Introduction to gas sensors and their dynamic operation

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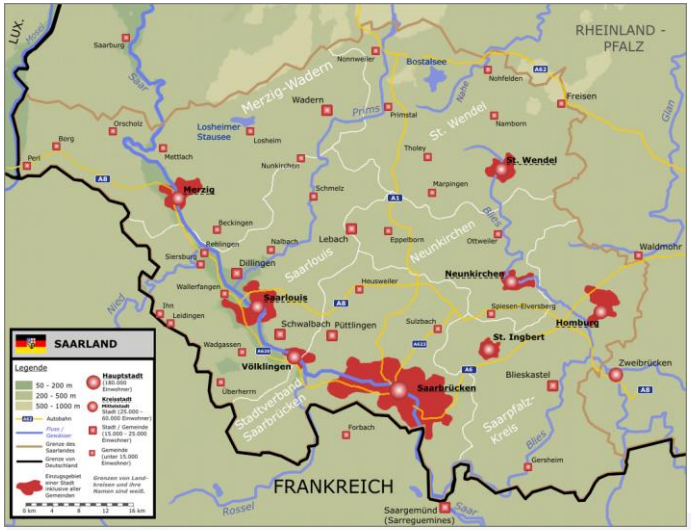
Outline

- Background
- Gas sensor applications
- Gas sensor function principles
- Dynamic sensor operation

Background: Who? Where? What?

- Personal background: applied physics, PhD in industry cooperation (CAQ)
- Since 2000 head of lab for measurement technology at Saarland University



Source: Wikipedia (above: from Roger Zenner - German Wikipedia, CC BY-SA 2.0 de)

- Primary research focus: **gas measurement systems** based on low-cost sensors (MOS, FET)
- Collaboration with R&D groups in sensor development, sensor manufacturers, end users
- Spin-off company 3S founded in 2006

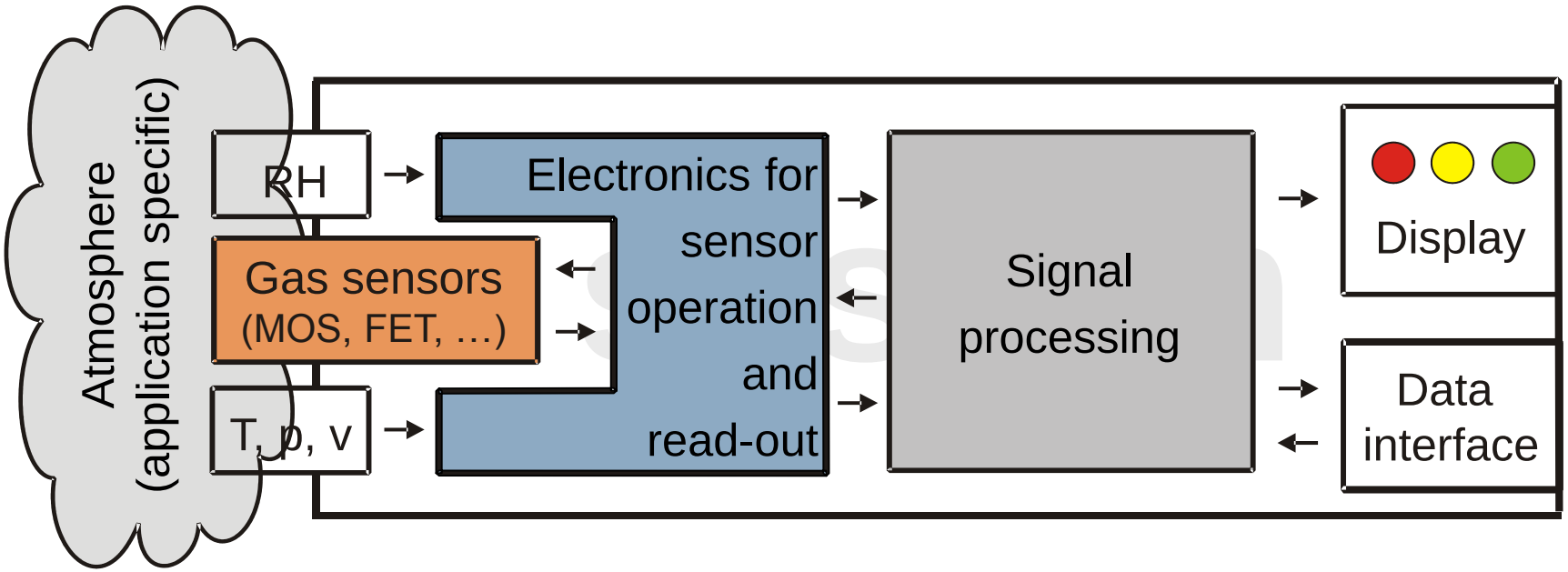
Research overview

- Dual sensor system for automotive **cabin air quality** (PhD project)
- EU project **Nanosensoflex** (5/2002 – 4/2005): development and testing of novel nanostructured semi-conducting metal oxide gas sensors
- **Outreach activities**, e.g. school labs, in sensors and microsystems (since 2002)
- Sin-off **3S – Sensors, Signal processing, Systems** founded 2006
- Projects on modular **gas measurement systems** and **sensor self-monitoring** (2006 – 2012) → main approach: Temperature Cycled Operation (TCO)
- Projects on (underground and building) **fire detection** using gas sensors
- Projects on **Indoor Air Quality** (VOC-IDS, 2011-14; SENSIndoor 2014-16) → improved VOC sensor systems with integrated pre-concentrator
- Projects on **odor nuisance monitoring** using human perception as reference
- **Simple physical model** for MOS sensors in TCO mode (**T. Sauerwald**, T. Baur)
- Comprehensive Matlab toolbox DAV^{3}E for sensor data fusion and analysis (**M. Bastuck**, T. Baur)
- Novel approach for onsite **VOC sensor (re)calibration** (**C. Schultealbert**, TS)

Selected publications

- A. Schütze et al.: Quantitative ozone measurement using a Pc thin film sensor and dynamic signal evaluation, Sensors & Actuators B 23 (1995) 215 - 218.
- A. Schütze et al.: Identification of Organic Solvents by a Virtual Multisensor System with Hierarchical Classification, IEEE Sensors J 4(6) (2004) 857-863.
- M. Lösch et al.: Ozone detection in the ppb-range with improved stability and reduced cross sensitivity, Sensors & Actuators B 130(1) (2008) 367-373.
- C. Bur et al.: Increasing the Selectivity of Pt-Gate SiC Field Effect Gas Sensors by Dynamic Temperature Modulation, IEEE Sensors J 12(6) (2012) 1906-1913.
- P. Reimann, A. Schütze: Fire detection in coal mines based on semiconductor gas sensors; Sensor Review 32(1) (2012) 47-58.
- **P. Reimann, A. Schütze, Sensor Arrays, Virtual Multisensors, Data Fusion, and Gas Sensor Data Evaluation; in: Kohl, Wagner (eds.): Gas Sensing Fundamentals, Springer, 2014.**
- **N. Helwig et al.: Gas mixing apparatus for automated gas sensor characterization; Meas. Sci. Technol. 25 (2014) 055903 (9pp)**
- M. Leidinger et al.: Integrated pre-concentrator gas sensor microsystem for ppb level benzene detection, Sensors & Actuators B 236 (2016) 988–996.
- **A. Schütze et al.: Highly Sensitive and Selective VOC Sensor Systems Based on Semiconductor Gas Sensors: How to?; Environments 4 (2017) 20.**
- **M. Bastuck: DAV^{3}E—A MATLAB Toolbox for Multivariate Sensor Data Evaluation, JSSS, 2018, acpt.**
- A. Schütze, T. Sauerwald: Dynamic Operation of Semiconductor Sensors, in: Raivo Jaaniso and Ooi Kiang Tan (eds.): Semiconductor gas sensors, 2nd ed. Elsevier, submitted.

Research focus: smart gas sensor systems



- Gas sensors: various function principles, multiple sensors, …
- Additional sensors (relative humidity, temperature, pressure, air flow)
- Electronics for sensor operation (heating, bias, light, …) & signal acquisition
- Signal processing (baseline & drift corr., gas identification & quantification)
- Data interface (bi-directional to set target gas, upload calibration data etc.)
- Sensor characterization and (on-site) calibration

Gas measurement systems: some history

- Gas measurement systems were originally required for (coal) mining operations to prevent explosions caused by methane (CH_4) and poisoning caused by carbon monoxide (CO)

- Historical warning systems used:

➢ The miner´s lamp (right)
These oil lamps would burn brighter, if additional fuel is present in the air (i.e. CH_4). To prevent setting off an explosion a tight metal mesh surrounds the flame.

➢ The canary
Miners would take along canary birds in a cage. Since the bird is more susceptible to CO poisoning it would drop from its perch, when high CO levels were encountered, warning the miners. Sometimes two birds were used for redundancy.

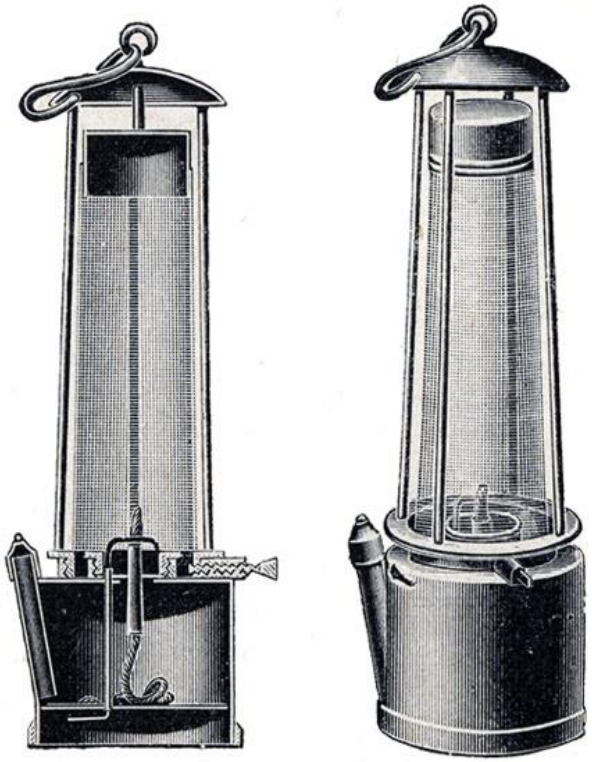


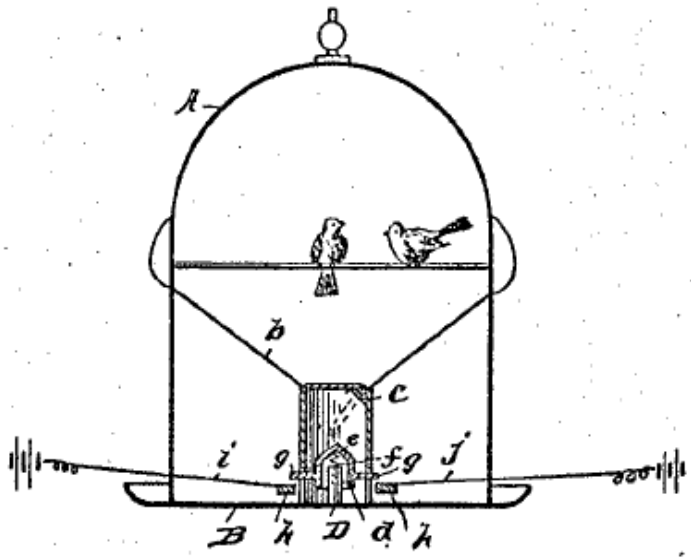
Fig. 192. Davysche Sicherheitslampe

Source: Wikipedia, „Grubenlampe“

Gas measurement systems: some history

The importance of redundancy is long since known, i.e. to prevent false alarms

Based on this patent from the year 1896 two canary birds are used to prevent false alarms: an alarm is only given, if both birds drop from their perch.



Eigenthum des Kaiserlichen Patentamts.

KAISERLICHES PATENTAMT.

AUSGEGEBEN DEN 16. JANUAR 1897.

PATENTSCHRIFT

— № 90083 —

KLASSE 74: SIGNALWESEN.

ROBERT WILLIAM JACOB KRAUS IN NEW-YORK
U. JOHN KOSTER IN BROOKLYN (N.-Y., V. ST. A.).

Verfahren und Vorrichtung zum Geben eines Signals beim Auftreten von Rauch oder schädlichen Gasen.

Patentirt im Deutschen Reiche vom 22. Februar 1896 ab.

Gas sensor systems today: hazardous gases

- Target gases: all potentially hazardous compounds, i.e. carbon monoxide (CO), hydrogen sulfide (H_2S), chlorine (Cl_2), benzene (C_6H_6), nitrogen oxides (NO_x), ozone (O_3), ammonia (NH_3), arsine (AsH_3), silane (SiH_4) etc.
- Normally, detection of a specific compound or class of compounds is required, therefore selective sensor systems are needed (expensive!).
- Typical units for measurement:
  - Volume fraction: ml/m^3,
    often in the form of ppm_V (parts per million) or ppb_V (… billion)
  - Mass fraction: mg/m^3 or $\mu g/m^3$ (also possible as ppm_m or ppb_m)
  - Conversion via mol volume (24.1 l at normal ambient cond.) and molecular mass
- Alarm levels are typically defined by legal constraints (i.e. maximum permissible workplace concentration). Examples: CO (in parking garages) 30 ppm; H_2S 10 ppm, SO_2 0,5 ppm, NO_2 5 ppm, AsH_3 50 ppb, Benzene 1ppb (WHO limit)
- Primarily electrochemical cells (EC) are used today, but also other sensor principles, NDIR-measurement or even chemical analysis systems.

Gas sensor systems today: explosion warning

- Target gases: hydrocarbons (HC), especially CH_4; hydrogen, H_2; but also solvents, fuels etc.
- The warning system has to detect dangerous mixtures of combustible gases or vapors in air (or oxygen) before they form explosive mixtures.
  Mixtures are explosive only in a certain concentration range; a minimum concen-tration is needed so that energy given off by one molecule reacting can spread the reaction to adjacent molecules causing a chain reaction, i.e. an explosion.
- Alarm level is typically at 5 - 10 % *LEL* (Lower Explosion Limit)
  LEL in air for: H_2 4%, CH_4 5%, C_4H_{10} 1,4%, i.e. typical alarm levels few 1000 ppm
- There is also an upper explosion limit (*UEL*; above a certain concentration, the oxygen concentration is too low to sustain an explosion) that is only of importance in select application (for example mine gas)
- Depending on the application, selective or broadband sensors are required.
- In industrial applications pellistors or IR-measurement are mostly used.
- Metal oxide semiconductor gas sensors were originally developed (and still used) for explosion warning in private households in Japan.

Some non-industrial applications

- Cabin air quality (CAQ) in cars
  - Sensor-based control of the air intake/recirculation flap in a car prevents high concentrations of hazardous (or smelling) gases from reaching the car interior
  - Today, dominating application in Europe and North America wrt to number of sensors
  - Comfort application with low demands on data quality
- CO_2 monitoring for indoor air quality and demand controlled ventilation
- TRSK 313 – fixed alarm for hazardous CO_2-concentrations (in bars and pubs)
  - Often NDIR- or EC-based systems warning against high CO_2 concentrations and for automatic venting of basement rooms
  - Legislation has created a completely new market
- Breath analysis (professional or personal)
  - Stationary system for dentists to diagnose halitosis (based on H_2S EC-cell: measure volatile S compounds, range up to 2000 ppb)
  - Low-cost-system for personal use based on MOS sensor for “fresh breath” (Asia) or breath alcohol (Europe, US)
- etc. (basically only limited by the ideas of developers!)

Gas sensor function principles

Overview over sensor principles

- NDIR sensor systems
- Electrochemical sensors
- Pellistors
- Mass-sensitive devices
- Gas-sensitive field effect devices
- Metal oxide semiconductor gas sensors

IR measurement systems I: basics

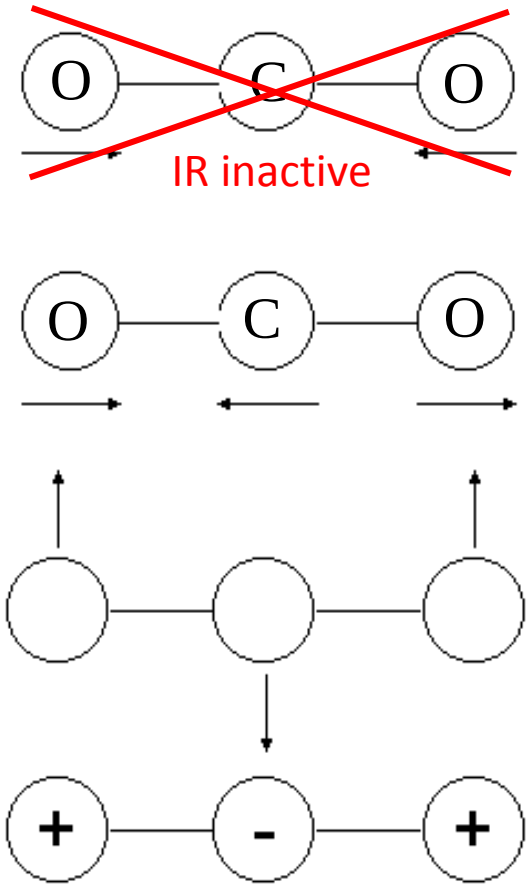
- Infrared light (i.e. heat radiation) induces molecular oscillations, light is absorbed in the process
- Only those wavelength are absorbed that couple resonantly with the molecule and induce oscillations:
  - Specific absorption spectrum („finger print“) for each gas
  - Absorption is described by the Lambert-Beer-Law:

$$I = I_0 \cdot e^{(-\alpha \cdot c \cdot l)}$$

$$-\ln\left(\frac{I}{I_0}\right) = \alpha \cdot c \cdot l$$

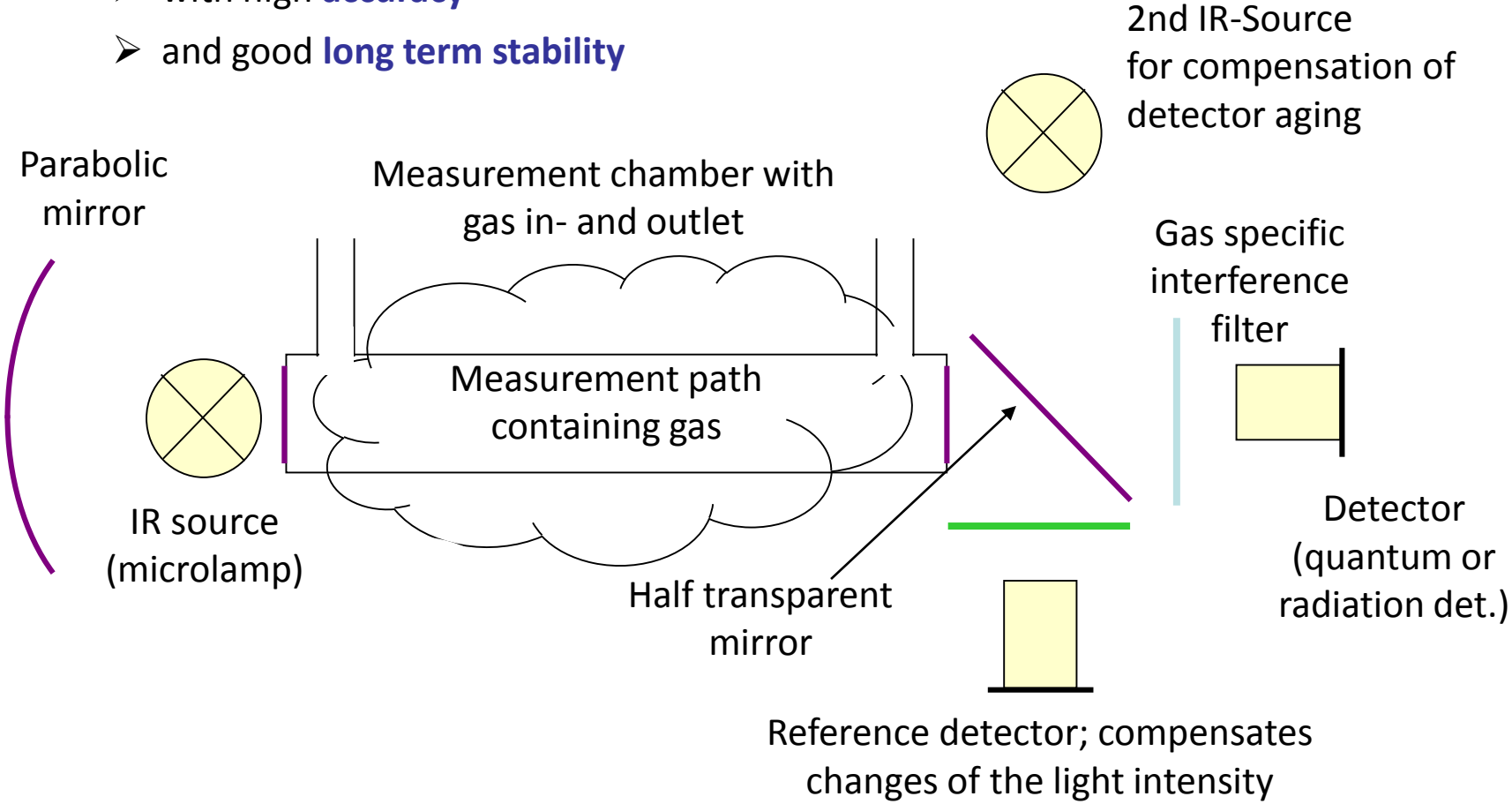
with: c: gas concentration
l: length of interaction path
α: extinction coefficient
(gas and frequency specific)

