanostructured metal oxide semiconductor (MOS) sensors.
Nanostructured MOS sensors

• Optimized micro-hotplates
• MOS sensors with PLD coated layers show high sensitivity in the ppb range
• Various layer types (SnO$_2$, WO$_3$) with and without noble metal catalyst in order to enhance selectivity
• Partner: SGX


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**SENSIndoor** has developed new gas sensitive SiC field effect transistors (SiC-FET) with nanostructured gate materials.
Nanostructured SiC-FET sensors

- Optimized platforms with integrated heater
- WO$_3$/Ir as gate material
- High response in the ppb range, especially vs. formaldehyde
- Additional contacts with metal electrodes to increase the stability
- Partners: LiU, SenSiC

D. Puglisi, J. Eriksson, M. Andersson, J. Huotari, M. Bastuck, C. Bur, J. Lappalainen, A. Schütze, A. Lloyd Spetz: Exploring the Gas Sensing Performance of Catalytic Metal/Metal Oxide 4H-SiC Field Effect Transistors, Materials Science Forum, 858, 997-1000

GasFET sample with WO$_3$ + Ir gate
**SENSIndoor** has developed a novel pre-concentrator concept based on metal organic frameworks (MOF).
Metal organic frameworks (MOF)

- Crystalline materials composed of metal centers & organic linkers
- Ultrahigh porosity
- Extremely large internal surface areas (up to several 1000 m²/g)
- Tunable chemical and physical properties
MOF pre-concentrators

- Pre-concentrators based on MOF shows two orders of magnitude higher sorption efficiency than conventional materials (e.g. Tenax TA)
- Efficient sampling of benzene to boost sensitivity and selectivity
- Partners: FhG-ICT, SGX, USAAR-LMT

M. Leidinger, M. Rieger, T. Sauerwald, M. Nägele, J. Hürttlen, A. Schütze: Trace gas VOC detection using metal-organic frameworks micro pre-concentrators and semiconductor gas sensors
EUROSENSORS 2015, Freiburg, Germany, September 6 to 9, 2015, doi: 10.1016/j.proeng.2015.08.719
SENSIndoor uses smart operation modes for sensor and data processing for detection and quantification.
Multiple signal generation by temperature cycled operation (TCO) and gate bias cycling (GBCO)

Data processing for detection (e.g. LDA) and quantification (e.g. PLSR)

Selective and quantitative VOC detection at ppb level

Partner: USAAR-LMT

Reference tests at JRC Ispra for benzene quantification

• MOS sensor systems w/o pre-concentrator, reference: PTR-MS

• Partners: USAAR-LMT 3S

Combination of MOS sensor with $\mu$PC

- SMD ceramic package (5x7 mm² footprint)
- Lid with gas access not shown

Left:
- $\mu$PC chip
- MOF material
  - $\varnothing \approx 300 \mu$m

Right:
- Dual gas sensor chip (SGX Sensortech)
  - 1x WO$_3$ undoped
  - 1x WO$_3$ doped

Cross section for simulations

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Simulation of adsorption/desorption cycles (Comsol)

Background gas concentration: $4 \times 10^{-7}$ mol/m³ (approx. 10 ppb)

Accumulation: 600 s
Desorption: 10 s

Simulations show approx. 2 orders of magnitude higher concentration

Note: colors show relative scales in each image

Operating mode for combined MOS sensor and µPC

ramp: “broadband measurement” (instead of temp. step)

compare desorption and resorption cycle to obtain sensor response and achieve differential measurement for higher selectivity

Application specific optimization: sensitivity, selectivity and power consumption

Note: sensor cool-down and µPC heat-up pushes gas to sensors (thermal expansion/contraction)
Experimental results (unpublished)

- Miniaturized integrated sensor system
- 3*3 mm² hot plate with 200 µm MOF layer (UiO-66)
- Commercial sensor (AS MLV)
- PC operation period 60 min: 3540 s adsorption 60 s desorption
- 30 times TCO of 120 s duration within one PC cycle
Experimental results (unpublished)

- Sensor response to benzene for two identical sensor temperature cycles
- Left: w/o PC desorption
- Right: with PC desorption at t=180 s
Experimental results (unpublished)

- Quasistatic sensor signals for gas concentrations 1 to 100 ppb
- PC increases sensor response by nearly two orders of magnitude
SENSInoor integrates sensor and pre-concentrator with electronic readout and data processing.
System integration: MOS w µPC

Simple integration concept for MOS sensors and micro-pre-concentrators – scale-up possible with proven technologies

MOS and µPC integration in an SMD package with controlled gas access (SGX, FhG-ICT, Univ. of Oulu, Picodeon)
System integration: electronics

- Integration of pre-developed electronics
- 3 independently controlled, fully synchronized analog resistance control loops (1 PC + 2 MOS) 1% accuracy
- Highly dynamic MOS read-out 250 Ω – 1 GΩ 300 digits / decade resolution
- CO₂ and μSD card extension
- Small series production for SENSIndoor field tests
Integrated micro-nano-sensor system

- Flush mount enabled design (50 x 40 mm) for unobtrusive installation
- μSD card and CO2 sensor extension for field test raw data collection
- Field calibration adapter attachable

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Novel concept for on-site calibration based on diffusion

- Easy to use mobile calibration standard
- Exploiting the vapor pressure of (highly) diluted solutions (Henry law)
  - Successfully tested by dilution series with Toluene ($C_7H_8$) and Squalane ($C_{30}H_{62}$) - non volatile liquid
  - Different dilution levels provide needed concentrations (also zero air)
- To Do:
  - Transferring results to target VOCs
  - Replacing liquid by a wax or gel

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Further information: www.sensindoor.eu

SENSIndoor selected as top-3 project in NanoFy! competition
Best project to be announced tonight at conference dinner.
European Sensor Systems Cluster – ESSC

“Renaissance of chemical and biological sensors”

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European Sensor Systems Cluster – ESSC

Human-centred sensor-system solutions

- Industrial process monitoring
- Indoor environment + energy efficiency
- Outdoor Environment (air pollution)
- Human health + comfort
- Agricultural monitoring
- Water monitoring
Overview – Environmental Sensors (WG1)

- Huge span of scenarios and activities
- Heavily cross-linked with other Working Group topics
- Major trends and opportunities

**INPUTS**
- ICT Infrastructure
- Citizen Science
- Improved Sensors
- Satellite Sensing
- Open Science

**Environmental Big Data**

**OUTPUTS**
- New Industries
- Innovative Services
- Effective Regulatory System
- Informed Society
European Sensor Systems Cluster – ESSC

Roadmap Towards European Leadership in Sensor Systems

SURVEY OF INDUSTRIAL NEEDS

Final 03/10/2016

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