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Novel Hand-Held Chemical Detector with Micro Gas Sensors (THREATGÅRDEN)

- New tool for effective protection of citizens against toxic chemicals
- Detection and identification of chemical warfare agents (CWA) and toxic industrial chemicals (TIC)
- Technology know-how and implementation has been raised to world-class leading edge level



Editor: Mikko Utriainen, Helsinki University of Technology

Participants

Finland

Environics Oy
Mikko Utriainen
R&D Manager

*Helsinki University of Technology
(HUT)*

*Micro and Nanosciences Laboratory
(MNS) at HUT*

Microfabrication Group (MFG) of MNS
Antti J. Niskanen
Research scientist

Electron Physics Group (EPG) of MNS
Aapo Varpula
Research scientist

Sergey Novikov
Senior research scientist

Pekka Kuivalainen
Professor

Juha Sinkkonen
Professor

*Micro and Nanofabrication Centre
(MINFAB) at HUT*
Veli-Matti Airaksinen
Director

Norway

Kitron Microelectronics AS
Arne Kuraas
Sales Manager

Lene Dahl
R&D Engineer

Sweden

AppliedSensor Sweden AB
Miodrag Kosovic
Sales Manager

Martin Einehag
Project Manager

Daniel Johansson
R&D engineer

*FOI, Swedish Defence Research
Agency*
Division of NBC Defence
Sune Nyholm
Research Officer

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Author(s): Mikko Utriainen (Editor), Aapo Varpula, Antti J. Niskanen, Juha Sinkkonen, Sergey Novikov, Veli-Matti Airaksinen, Martin Einehag, Daniel Johansson and Sune Nyholm		
Institution(s): Environics Oy, Helsinki University of Technology, AppliedSensor Sweden AB and Swedish Defence Research Agency		
Abstract: Within the framework of the joint Nordic project "Novel Hand-Held Chemical Detector with Micro Gas Sensors ", a technology feasibility study of implementation of novel micro gas sensors to the existing hand-held chemical detector concept has been carried out. A scope of the application area of the chemical detector was the detection and identification of highly toxic chemical substances, such chemical warfare agents (CWA) and toxic industrial chemicals (TIC). The study was predominantly focused to the state-of-art silicon fabrication technology-based solid-state semiconductor gas sensors, more precisely micro hot plate –based metal oxide semiconductor (MOS) and field effect (FE) gas sensors. The study involved all aspects from the fabrication and packaging of sensors to the wide range of functional testing as well as physical modeling. Furthermore, a novel chemical detector prototype based on the new micro gas sensors and ion mobility spectrometry combination was constructed and tested. The main outcome of the project is better understanding of the micro gas sensors' functionality in the CWA-TIC detection and identification applications. The sensitivity and selectivity of the new micro gas sensors to highly toxic agents was studied comprehensively for the first time. For example, the sensors showed promising sensitivity and selectivity to VX nerve gas and mustard gases. It was also shown promising sensitivity and selectivity to highly toxic TIC classified agents such as phosgene, cyanides and arsine. When these new sensors are implemented to the CWA-TIC detector concept, the advantages such as wider detection capability and improved identification shall be expected. That should give a new tool for authorities to protect more efficiently citizens against toxic chemicals, either released in accidents or in terrorist attacks.		
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Distributed by: Nordic Innovation Centre Stensberggata 25 NO-0170 Oslo Norway		Contact person: Mikko Utriainen R'n'D manager Environics Oy PO Box 349, 50101 Mikkeli, Finland tel. +358 201 430 430 direct. +358 40 8361471 email: mikko.utriainen@environics.fi

Executive Summary

The project was one of eight projects in the “Everyday Nano” project portfolio of the Nordic MINT initiative. The aim of the initiative is to help commercialise existing micro- and nanotechnology research relating to lifestyle, well-being and healthcare, and safety.

The project was based on the existing technologies being developed by Environics Oy and the other partners of the project group, in particular within the CBNS technology programme coordinated by Environics Oy for the Finnish Ministry of Defence.

Objectives

The objective of the project was to form a network to develop and commercialise existing research and development. The idea was to combine an array of specially designed and novel metal oxide semiconductor micro gas sensors and field effect gas sensors with the ion mobility spectrometer in a hand-held chemical detector. With the implementation of new sensors the aims were to improve toxic agent detection and identification performance of the chemical detector.