Example: CO_2



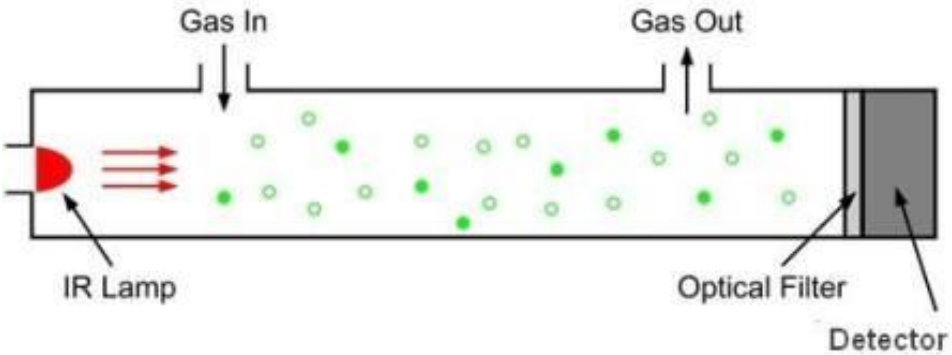
IR measurement systems II: NDIR setup

- High performance Non-dispersive IR absorption measurement requires elaborate setup
- Compared to chemical sensors NDIR allows quantitative measurements
  - with high **accuracy**
  - and good **long term stability**



Low-cost NDIR sensors

- Available for CO_2 and CH_4
  - Single wavelength only: no compensation of light source deterioration or dirt
  - ABC algorithm (automatic baseline correction): lowest value is set to background concentration



Available without pins (special order)

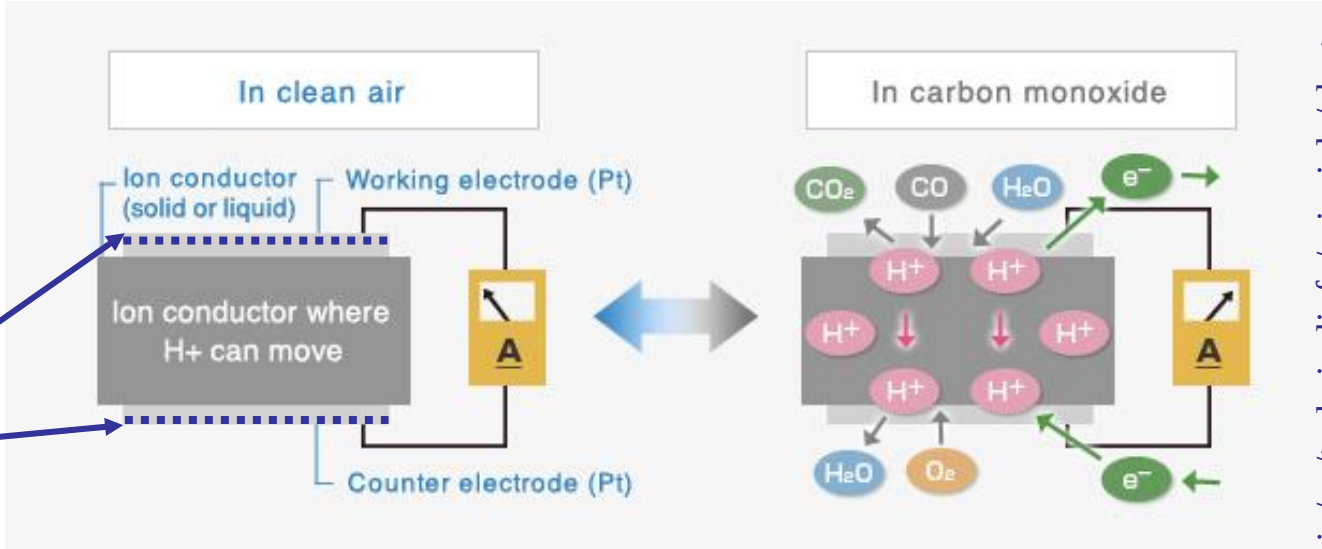
LP8 sensor back (magnified)

- Low resolution ~ 50 ppm → not suitable for trace gas monitoring
- Power consumption ~ 50 mW
- Manufacturers:
  SenseAir (S), Alphasense (UK), Honeywell (USA), Dräger (D),…

Electrochemical cells I: function principle

- Gas molecules are ionized at the working electrode, electrolyte in the sensor allows ions to reach the counter electrode, the resulting current is measured.
- Selectivity can be influenced by choice of the electrolyte, working electrode material and the electrical potential.
- Detection limit ~1-10 ppm, linear response, i.e. constant sensitivity

Source: Alphasense



Diffusion limited gas access, i.e. reaction is limited by gas reaching the electrode (leading to better long term stability).

- Potentiostat controls voltage between working vs. counter electrode, additional reference electrode for defined potential
- Simple cells with only two electrodes (w/o reference electr.) are less temperature stable, but more compact & cheaper.

Source: www.figaro.co.jp/en/technicalinfo/principle/electrochemical-type.html

Electrochemical cells II: assessment

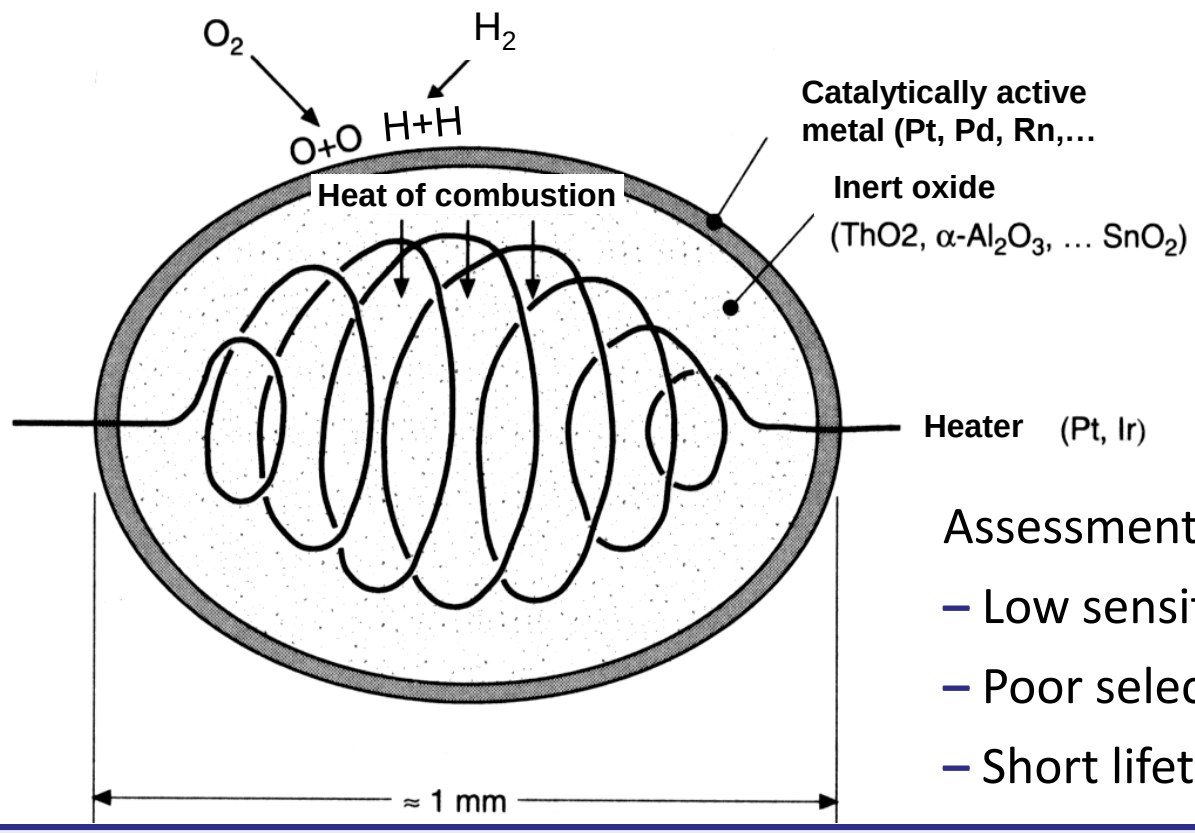
- Advantages
  - For many applications sufficient selectivity (i.e. CO detection)
  - Good sensitivity (detection threshold 1-10 ppm)
  - Low power consumption, relatively compact, therefore well suited for portable devices.
- Disadvantages
  - Comparatively costly due to complex manufacture
  - Short lifetime (typically a few months up to 2-3 years max.)
    - ➢ Electrolyte is consumed, especially when target gas is continuously present or high concentrations are repeatedly measured
  - Operation at high ambient temperature is very problematic (electrolyte dries out)
  - Cross sensitivities are there (even though they are often ignored)
    - ➢ CO vs. H_2, Ozone vs. NO_2
  - Limited innovation potential
    - ➢ Especially miniaturization is limited (reduces lifetime further)
    - ➢ Manufacturing automation, little potential left for reducing cost

Source: Dräger

Source: Alphasense

Pellistors I: function principle

- Sensor temperature changes when combustible gases react with oxygen on the catalytic surface (operating temp. 200 – 600°C)
- Heater is simultaneously used as temperature sensor for measurement
- Selectivity can be influenced by catalyst material and temperature



Source: H. Schaumburg, *Sensoren*, Teubner

Pellistor = **pell**et res**istor**

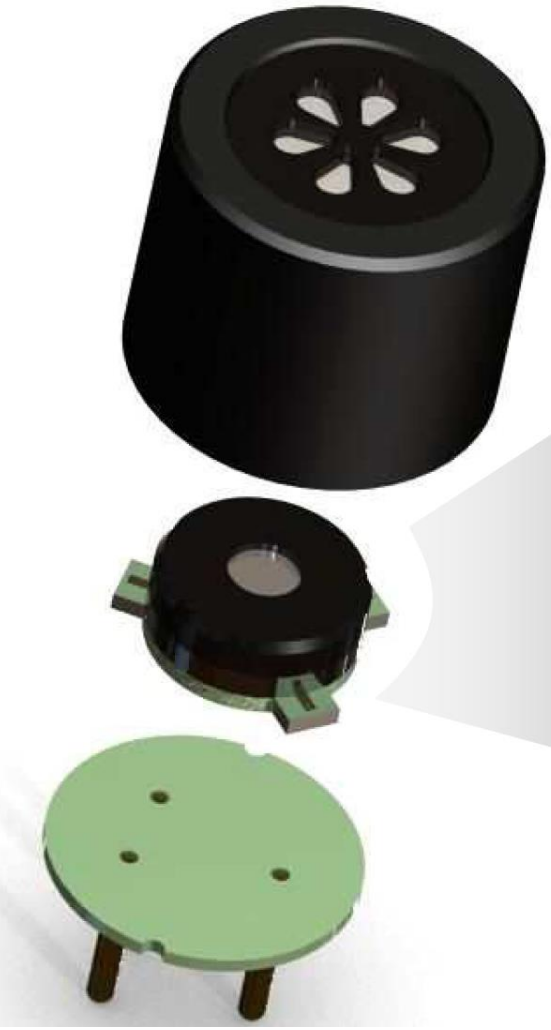
Measurement signal is either
- Temperature change at constant heating power or
- Change of heating power at constant temperature (faster, no self-destruction of sensor @high concentration)

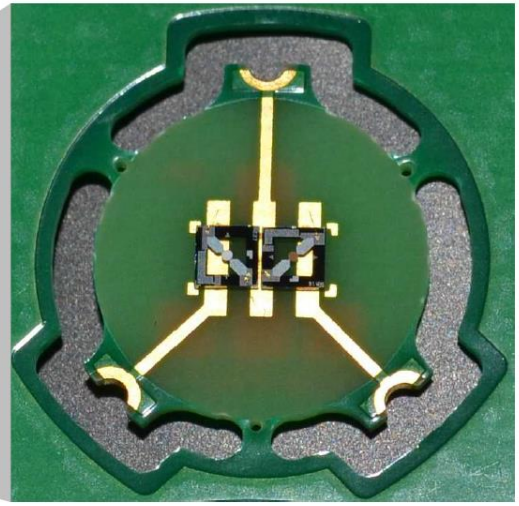
Assessment:
- Low sensitivity, poor detection limit
- Poor selectivity (combustion only)
- Short lifetime (typ. 6 months)

Pellistors II: miniaturization

Planar pellistor on MEMS micro hotplate

- First commercial offer
- Size reduction approx. 1/10, power reduction approx. 1/3
- Vibration resistance approx. 1000x higher





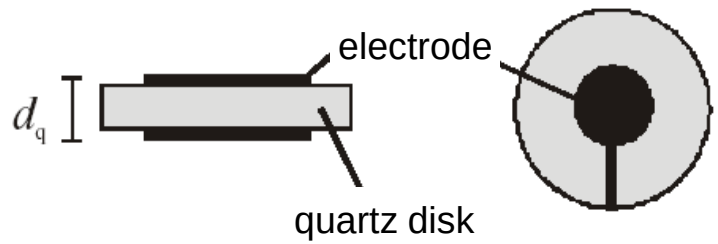
Source: SGX Sensortech, Corcelles, CH

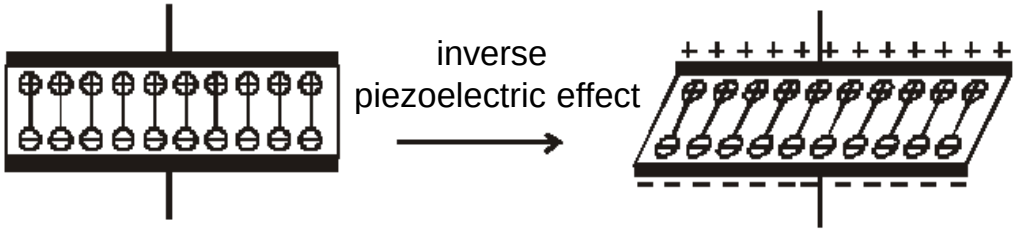
Mass sensitive devices I: function principle

- Sensor is basically a piezoelectric mechanical resonator, often quartz
- Resonance frequency is determined by mass loading (→ micro balance)
- Gas adsorption on the sensitive layer changes the mass loading
- Different construction principles based on
  - **Volume oscillations**
    „**BAW**“ bulk acoustic wave →
  - **Surface oscillations**
    (shear waves, Rayleigh waves, Love waves):
    „**SAW**“ surface acoustic wave
- Frequency behavior determined by Sauerbrey equation:

$$\Delta f = -\frac{\boxed{2 f_0^2}}{\sqrt{\rho_q \mu_q}} \frac{\Delta m}{A_q} = -S_f \frac{\Delta m}{A_q}$$

ρ_q, μ_q, A_q: density, shear modulus and area of the quartz
S_f: Sauerbrey constant (sensor specific)

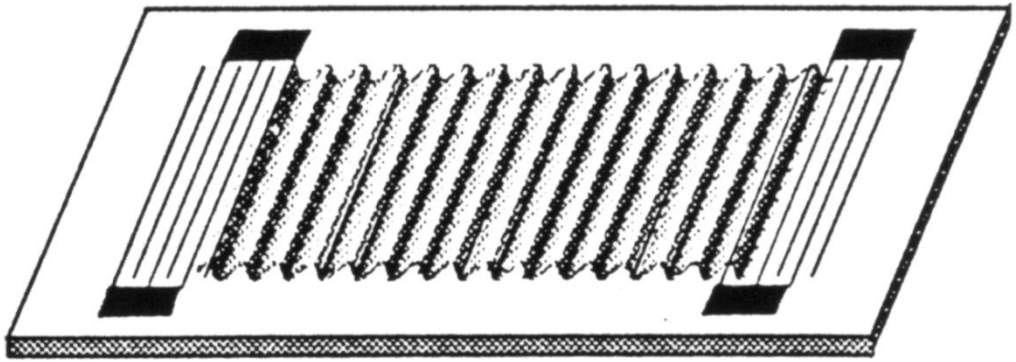




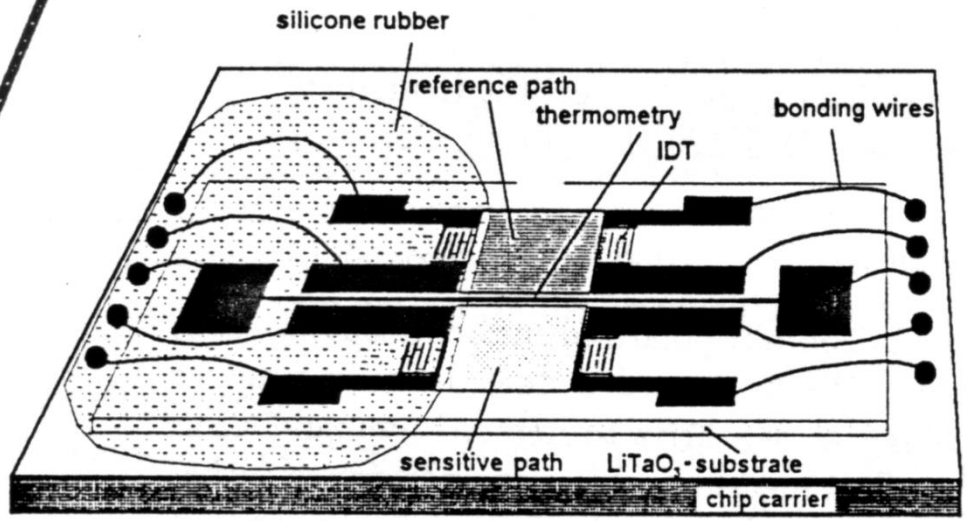
Source: Quarzmikrowaage, Uni Mainz, online

Mass sensitive devices II: function principle

- BAW oscillators have typical resonance frequencies of 5 – 20 MHz
  - Frequency resolution ~ 1 Hz ⇒ Sensitivity increases with resonance frequency
  - Experimental data for S_f: 0.036 Hz cm²/ng
  - for 1 cm² quartz surface area therefore: $\Delta m = \Delta f / S_f = 28$ ng/cm²
- SAW oscillators have typical resonance frequencies of several 100 MHz
  - Higher sensitivity, but also higher effort for electronics design and components



Interdigital transducers (IDT) inject a wave, wave frequency influenced by mass loading of the path; reference path allows differential measurement



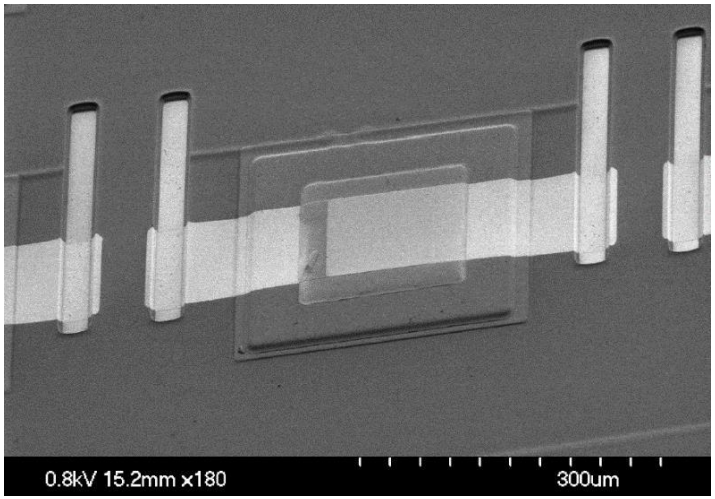
Assessment:

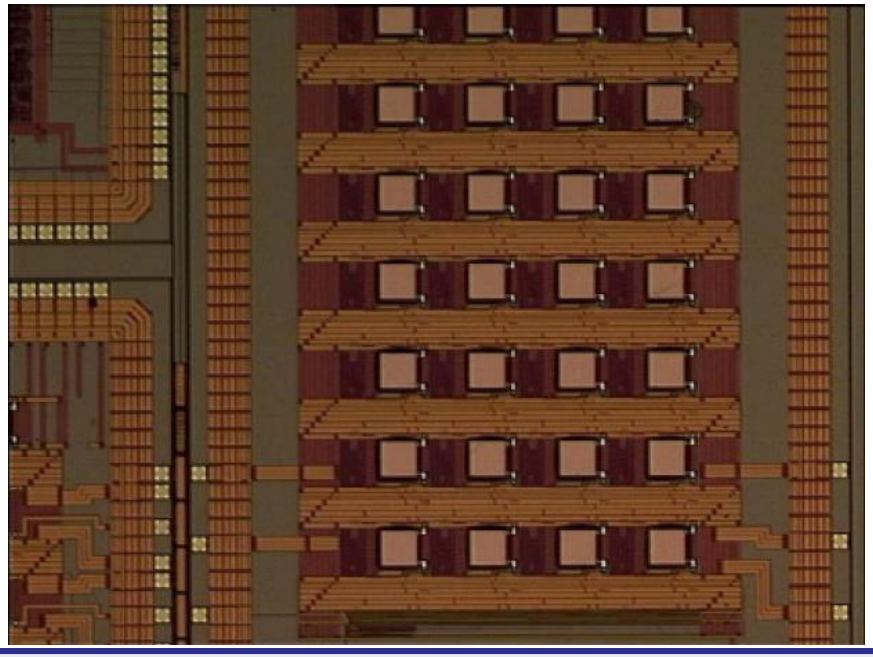
- Low sensitivity, poor detection limit
- Trade-off between selectivity and reversibility
- (costly electronics for SAW)

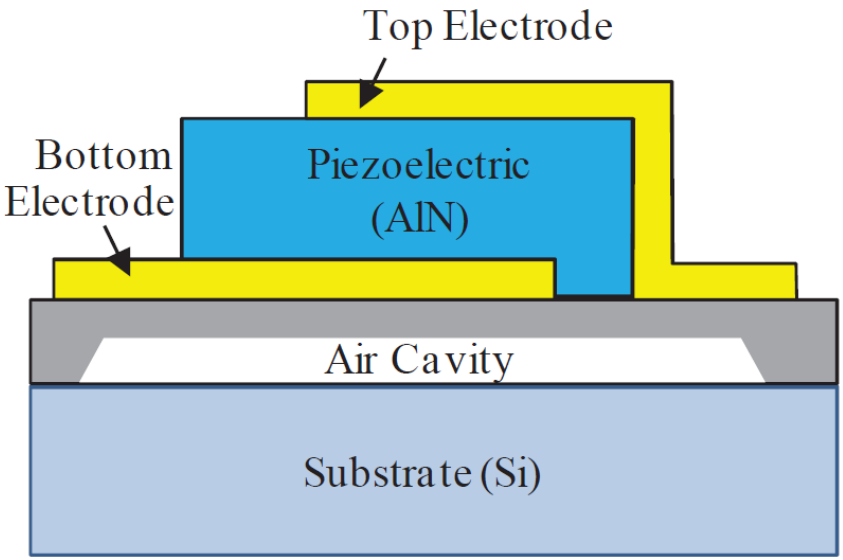
Source: H. Schaumburg, *Sensoren*, Teubner

Mass sensitive devices III: FBAR microsensors

- Miniaturization:
  thin film bulk acoustic resonator (FBAR)
- Resonance frequency is measured with CMOS oscillator integrated underneath the FBAR structure
- Microarrays possible, but functionalization is critical



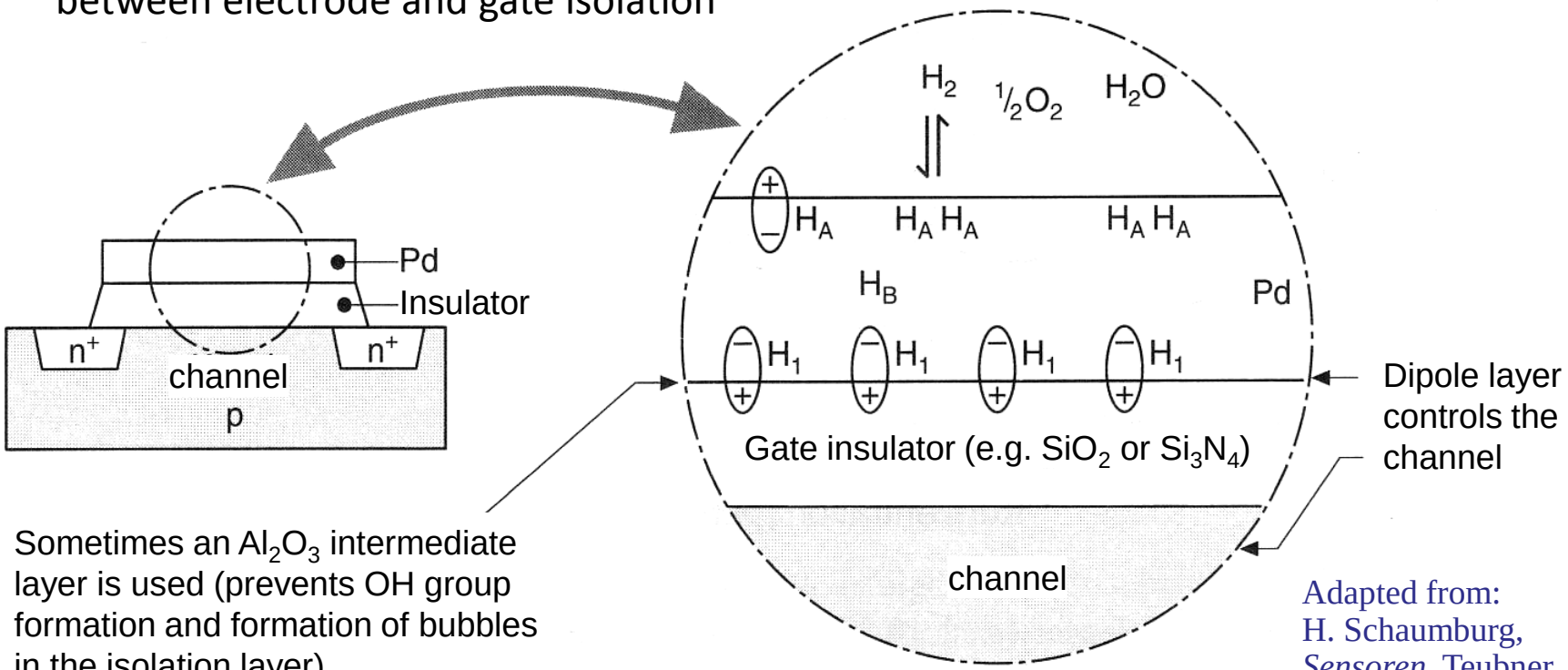




Sources: Johnston, MEMS 2012, Paris 846 (2012)
Tukkiniemi, Procedia Chem. 1 1051 (2009)
Lee, Sensors IEEE, 1 (2015)

Field effect devices I: function principle

- Instead of being controlled by a gate voltage, the channel resistance of a field effect transistor (FET) is controlled by adsorbed chemicals forming dipoles
- Classic sensor element: H_2 sensor based on a Pd gate electrode
  - Hydrogen (protons) diffuses through the Pd electrode to the isolation layer
  - A dipole layer controlling the FET behavior is formed In the boundary layer between electrode and gate isolation

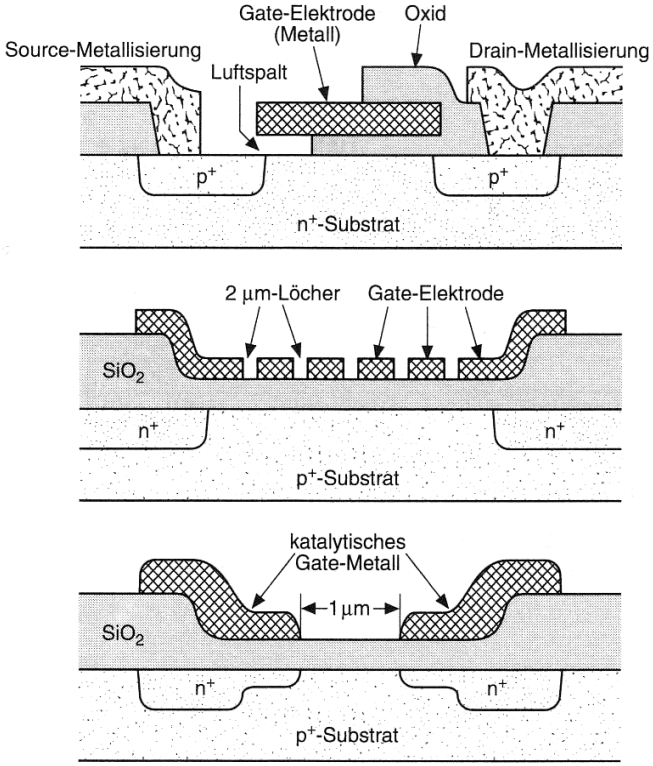


Sometimes an Al_2O_3 intermediate layer is used (prevents OH group formation and formation of bubbles in the isolation layer)

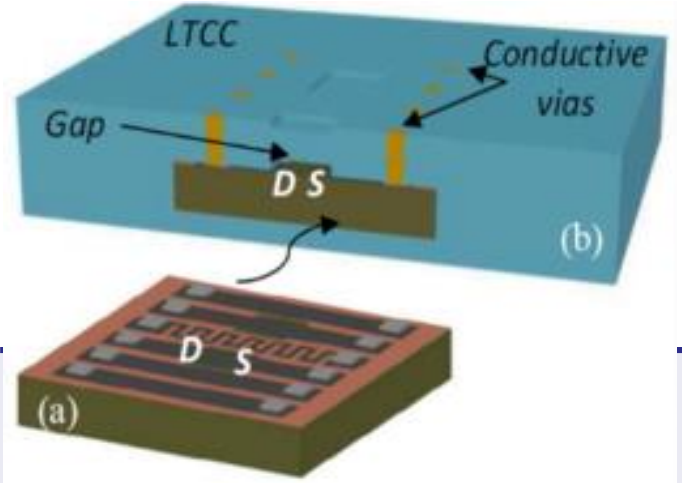
Adapted from: H. Schaumburg, *Sensoren*, Teubner

Field effect devices (GasFET, ChemFET) II: gate variations

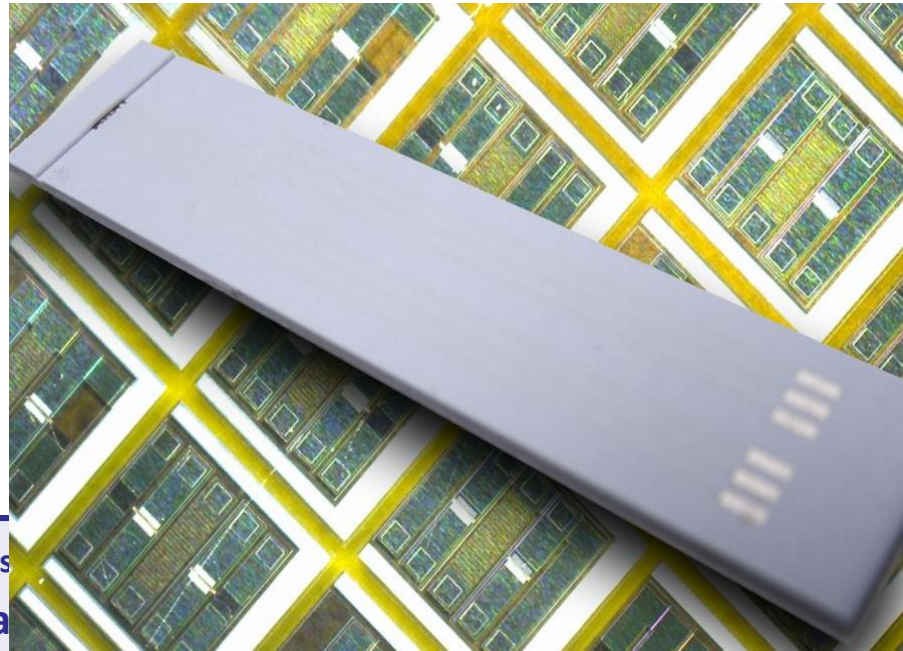
- To overcome the basic limitation (sensitive only to H_2 and hydrogen containing gases), different gate variations are used, i.e.
  - perforated or **porous** gate
  - suspended gate
- Selectivity and sensitivity can be influenced and improved with suitable gas sensitive (chemically active) layers covering the gate to absorb the gases to be detected.
- SiC as substrate material allows operation at elevated temperatures and in harsh environments



Source: H. Schaumburg, *Sensoren*, Teubner



SiC-GasFET integrated in LTCC package, Linköping Univ., Applied Sensor Science, SenSiC AB

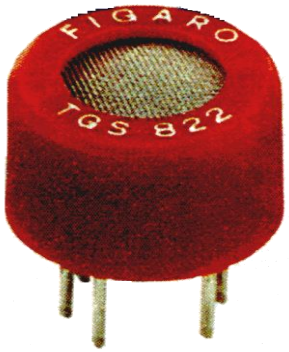


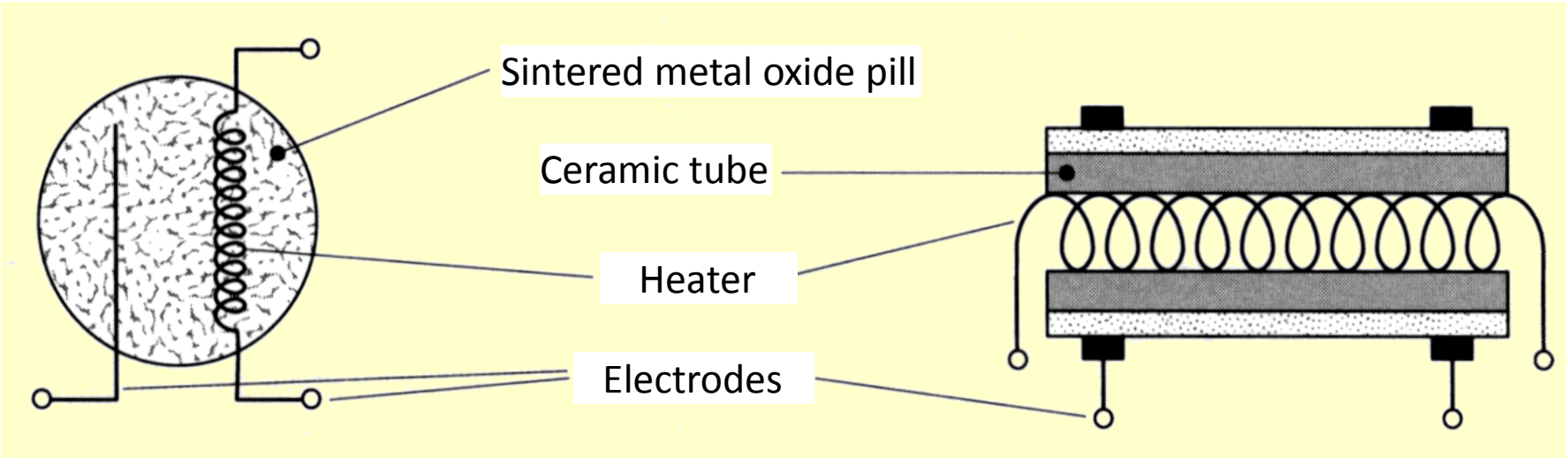
Field effect devices III: assessment

- Advantages
  - Separation of chemical recognition through gate materials on the one hand and signal generation (transduction) on the other hand allows separate optimization and a broad spectrum of gas sensitive layers with one base technology
  - CMOS GasFET perfect for direct integration with microelectronic systems (chemically sensitive layer is deposited in post-processing) allowing high sensitivity (integrated amplifiers) and offering the basis for (very) low cost (at high volumes)
  - Low power consumption for room temperature operation
  - **SiC-FETs have shown ppb-level detection limits**, e.g. for formaldehyde, benzene
  - **SiC-FETs suitable for exhaust gas monitoring** (cars, power plant, stove)
- Disadvantages
  - CMOS GasFET: poor long term **stability** due to irreversible adsorption
    → periodic heating required for surface cleaning
  - CMOS GasFET: strong influence of ambient temperature on baseline and sensitivity
    → elevated temperature increases sensitivity, stability (and power consumption)
  - Technology requires **high volume applications** to achieve cost benefits; development and manufacturing costs are relatively high for niche applications

Semiconductor gas sensors: overview

- Gas adsorption/-reaction changes electrical properties (impedance) of the semiconducting gas sensitive layer
  (however, often only the “ohmic” resistance is evaluated)
- Gas sensitive materials:
  - **Metal oxide semiconductor (MOS)**
    (i.e. SnO_2, Ga_2O_3, WO_3, In_2O_3) with additional catalysts
  - organic semiconductors (Phthalocyanine, polypyrroles)
- Manufactured at first as pressed composites, see below
- Today, screen printing is most widely used

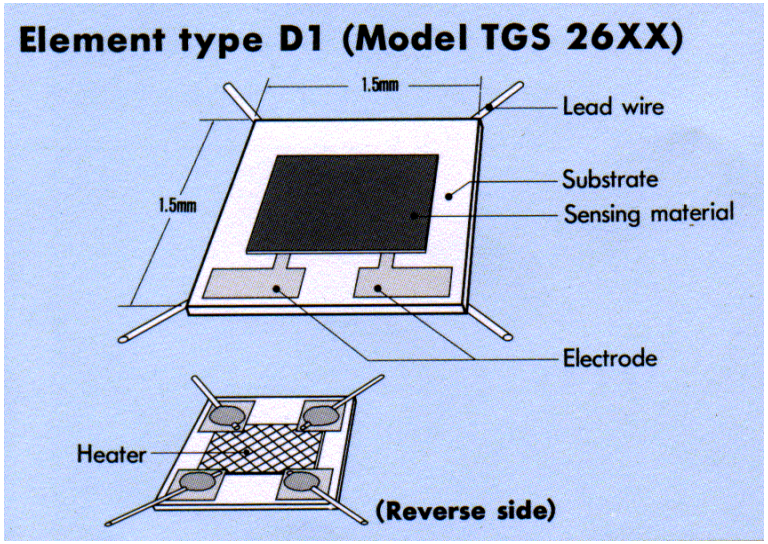




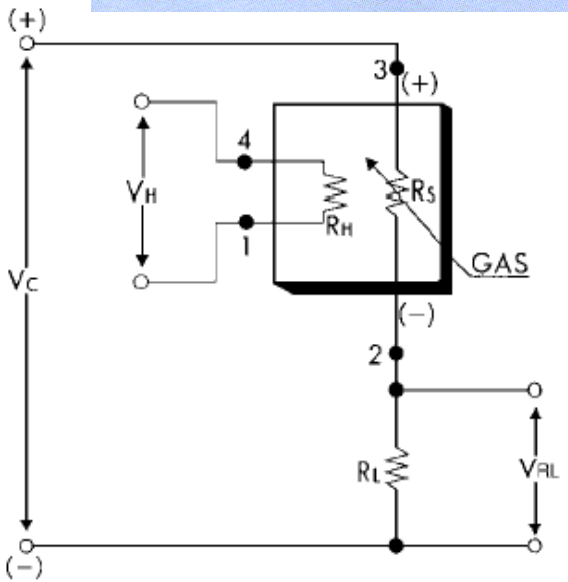
Source: Figaro, Inc.

MOS sensors: basic construction

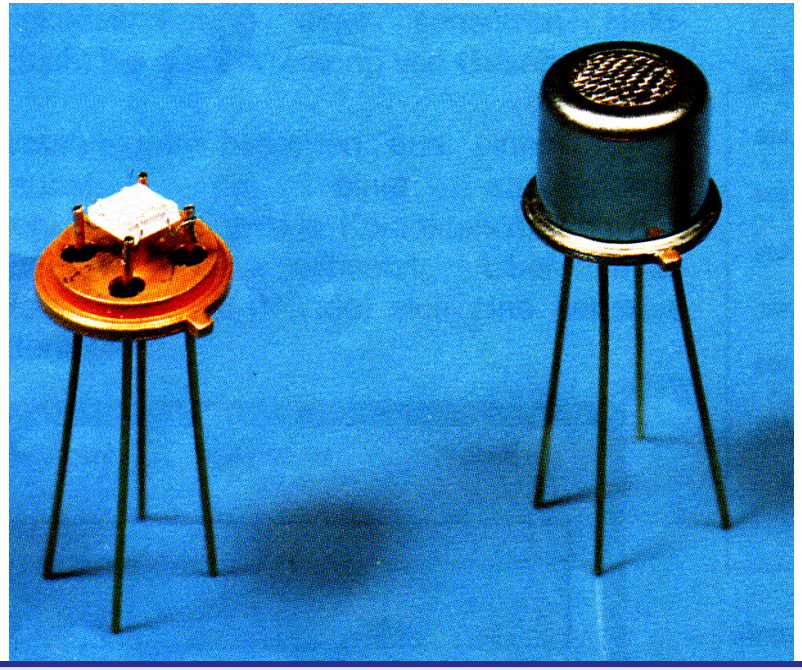
Source: Figaro, Inc.



- Modern fabrication using screen printing allows smaller and cheaper sensors
- Al_2O_3 is mostly used as substrate material with sputtered Pt for heater and electrodes
- Typical packaging of current semiconductor gas sensors in TO-5 cans with metal mesh to mechanically protect the sensor



Simple read-out circuit with constant heater voltage V_H and measurement voltage V_C for a voltage divider consisting of the sensor resistance R_S and a load resistor R_L

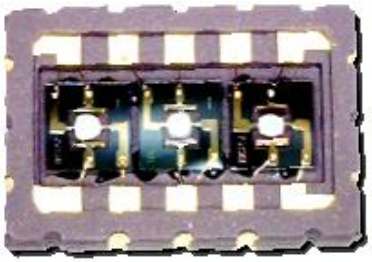


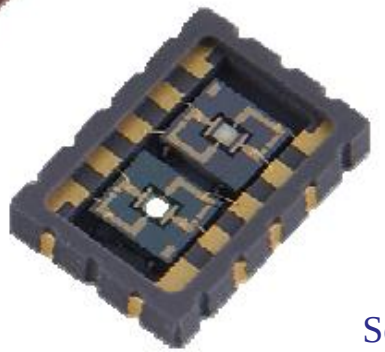
Source: UST Umweltsensortechnik GmbH

MOS sensors II: MEMS microsensors

Metal oxide semiconductor sensor in MEMS technology

- Micro hotplate: reduced power and time constant
- Gas-sensitive layer deposited via screen-printing, drop dispension or PLD (pulsed laser deposition)



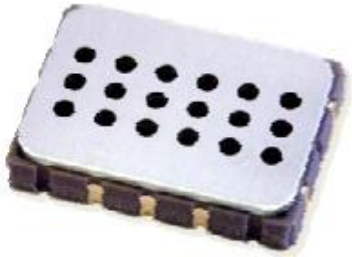


Primary application today

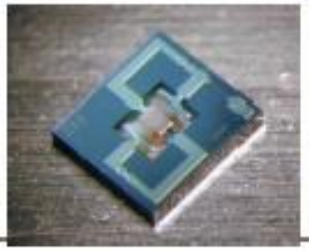
- Automotive Cabin Air Quality

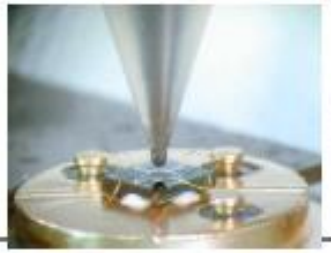
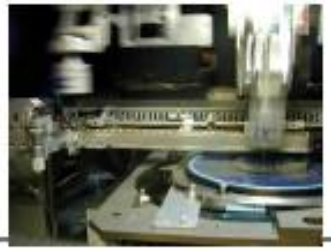
Future applications?

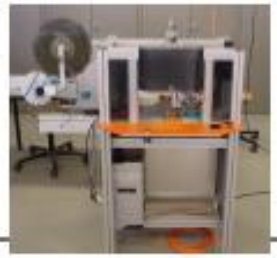
- Fire detection
- Indoor Air Quality
- Smartphone integration



Source: SGX Sensortech, Corcelles, CH

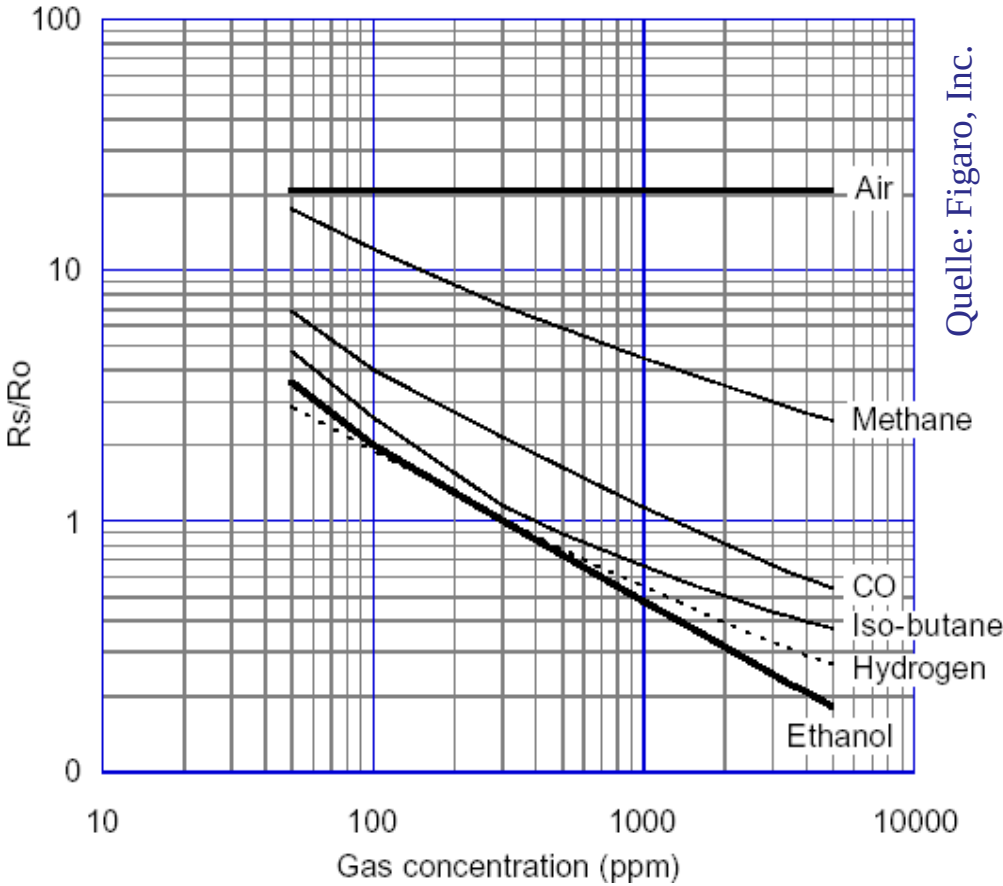




MOS sensors III: (first) assessment

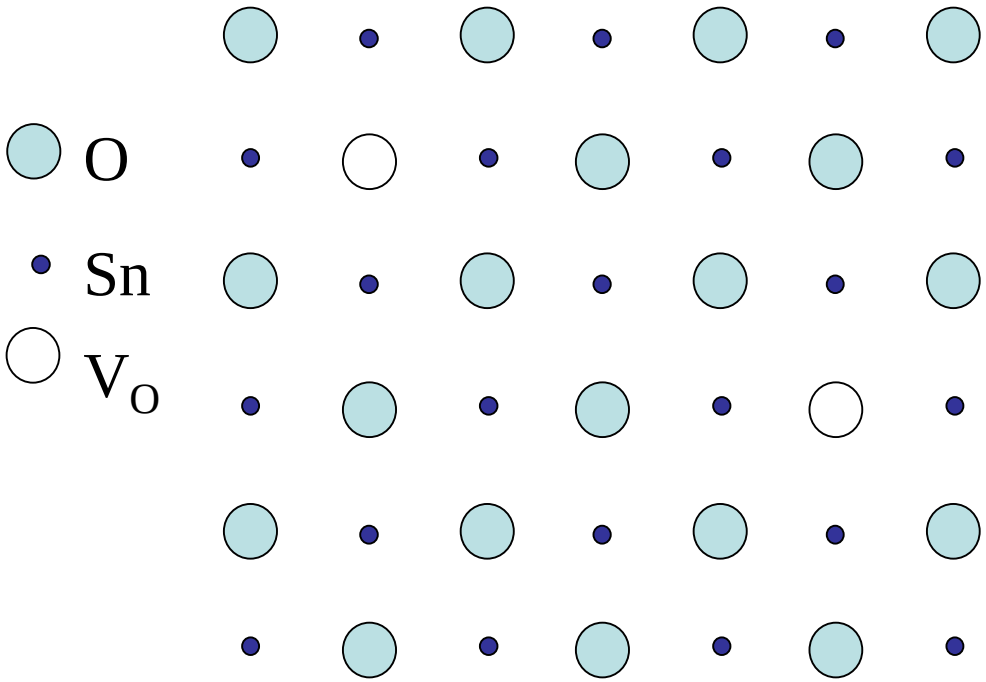
- Advantages
  - robust: proven lifetime of more than 10 years
  - Low cost: sensor elements in small quantities are ~ $ 10,- incl. package; large volume (automotive) ~ $ 1
  - high sensitivity: typically << 1 ppm
- Disadvantages:
  - **Selectivity**: the function principle leads to a broad reaction spectrum to many reducing and oxidizing gases; interferents lead to false results
  - **Stability**: reproducibility in general poor compared to physical sensors



  - **Power consumption**: operating temperatures between 200 and 800°C require comparatively high heater power (typically 1 W for ceramic thick film sensors, several 10 mW for MEMS sensors)

MOS sensors IV: a deeper look

- Original Figaro material and still dominating today: SnO_2
  - n-type semiconductor, primarily used for reducing gases (CO, CH_4,…)
  - Semiconductor behavior is the results of oxygen vacancies V_O



The large electronegativity of oxygen localizes the electrons of the SnO_2 lattice near the oxygen atoms (O^{2-}).

Oxygen vacancies act as donor sites → n-type conduction.

Effect is similar to the doping of Si with atoms from the fifth main group of the table of elements (i.e. N, P).

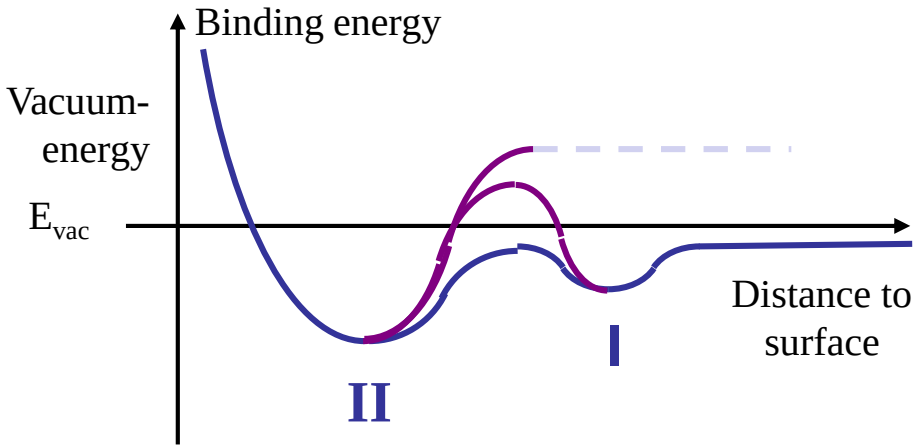
- Many other metal oxides have been studied and some are **commercially used**
  Examples: ZnO, **WO_3**, **In_2O_3**, TiO_2, **Ga_2O_3** (req. very high temp.), Cr_2O_3, Co_3O_4, Fe_2O_3, ...

Interaction between gas and solid

Three relevant phases for approach of an atom/molecule to the surface of a solid:

I Physisorption:

- Weak binding, primarily due to *van der Waals* forces (induced dipoles)
- No charge transfer and therefore basically no electrical sensor reaction
- Atom/molecule can move along surface



II Chemisorption:

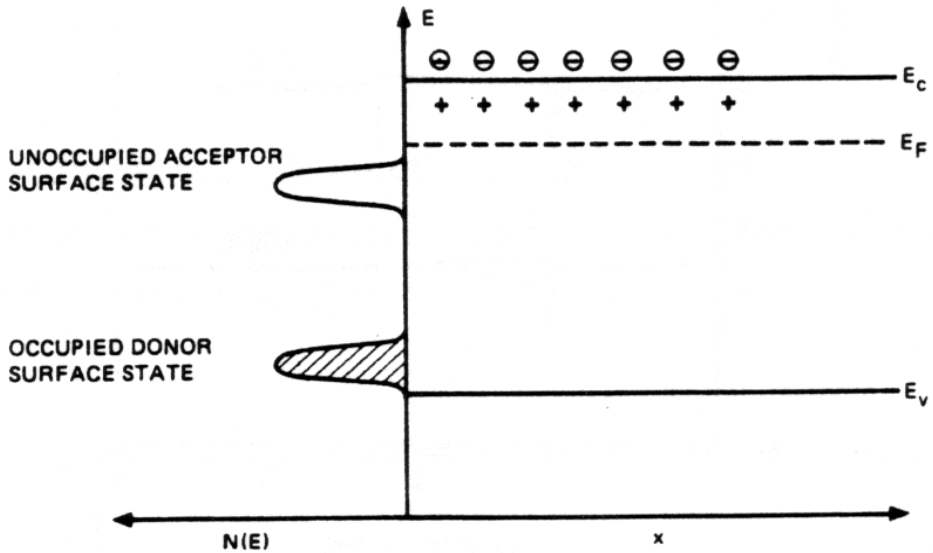
- Stronger adsorption to the surface due to charge transfer (covalent binding)
- Charge transfer induces an electrical sensor reaction
- Molecules remain unchanged
- Example: $O_2 + e^- \rightarrow O_2^-$

III Reaction:

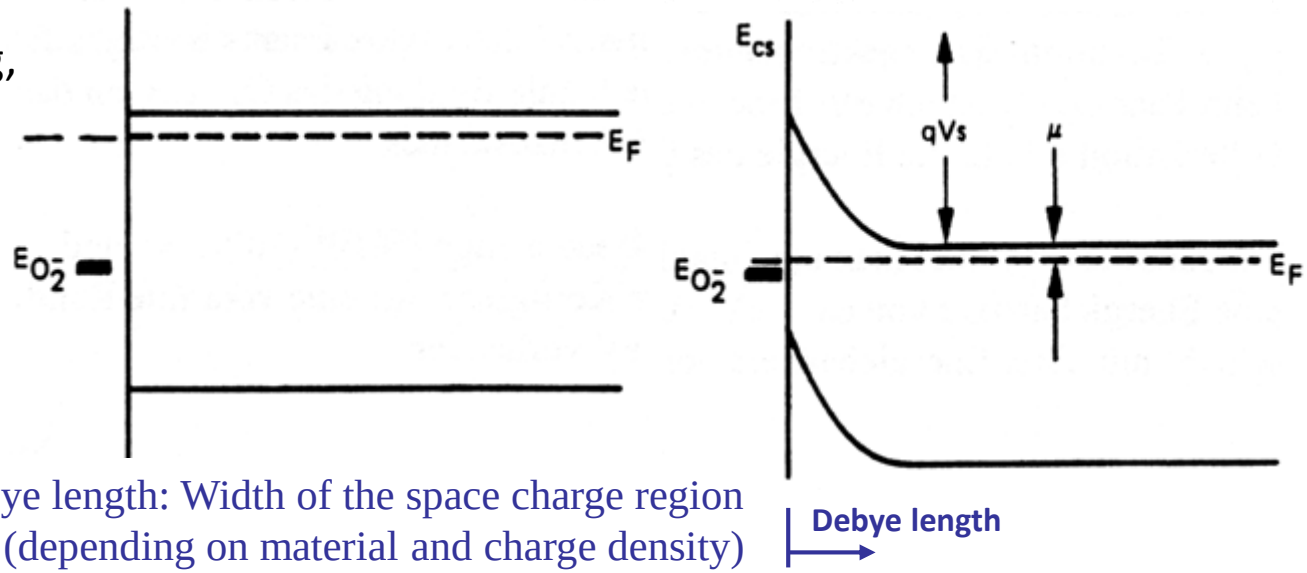
- Atom/molecule reacts with sensor material or adsorbed species, i.e. $CO + O^- \rightarrow CO_2 + e^-$
- Charge carriers are set free, which can again lead to an electrical sensor reaction

MOS sensors V: surface states

Additional electron energy levels exist only at the surface of a solid (hence called surface states); these can be occupied for example by a molecule adsorbing on the surface, transferring charge into the surface state. This changes the number of charge carriers available in the solid.



The charge transfer induces a band bending, lifting the surface state above the fermi level for large coverage. This effectively limits the coverage on the surface, for example O_2^-:
→ "Weisz limit"

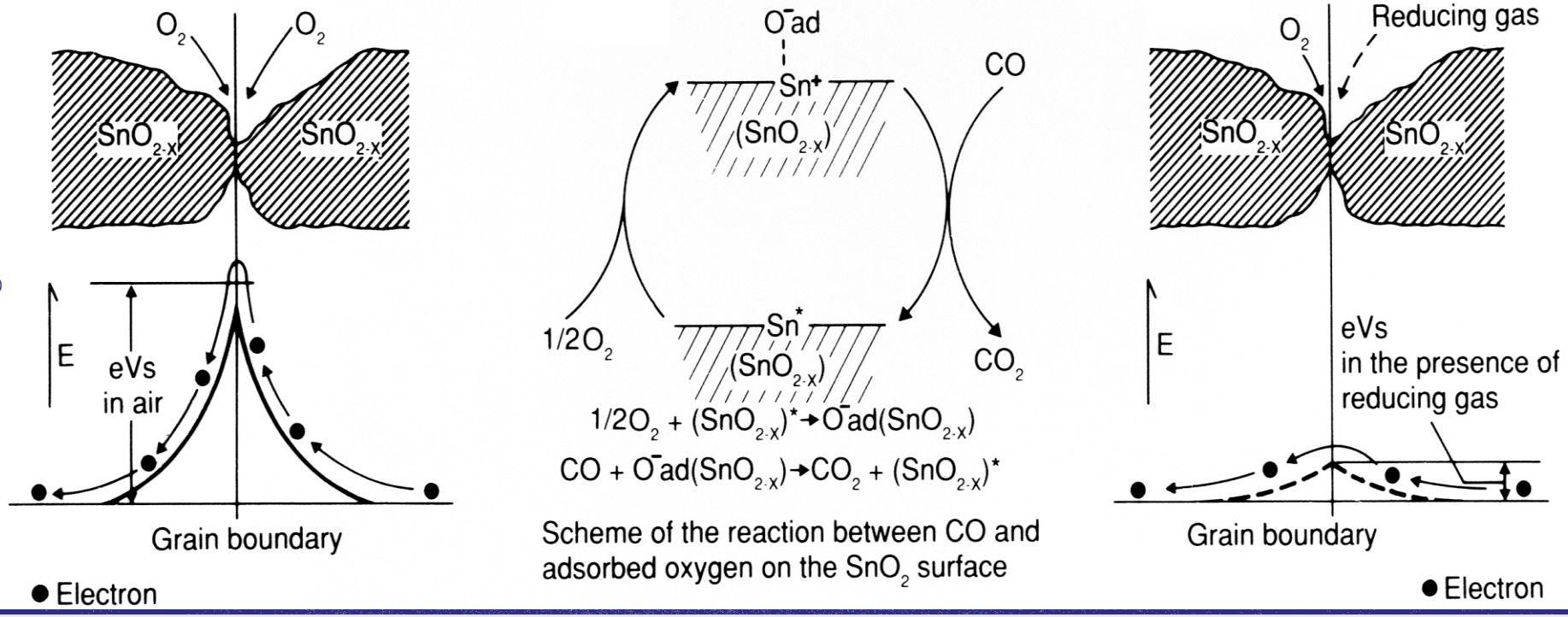


Debye length: Width of the space charge region (depending on material and charge density)

Source: MJ Madou, SR Morrison: Chemical sensing with solid state devices, Academic Press, 1989

MOS sensors VI: grain boundary effect

- Electrical properties of the sensitive layer are changed by adsorption or reaction of gases on the sensor surface.
- The resistance change is primarily induced by the grain boundary effect, not by the number of available charge carriers in the sensitive layer.
- Adsorbed oxygen leads to a double depletion layer forming an energy barrier between grains, which is modified by reducing/oxidizing gases → high sensitivity

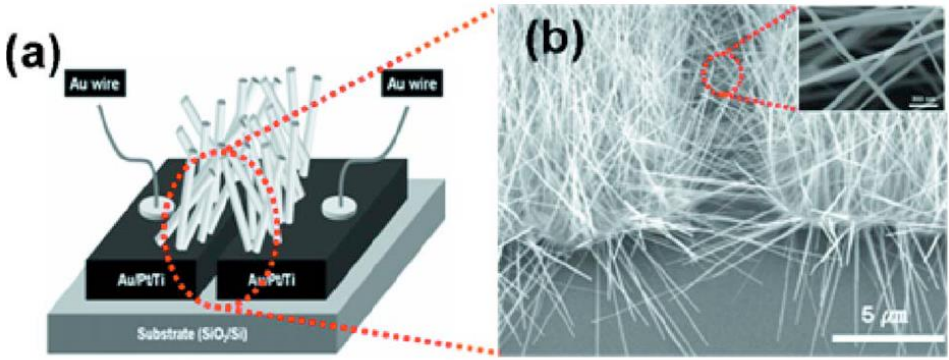


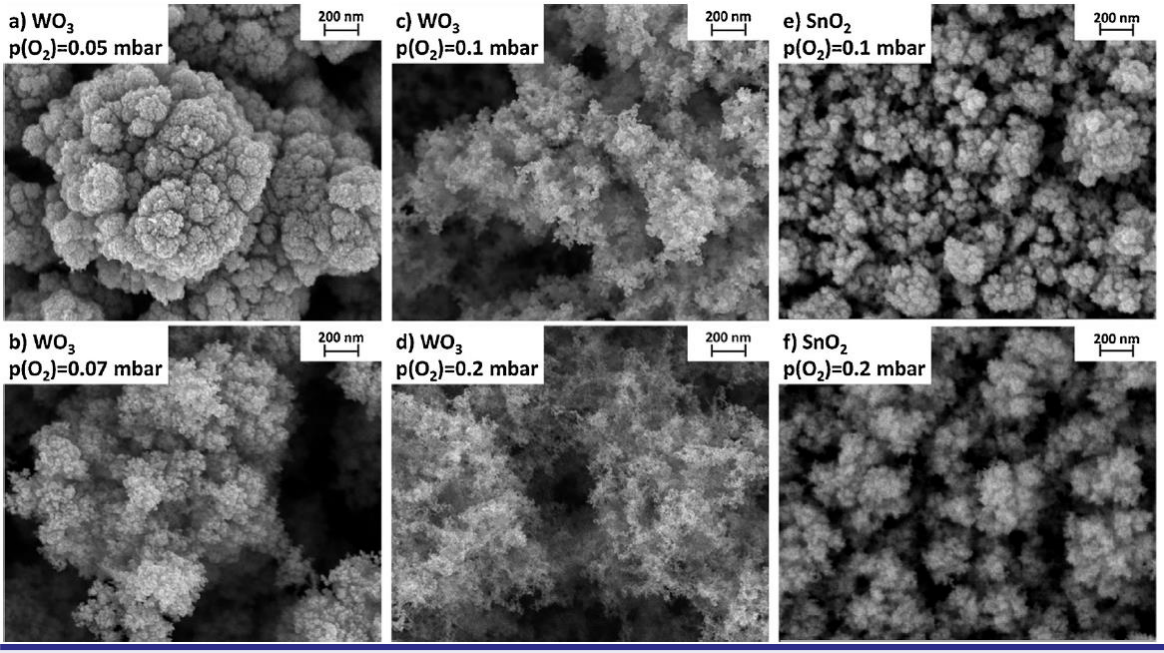
Source: Figaro, Inc.

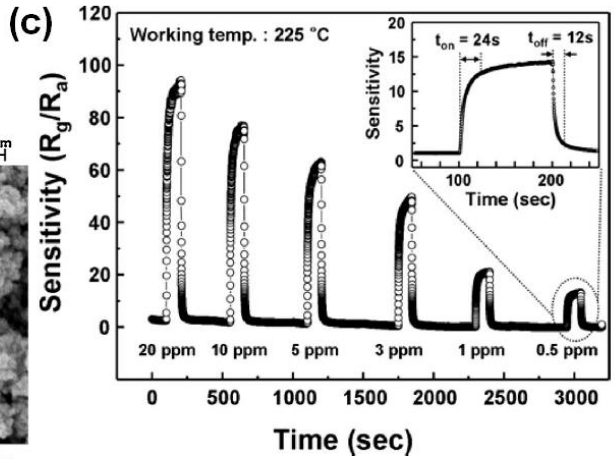
Improving performance by material optimization

Advanced gas sensing layer preparation targets sensitivity, selectivity and stability

- Nanowires, graphene, …
- Pulsed Laser Deposition (PLD)
- …







By Wan et al.: "Semiconducting Oxide Nanowires: Growth, Doping and Device applications", in: Abbass Hashim (ed.) "Nanowires - Implementations and Applications", ISBN 978-953-307-318-7 (2011)

J. Huotari et al.: Pulsed laser deposition of metal oxide nanostructures for highly sensitive gas sensor applications, Sensors & Actuators B 236 (2016) 978–987

MOS sensors: challenge selectivity

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  - Low cost: sensor elements in small quantities are ~ $ 10,- incl. package; large volume (automotive) ~ $ 1
  - high sensitivity: typically << 1 ppm
- Disadvantages:
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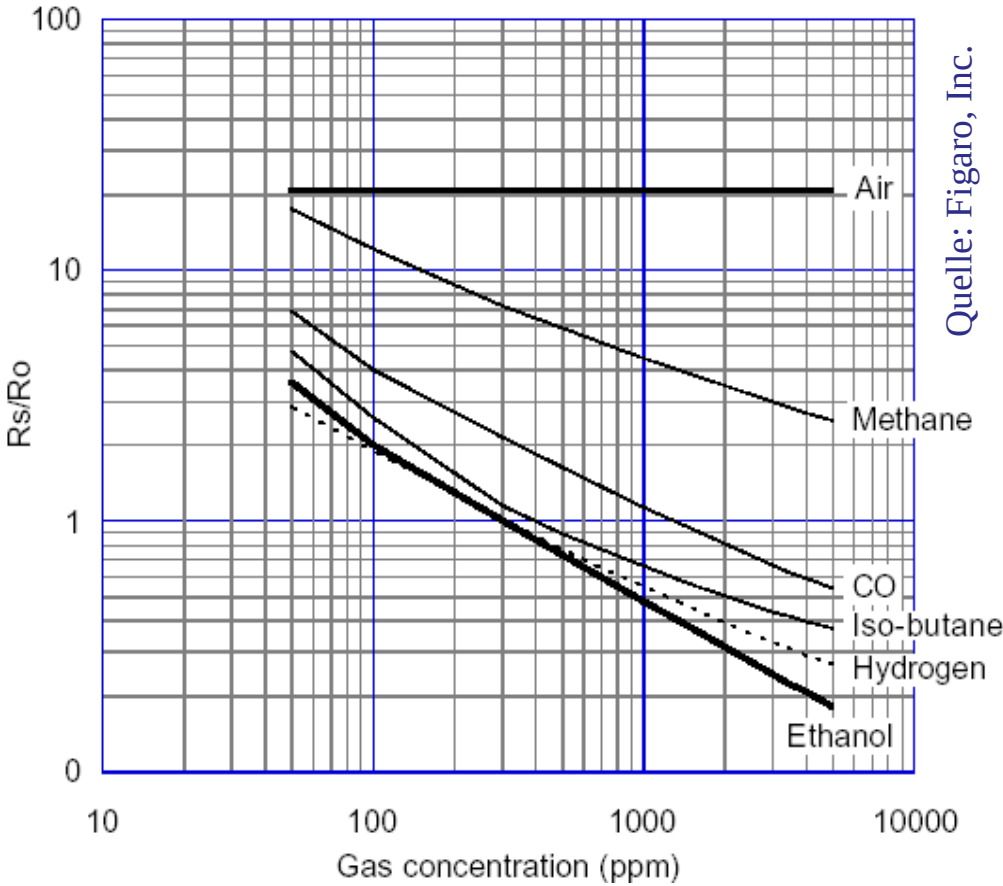


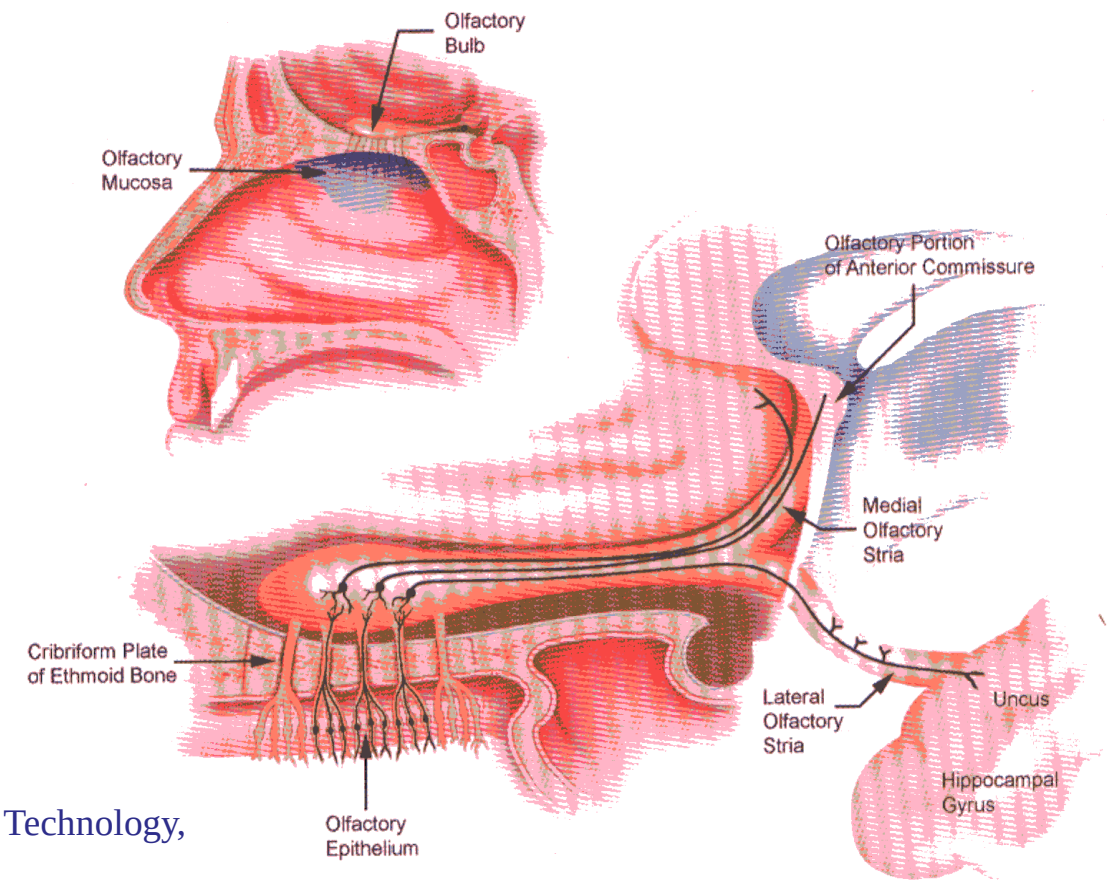
  - **Power consumption**: operating temperatures between 200 and 800°C require comparatively high heater power (typically 1 W for ceramic thick film sensors, several 10 mW for MEMS sensors)

Achieving selectivity with multi-sensor arrays

- Insufficient selectivity of individual chemical sensors is the biggest challenge
- Multi-sensor systems (not only MOS sensors!) offer possible solution
  - Many chemical sensors have a very broad response spectrum, i.e. they react to many different chemical substances with a signal or a change of their signal.
  - But the signal of a (MOS) sensor can be influenced through the variation of
    - sensor material,
    - preparation process (i.e. grain size, layer thickness, sintering, preconditioning),
    - catalytic additives,
    - sensor temperature,
    - electrode structure,
    - sampling and sample preparation.
  - Several different sensors used in parallel ("multi-sensor arrays") thus provide signal patterns that are different for different substances due to variations in the interaction.
  - These patterns can be used for the identification/classification of the substance.
- **Note: this added information can also be used for checking the correct function of the sensor system (self monitoring).**

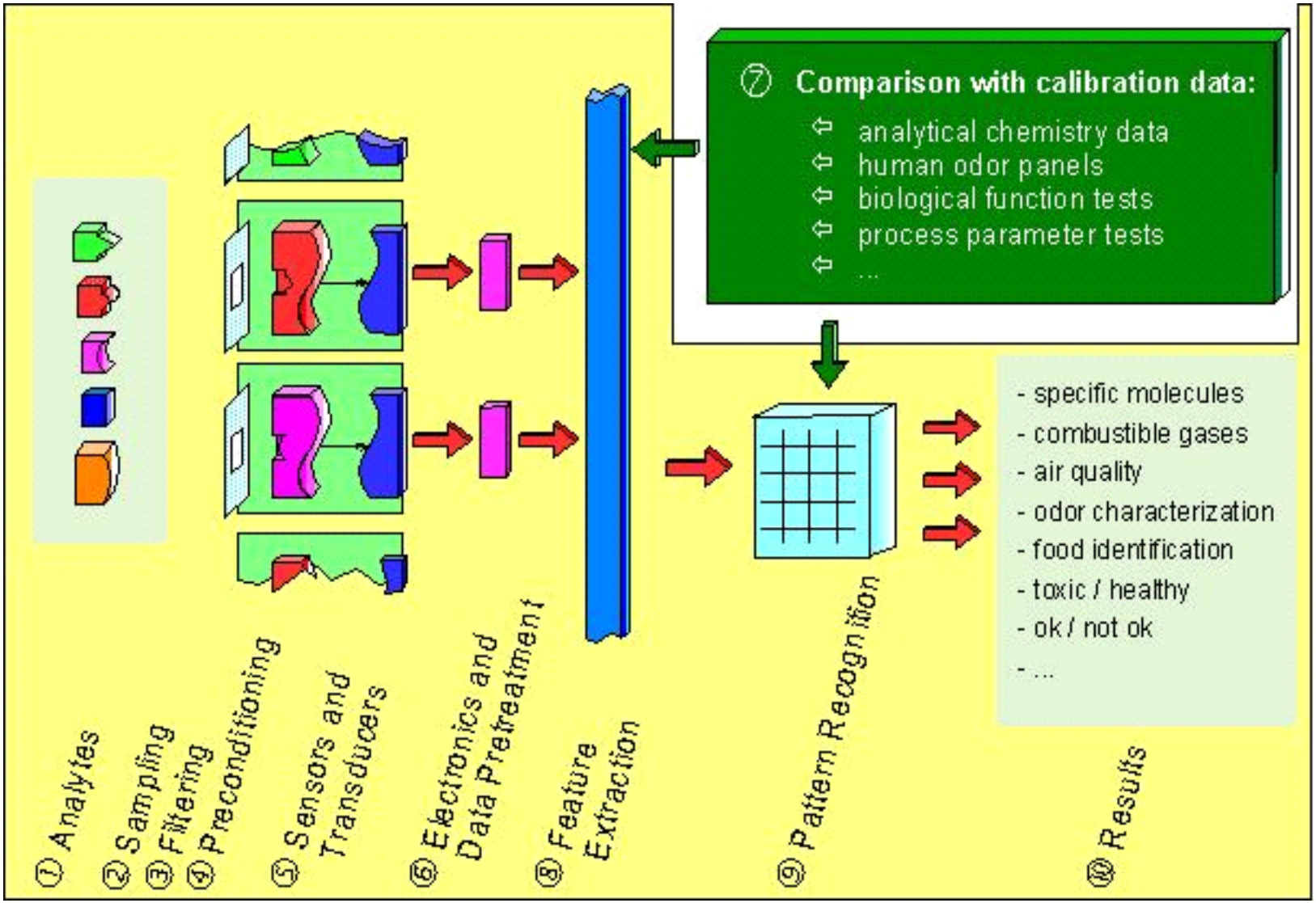
Biology: model for multi-sensor systems

- Nature - as so often - gives the best example:
  - Human nose: approx. 400 different receptors to detect molecules/functional groups
  - However, a skilled perfumer can distinguish up to 10.000 different aromas/smells
- Not every smell has its own specific receptor ("sensor"), instead the information is coded in the signal pattern (= reaction of several sensors).
  - The necessary signal inter-pretation is performed by the olfactory bulb in the brain.
  - The response threshold for different aromas/molecules can be well below 1 ppb (for example for mercaptans).



Handbook of Machine Olfaction – Electronic Nose Technology, Wiley, 2002

“Electronic noses”: the basic concept



Source: www.ipc.uni-tuebingen.de/weimar/research/maintopics

“Electronic nose”: application fields I

- Environmental monitoring, i.e. detection of hazardous or toxic compounds
  - For example fast appraisal of soil contamination during construction work
    A sensor in the excavator dipper decides if this is contaminated or normal soil.
- Medical diagnostics and health monitoring
  - For example disease diagnosis based on breath analysis (for diabetes or cancer)
- Food and beverage quality assurance
  - For example assessing the freshness of fish or mold contamination of cereals
- Process monitoring
  - For example control of fermentation processes in bio reactors
- Automotive and aerospace applications
  - For example assessment of the “new car smell” in vehicles
  - For example monitoring air quality in spacecraft
- Detection of explosives, chemical/biological warfare agents, drugs
- Cosmetics and fragrances

→ Most applications require sensitive detection of VOCs

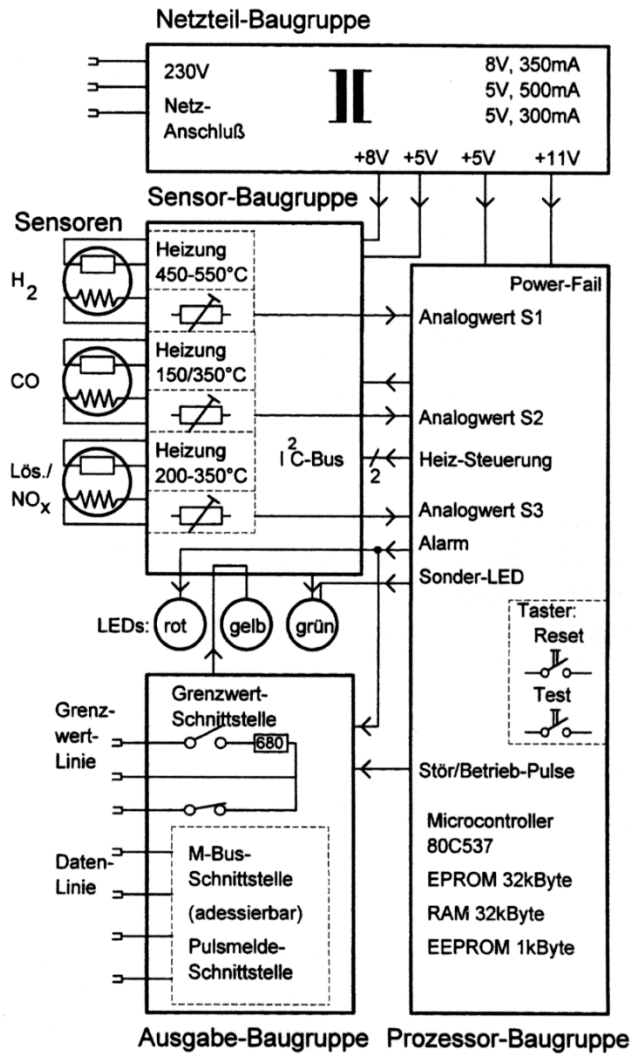
List based on: Handbook of Machine Olfaction – Electronic Nose Technology, table of contents

Drawback of multi-sensor arrays

Stability is a huge challenge for multi-sensor arrays (even a few days!)

- Even a single sensor that is poisoned or drifting changes the response pattern
  → false results of pattern recognition!
- Frequent recalibration required
  → huge effort for practical application

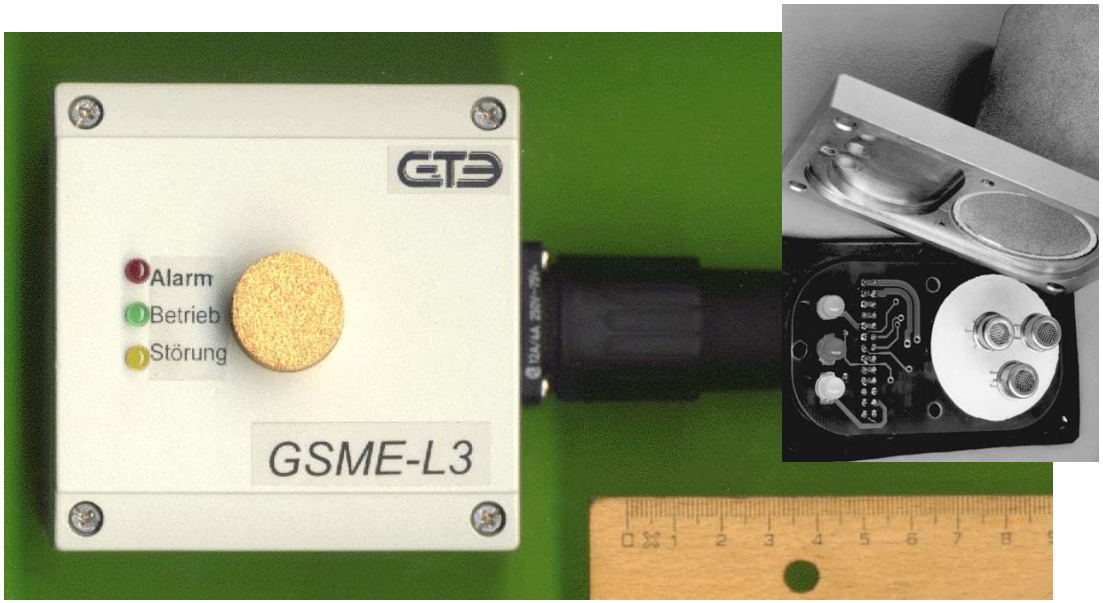
“Electronic nose”: application fields II



J. Kelleter, Ph.D. thesis, JLU-Gießen 1996

Commercial fire detector for coal power plants:

- Based on 3 SnO_2 MOS sensors optimized for detection of H_2, CO, organic solvents/NO_x by dynamic operation
- Stable discrimination between smoldering coal and potential false alarm situations, i.e. vulcanization of transport belts, welding, cleaning etc.
- Approved by the leading association of insurances



GTE mbH, Viersen

Drawback of multi-sensor arrays

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Dynamic operation is a possible approach to improve the "**3S**"

- **Stability** – proven over several months in various applications
- **Sensitivity**
- **Selectivity**

→ **"Virtual multi-sensor"**

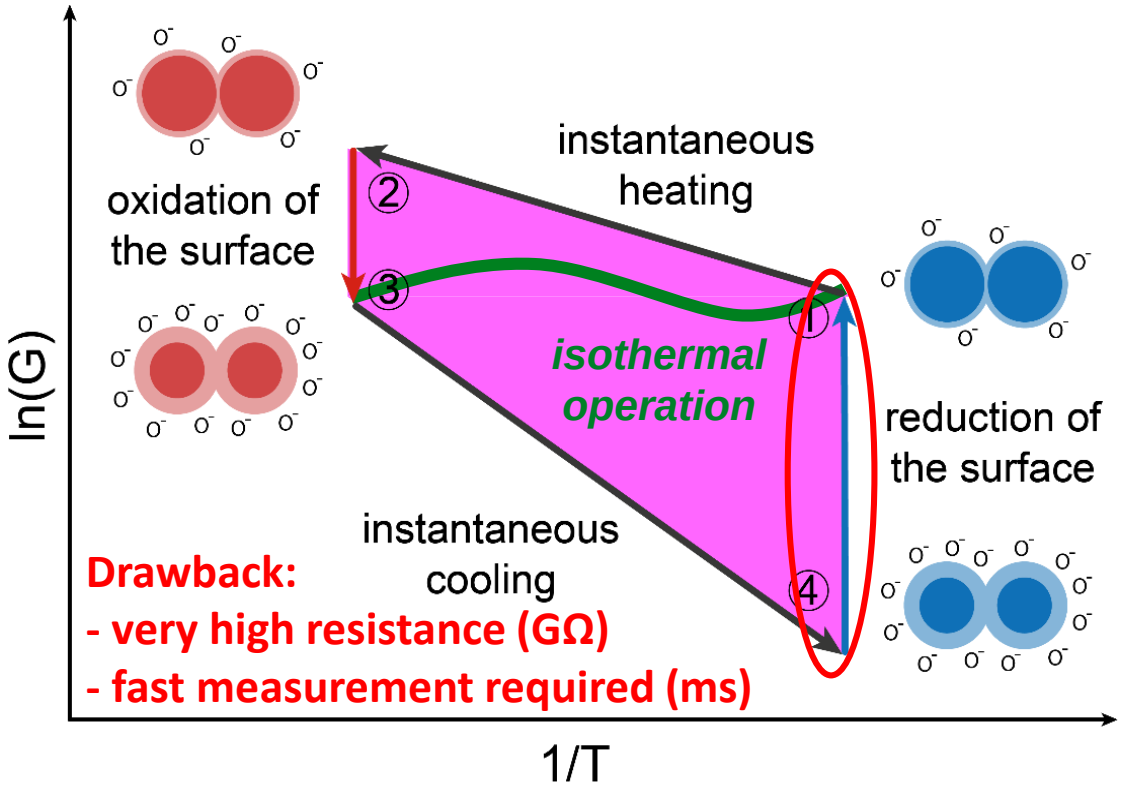
Dynamic operation of MOS and GasFET sensors

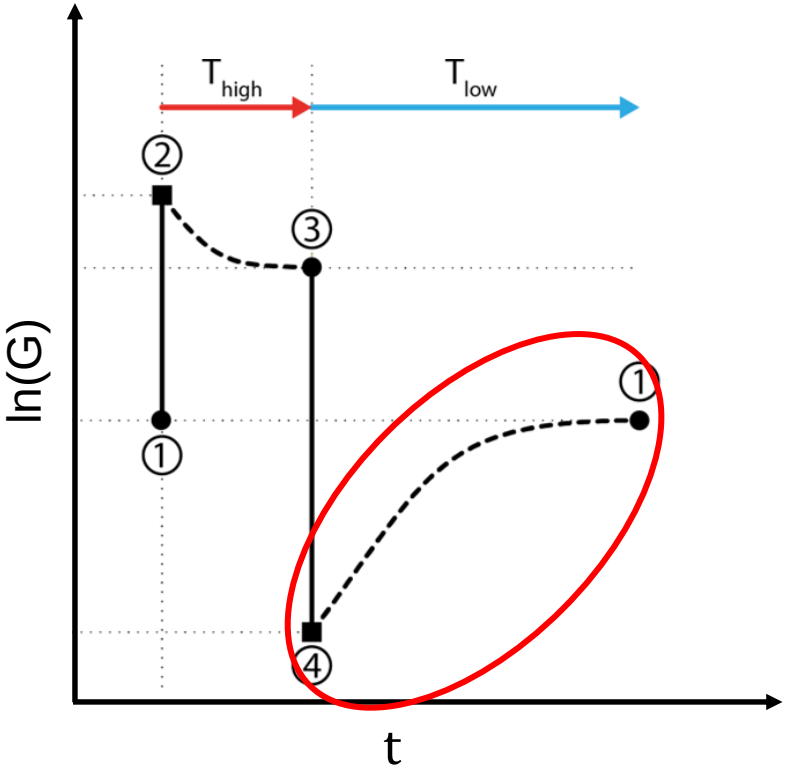
Overview

- Temperature cycled operation (TCO)
- Gate bias cycled operation for GasFET sensors
- Electrical impedance spectroscopy
- Pre-concentration

Boosting the 3S: dynamic operation (TCO)

- Change of sensor temperature causes change of surface charge, energy barrier and conductivity as well as reactivity vs. target and interfering gases
- Interesting behavior after rapid change from high to low temperature
  → highly sensitive vs. reducing gases, i.e. VOC



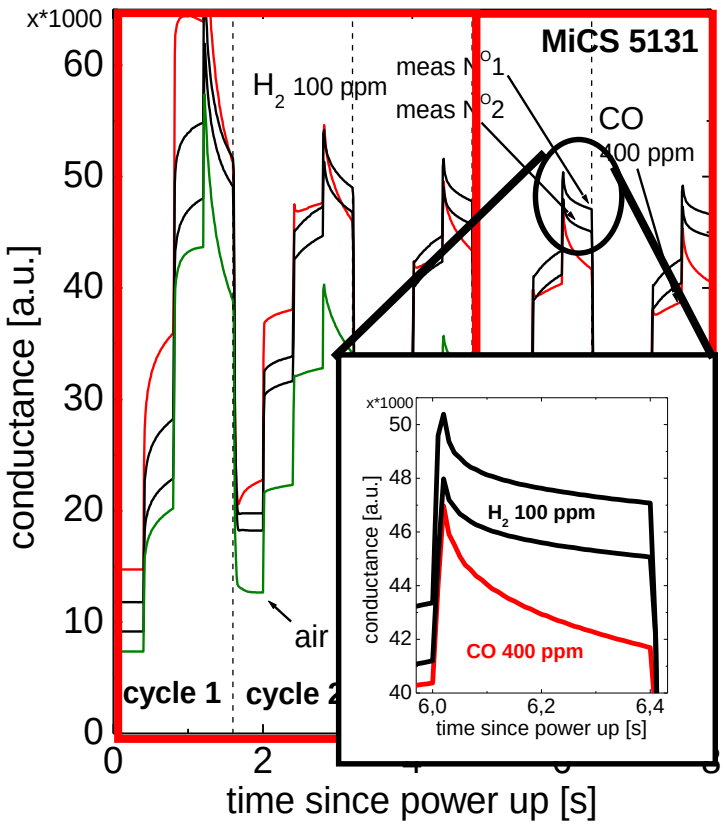


adapted from: A. Schütze et al.: Environments **2017**, *4*, 20; doi:10.3390/environments4010020

Dynamic operation to boost selectivity I

- Fast identification and quantification after sensor power-up

Setup: - 5 T-cycles after sensor power-up
- 4 T steps (20°C - 450°C) / 400 ms per step / 10 ms data acquisition



2 distinct areas in the sensor response:

- First three cycles: sensor stabilization
  → Desorption of adsorbates (@ high temperatures)
- Cycles 4 – 5 after power-up used for evaluation
  → Characteristic curves for air and test gases

Different absolute sensor conductance values for repeated measurement,

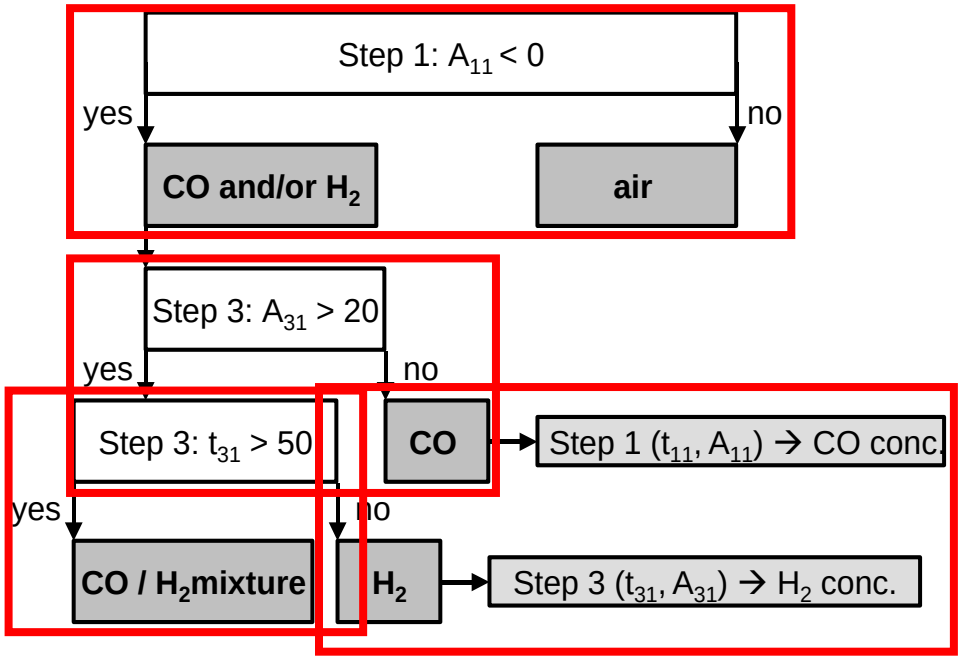
but very similar curve shapes.

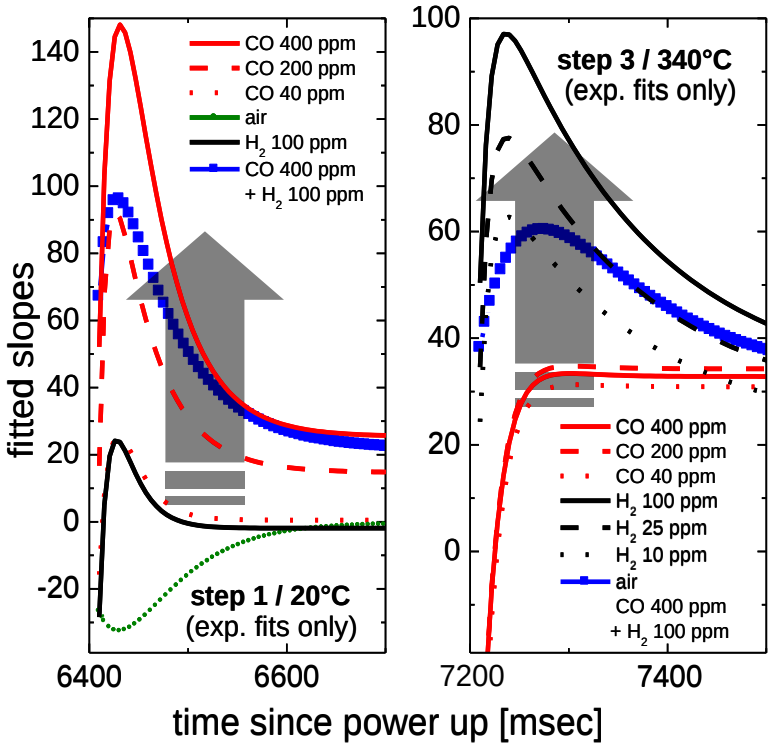
⇒ **Evaluate the slopes of the cond. on each step**

$$Slope(t) = G(t) - G(t - \Delta t)$$

M. Baumbach, T. Kammerer, A. Sossong, A. Schütze: Proceedings IEEE Sensors 2004, Vienna, Austria, Oct. 25-27, 2004.

Dynamic operation to boost selectivity II





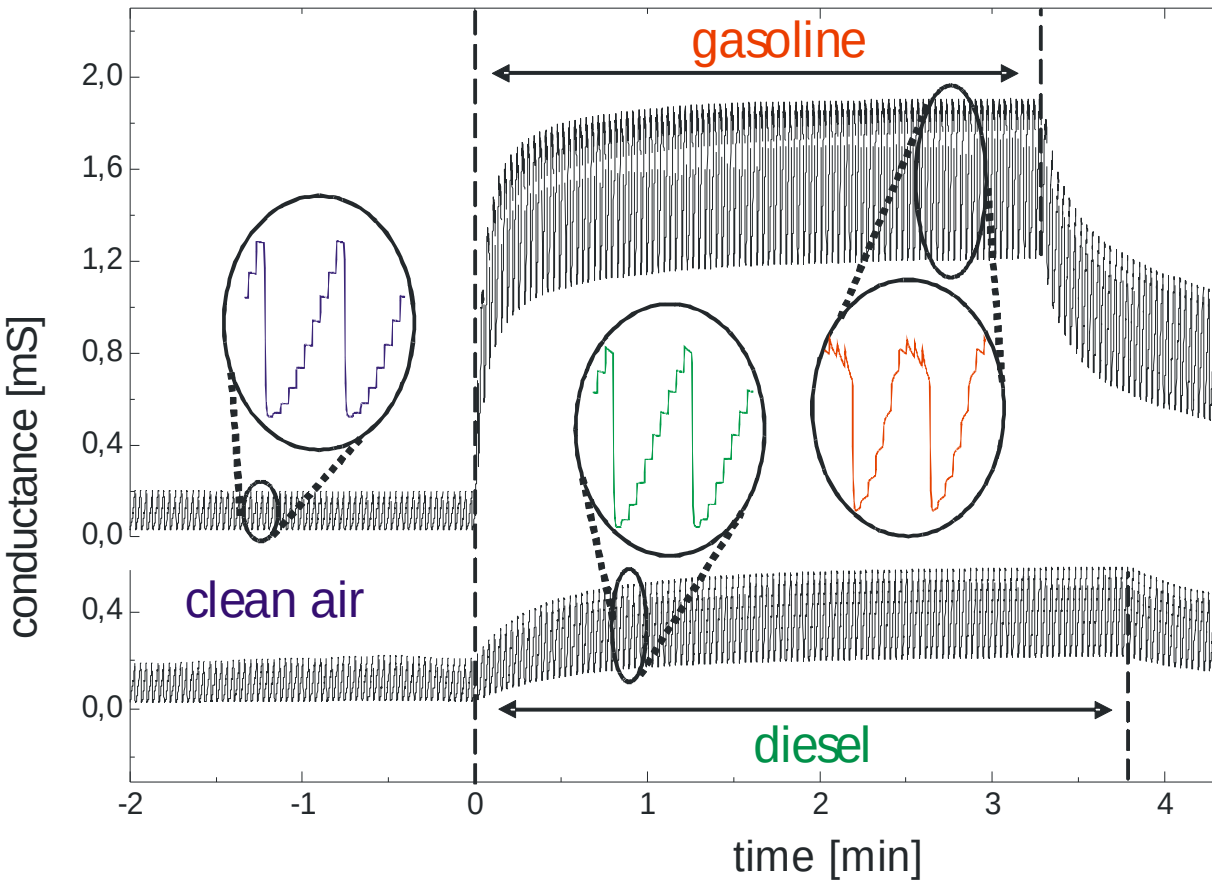
- 1st decision: air vs gas → step 1 / „slow“ sensor reaction (A_{11})
- 2nd decision: CO vs H_2 → step 3 / „slow“ sensor reaction (A_{31})
- Estimate of the gas concentration:
  CO → step 1 / H_2 → step 3 / again slow sensor reaction (A_{11}/ A_{31})
- **Mixtures show CO effect after step 1 and H_2 effect after step 3**

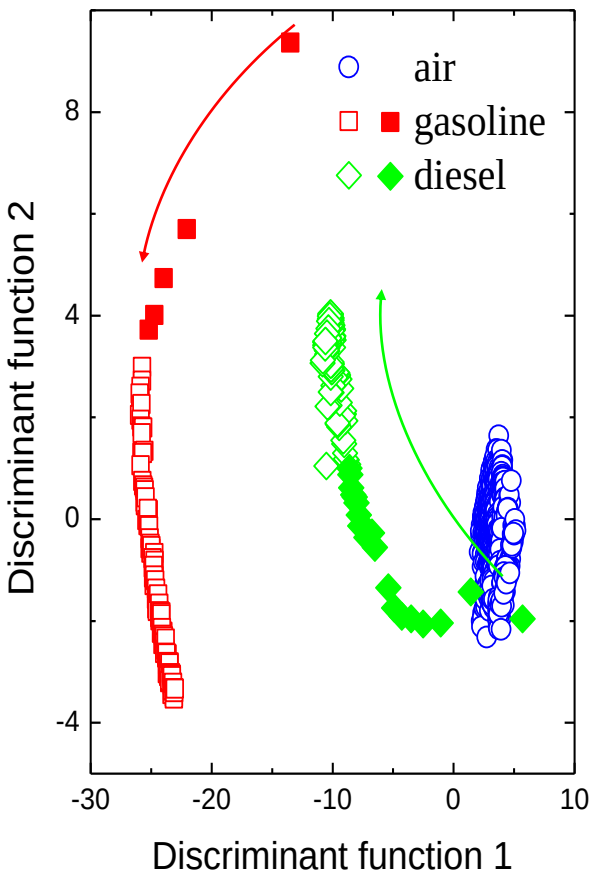
M. Baumbach, T. Kammerer, A. Sossong, A. Schütze
Proceedings IEEE Sensors 2004, Vienna, Austria, Oct. 25-27, 2004.

Potential of virtual multi-sensor approach

Dynamic operation can even improve overall system response time

- Identification of fuel type for gas stations requires very fast classification (less than 5 s)
- Time constant of absolute values ~ 30 s, classification based on T-cycle after 1 cycle (2 s)

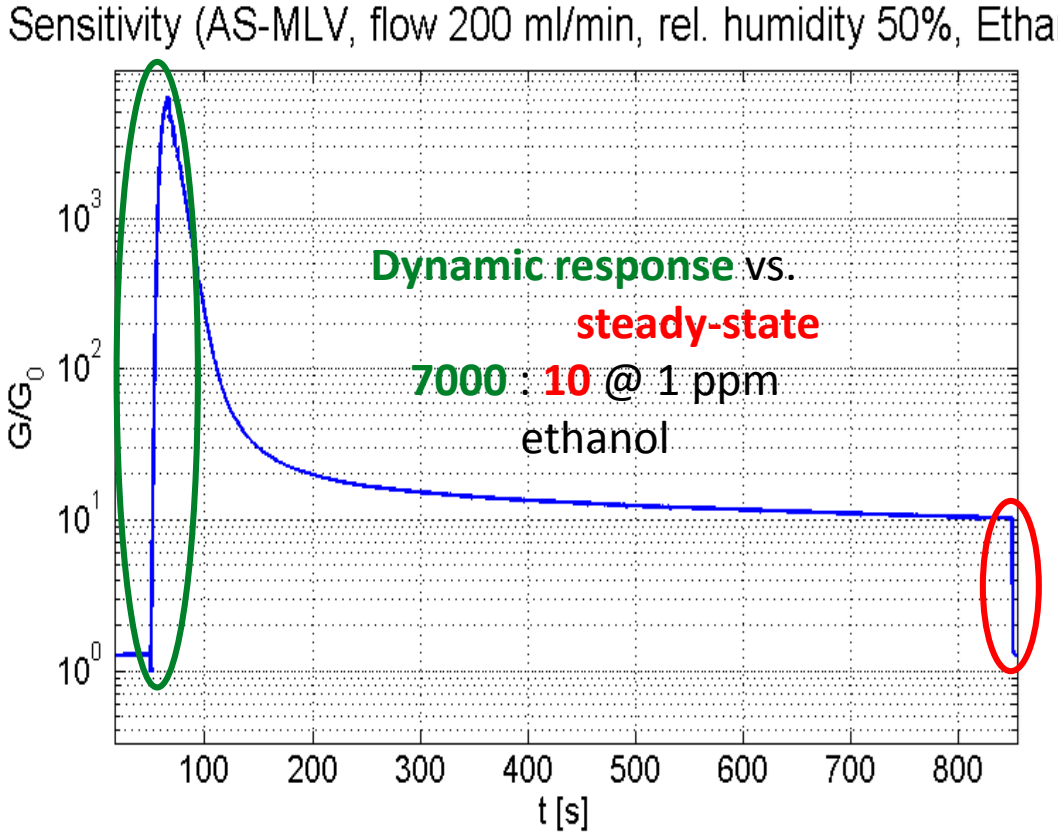


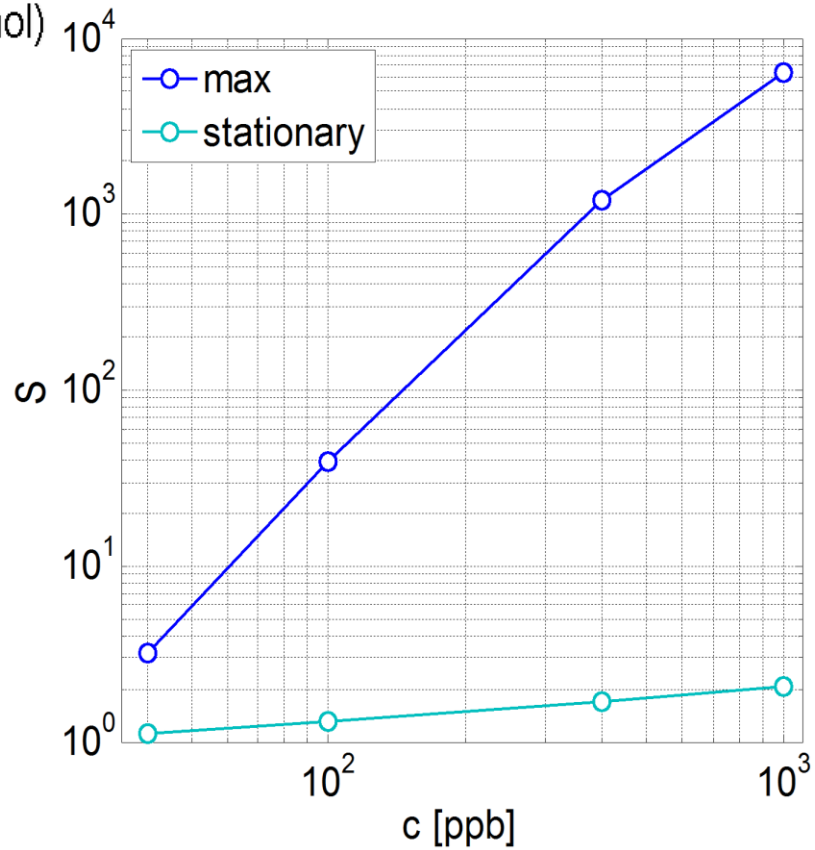


T. Kammerer, M. Engel, A. Schütze, Proceedings IEEE Sensors 2003, Toronto, Canada, Oct. 22-24, 2003.

Dynamic operation also boosts sensitivity

- Temperature step change from 450°C to 150°C
  - → Sensor response in dynamic operation significantly higher than steady-state
  - → Sensitivity boost strongly concentration dependent



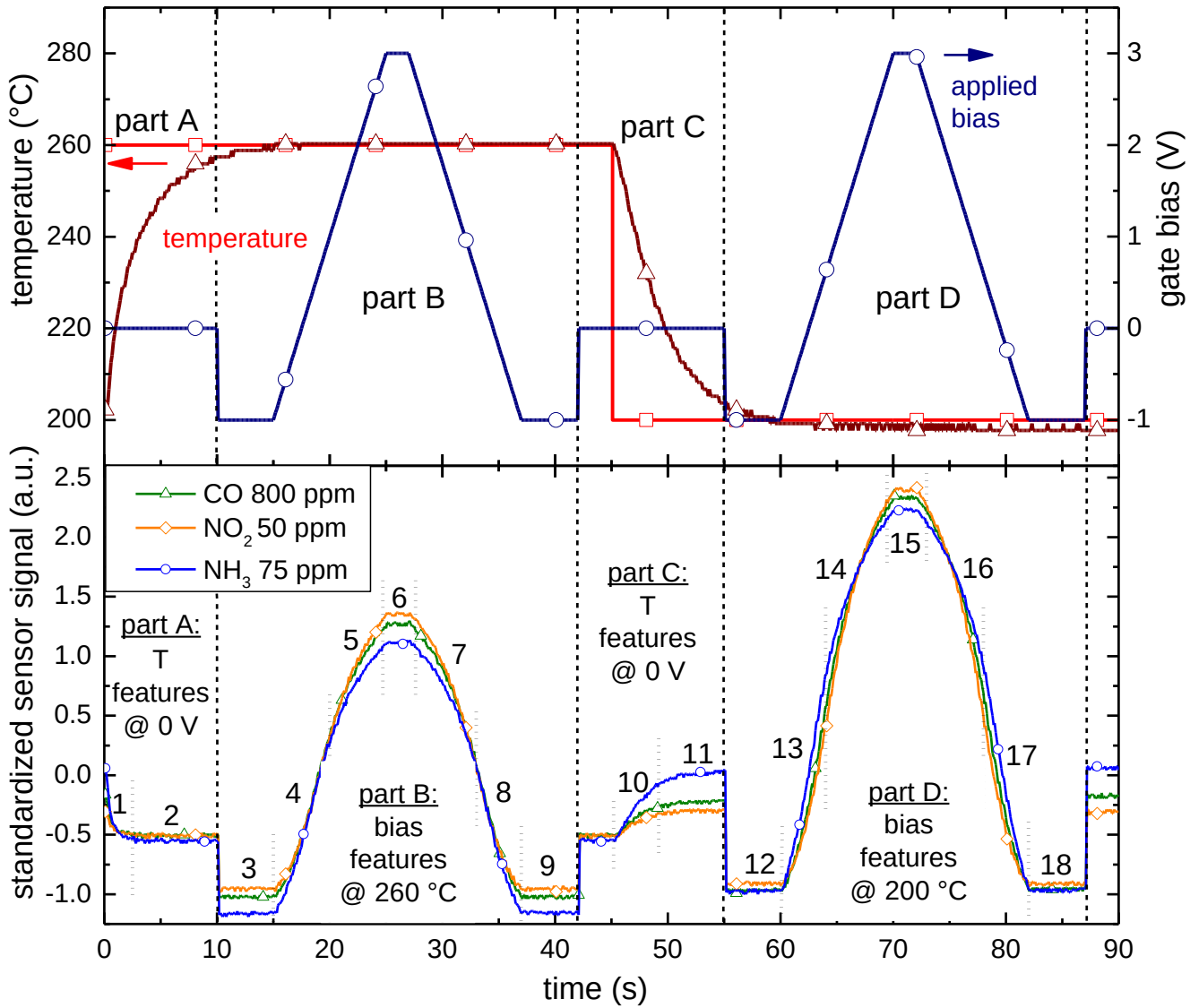


T. Baur: Optimierung des temperaturzyklischen Betriebs von Halbleitergassensoren, tm - Technisches Messen, 82 (4), 187–195 (2015); doi: 10.1515/teme-2014-0007

SiC-FET: combination of TCO and GBCO

Dynamic operation for SiC-FET sensors:

- Temperature Cycled Operation (TCO)
- Gate Bias Cycled Operation (GBCO)
- Combination of TCO and GBCO for optimized selectivity



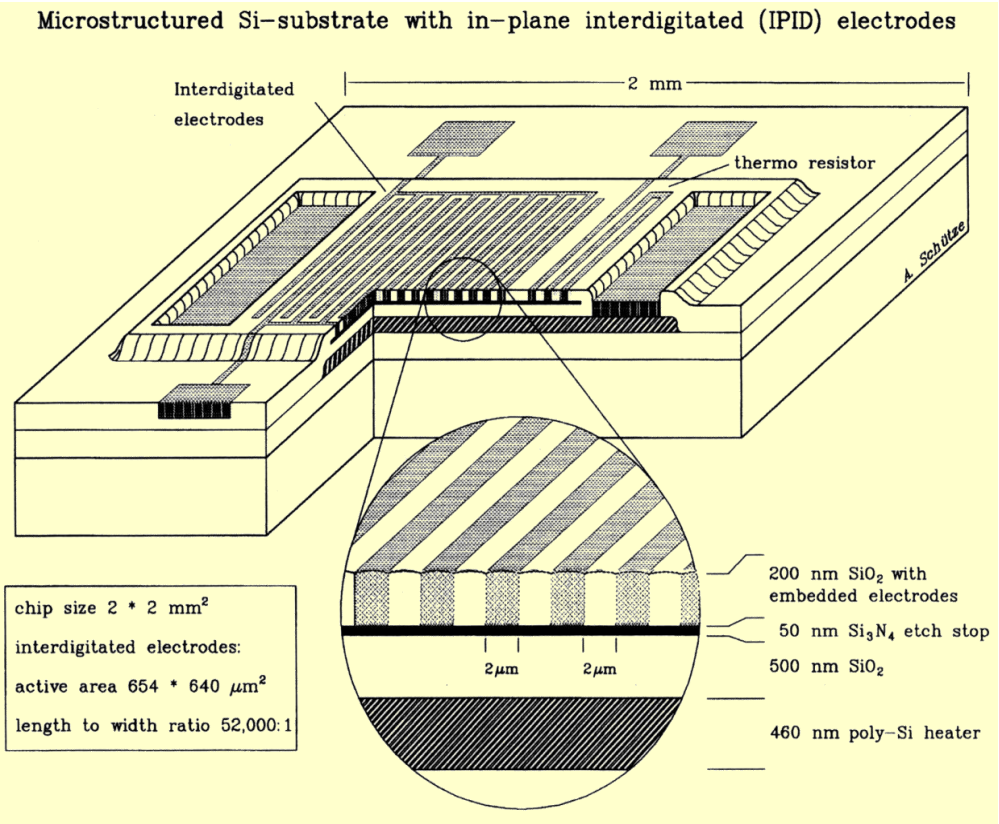
Three terminal depletion type Pt-gate SiC-FET, V_{DS} = const.
Background:
5 % O_2 in dry N_2

C. Bur et al., Sens. Actuators B, vol. 193, pp. 931-940, 2014.

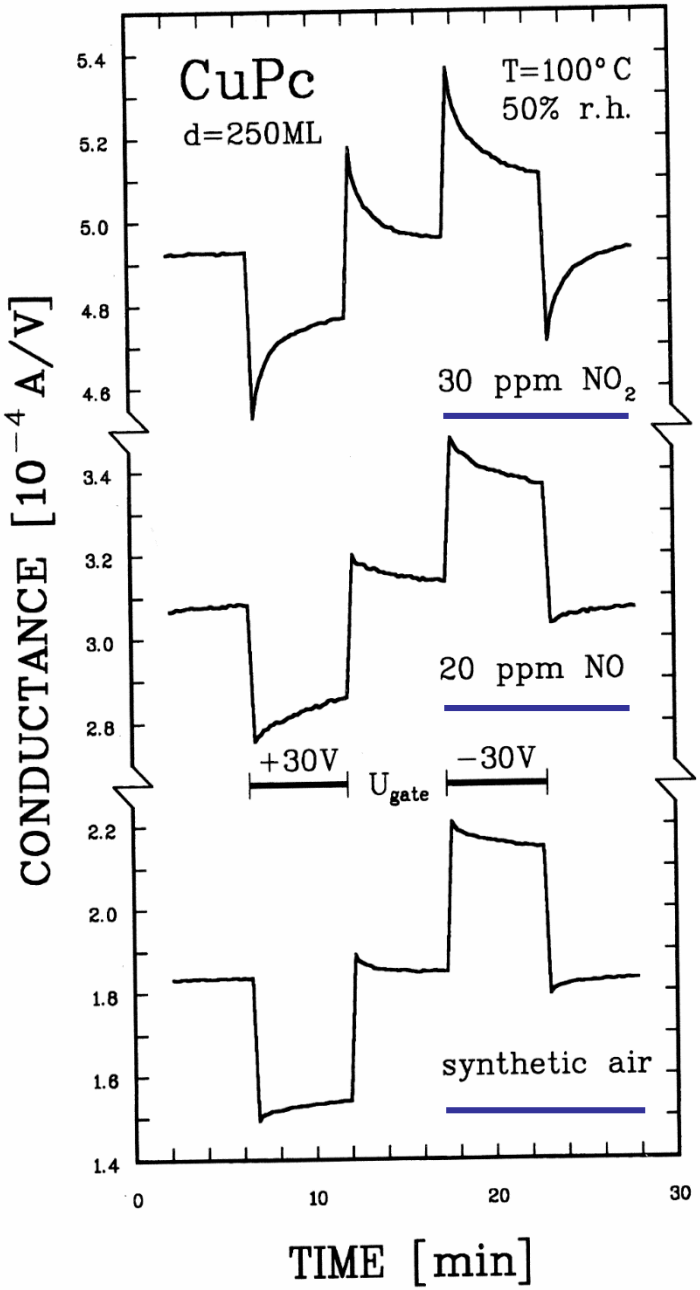
Field effect for dynamic excitation

Excitation of the sensor with a field effect setup influencing the charge carriers in the semiconductor:

Influence of gas type on the field effect measured with a microstruc. Si substrate (heater used as field electrode).



A. Schütze, Dissertation, JLU-Gießen 1994



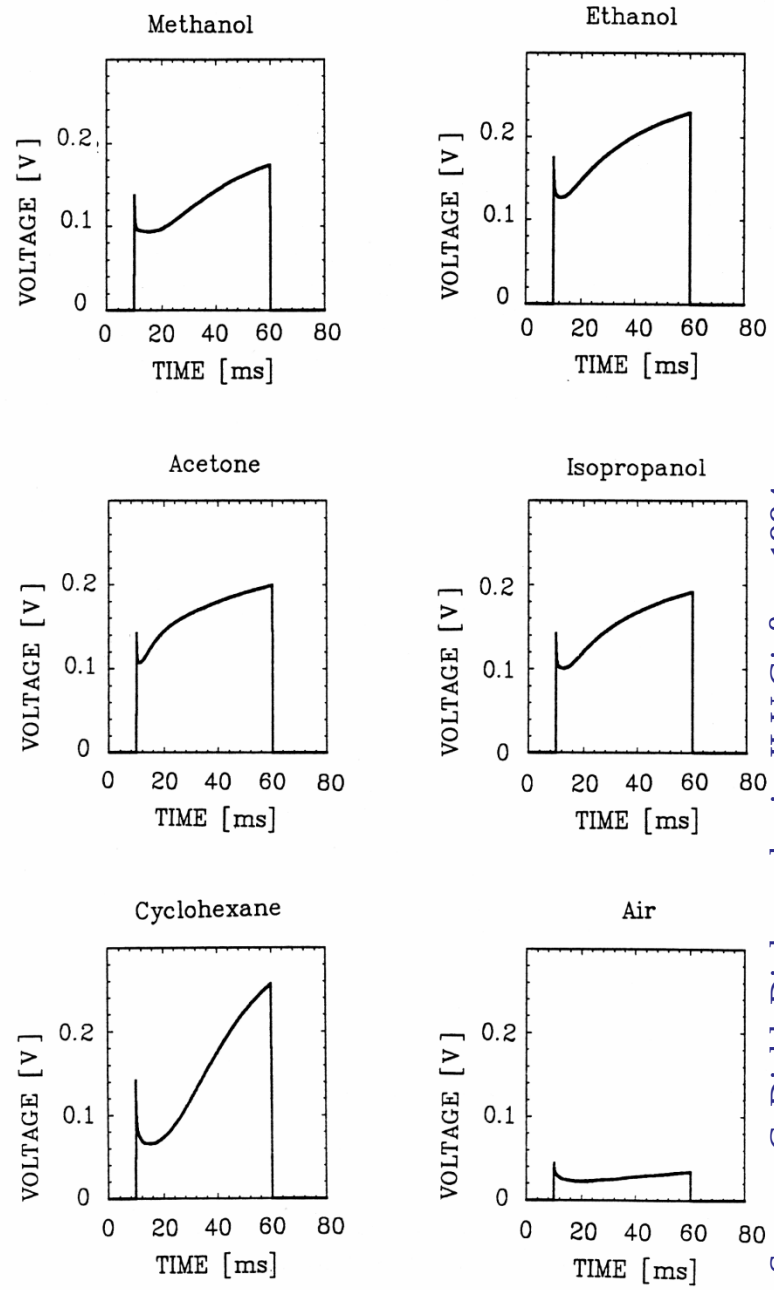
Dynamic excitation with voltage pulse

Excitation of the sensor with a voltage pulse across the electrodes:

Similar to the (pulsed) temperature variation, different signal patterns result for different gases, which are determined by the RC time constants. However, these patterns can be measured much faster than either temperature cycling or impedance measurements, so that this method can also be used for rapidly changing ambient conditions and gas concentrations. Also, evaluation, i.e. for alarm generation, can be much faster.

Using this approach, impedance measurements can be integrated in sensor electronics with less effort on the part of the driving electronics, but very fast data acquisition is necessary.

Signal evaluation is then based on characteristic features of the response patterns.

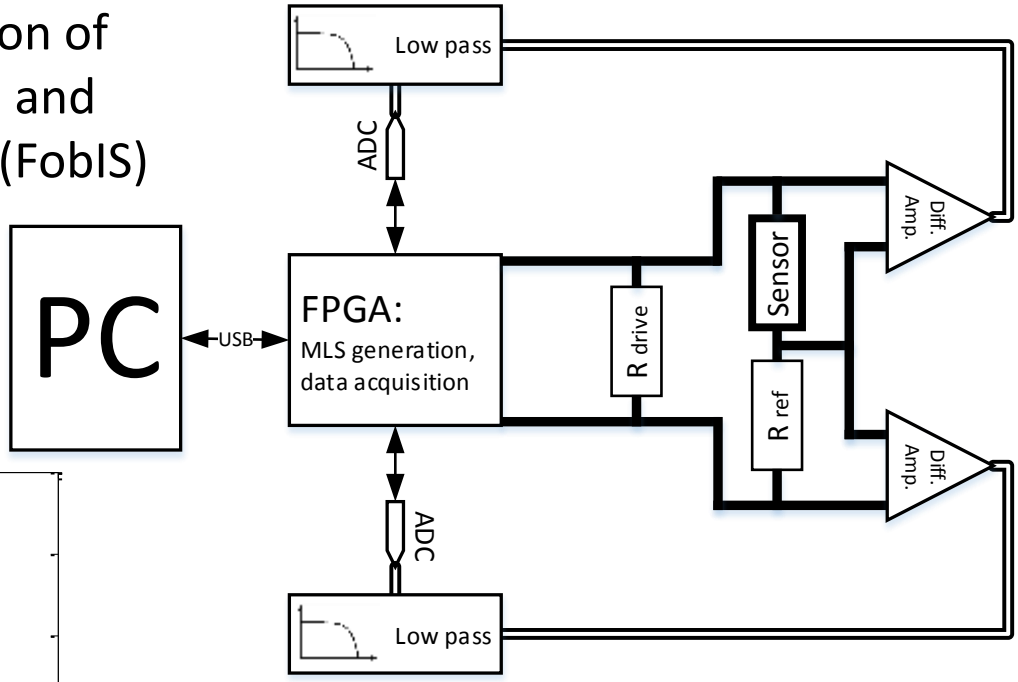


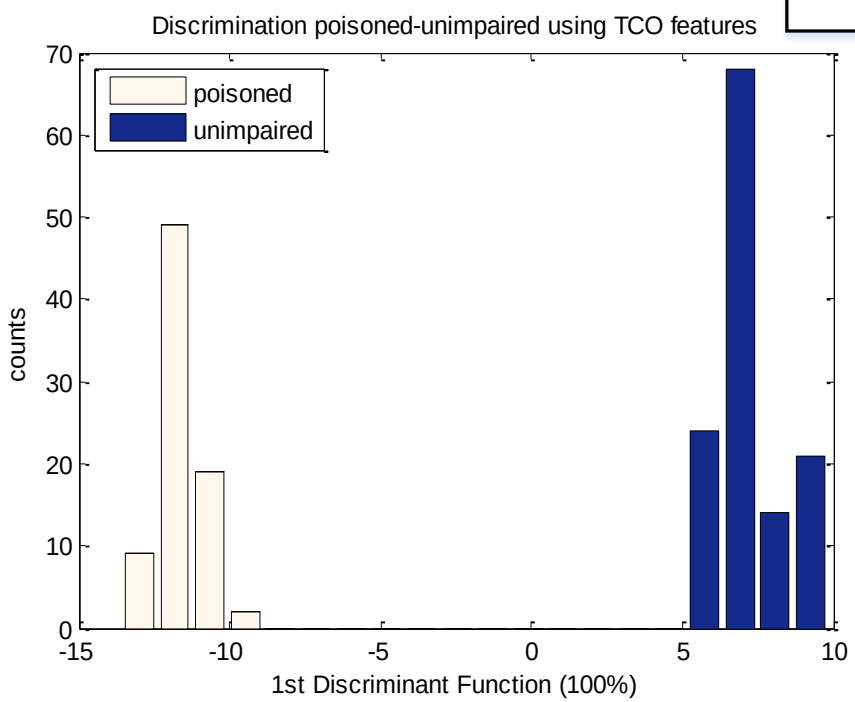
Source: C. Diehl, Diploma thesis, JLU Gießen, 1994

One step further: impedance spectroscopy

Sensor self-test based on combination of temperature cycled operation (TCO) and Fourier-based imped. spectroscopy (FobIS)

- Frequency range 40 kHz – 125 MHz
- Fast acquisition of spectrum 16 µs
- Tested for HMDSO poisoning





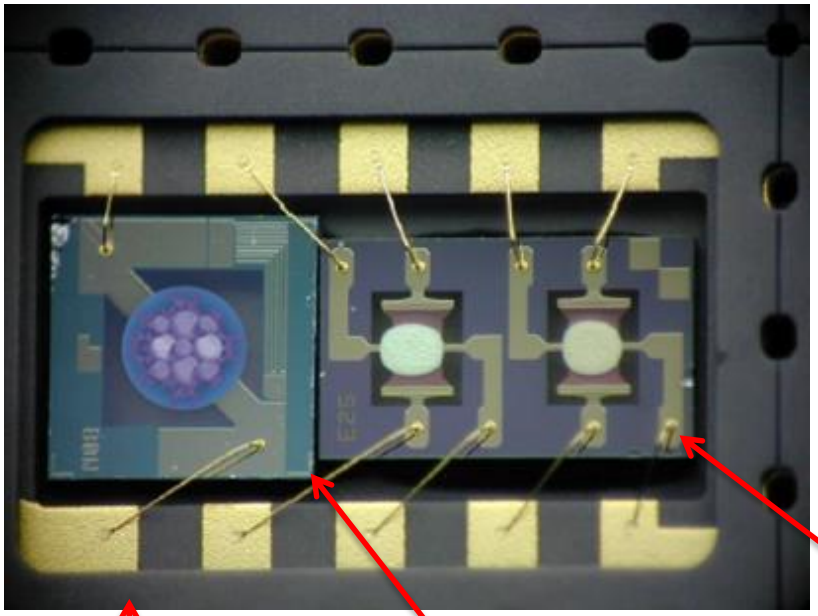
M. Schüler et al.: J. Sens. Sens. Syst., 3 (2014), pp. 213-221; doi: 10.5194/jsss-3-213-2014

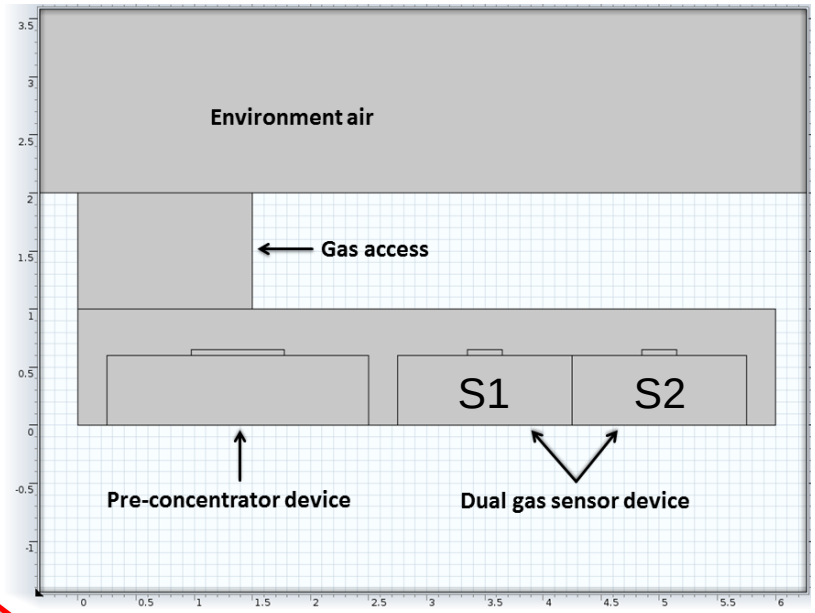
Similar approaches demonstrated for

- Amperometric oxygen sensor (M. Bastuck et al.: Sens. & Act. B 214 (2015) 218–224)
- Pellistors (T. Fricke et al.: Study of Pulsed Operating Mode of a Microstructured Pellistor to Optimize Sensitivity and Poisoning Resistance, Proc. IEEE SENSORS Conference, Nov. 2-5 2014, Valencia, Spain

Boosting sensitivity: pre-concentration

- Pre-concentration is widely used for analytical methods (sampling on Tenax TA)
- Novel low-cost concept based on diffusion (passive transport w/o pump)



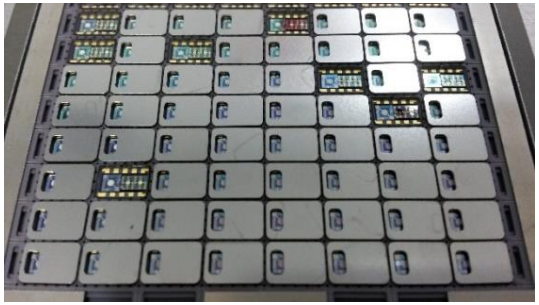


SMD ceramic package
(5 x 7 x 1.5 mm³)

µ preconcentrator chip
(SGX Sensortech)

coated with MOF
material Ø 800 µm

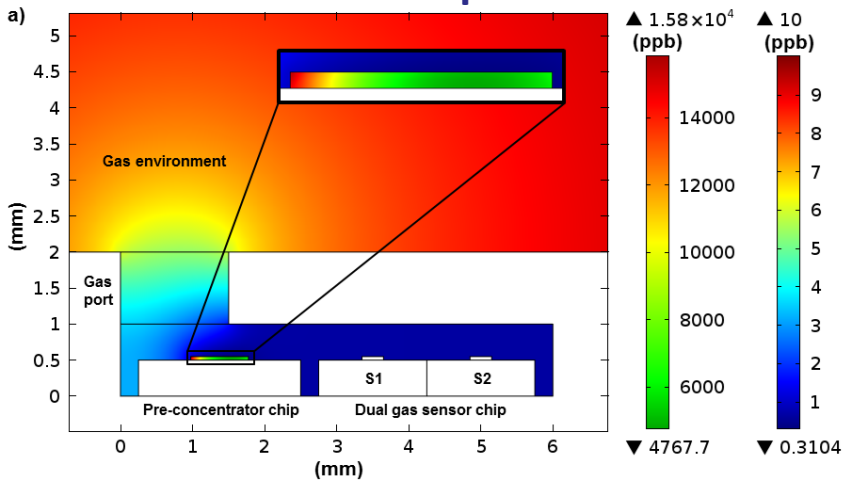
dual gas sensor chip
(SGX Sensortech)



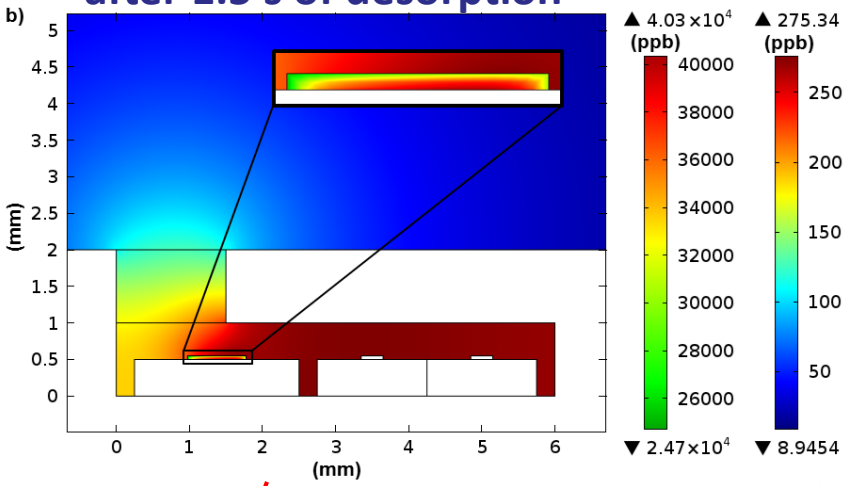
SENSIndoor

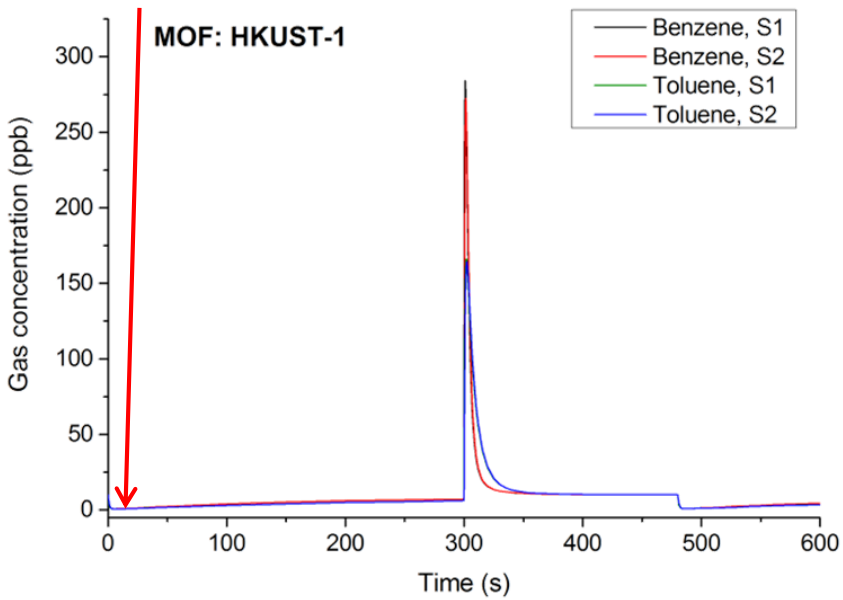
Boosting sensitivity: pre-concentration

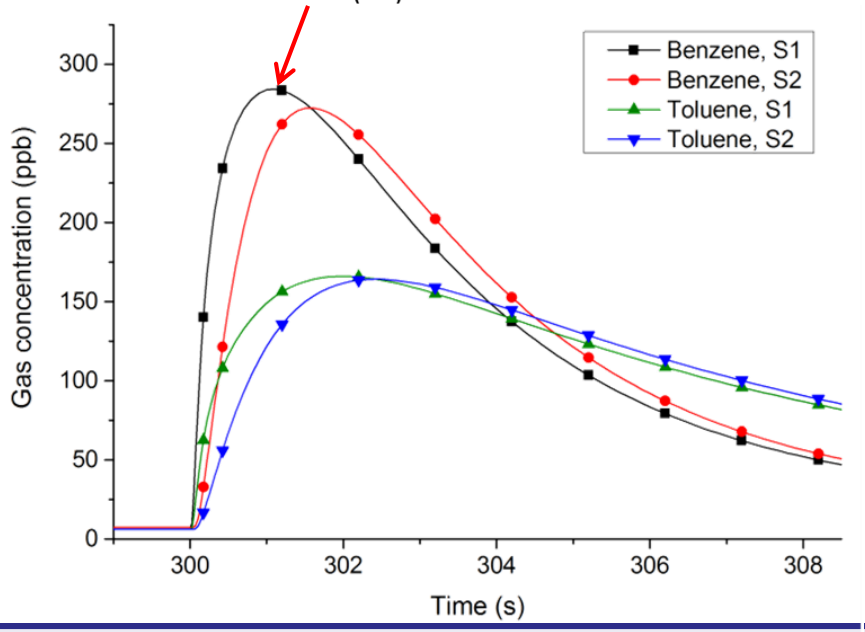
after 6.5 s of adsorption



after 1.5 s of desorption







M. Leidinger et al., Sens. & Act. B 236 (2016) 988–996, http://dx.doi.org/10.1016/j.snb.2016.04.064

Introduction to gas sensors and their dynamic operation

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Saarland University, Lab for Measurement Technology

Outline

- Background
- Gas sensor applications
- Gas sensor function principles
- Dynamic sensor operation

Conclusion: (virtual) multi-sensor arrays provide response patterns & require multiparameter signal evaluation