Methods and implementation

The project organization and tasks are presented in Fig.1. The coordinator of the work was Environics Oy (Finland). The partners carried out specific tasks as follows: Environics was developing chemical detector prototypes and involved practically to all parts of work, AppliedSensor Sweden AB and Kitron Microelectronics AS (Norway) provided sensors, sensor packaging and sensor module design solutions, Swedish Defence Research Agency (FOI) provided end-user expertise as well as comprehensive highly toxic chemical agent testing expertise for the developed detector prototypes. Helsinki University of Technology carried out academic research for all aspects of micro gas sensors including sensor fabrication, functional studies and modeling.

Results and conclusions

The main result of the project is better understanding of the micro gas sensors’ functionality in the chemical detector applications. Especially the technology know-how and implementation of the micro hot plate –based metal oxide semiconductor (MOS) gas sensors and field effect (FE) –type gas sensors, in the context of detection and identification of chemical warfare agents (CWA) and toxic industrial chemicals (TIC), has been raised to world-class leading edge level.

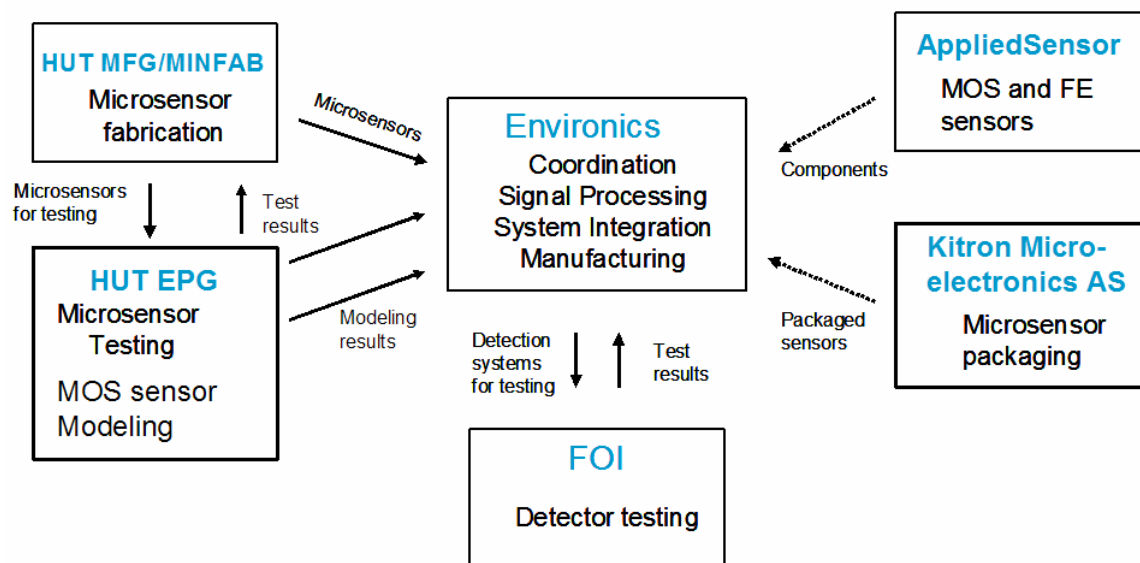


Fig.1. Project organization and tasks.

The sensitivity and selectivity of the new type of micro gas sensors against wide variety of toxic CWA and TIC agents was studied comprehensively for the first time. The results are promising and prove the feasibility of these low power and small size sensor technologies in this demanding application area. For example, the new sensors showed extraordinary good sensitivity, selectivity and stability to VX nerve gas and mustard gases. It was also shown promising sensitivity and selectivity to highly toxic TIC classified agents such as phosgene, cyanides and arsine. When these new sensors are implemented as additional sensors to the ion mobility spectrometry- and multiparameter output based CWA-TIC detector concept, the advantages such as wider detection capability and improved identification performance shall be expected. That should give a new tool for authorities to protect more efficiently citizens against toxic chemicals, whether the chemicals are released in accidents or in terrorist attacks.

Furthermore, it was also found new potential concerns related to micro hot plate MOS gas sensor technology, in general. Those include extraordinary high demands for the fabrication process to produce reliable sensors. One of the evidences of these demands is sensitive layer material dependences on selectivity and stability towards CWAs, TICs and also towards interferences. The concerns are clearly dependent on the applied materials and fabrication process details. However, the results indicate also that with the properly developed fabrication processes and applied materials the concerns can be overcome. The identification of the main concerns gives also good basis to focus the future research and development to the most important issues.

Most of the project partners have strong intention to continue work. Industrial partners have ideas to commercialize the results and bring them available to markets. Also academic partners are interested to continue the work carried out so far by disseminating the results, finalizing dissertations and by providing their services to the new projects.

Recommendations

By the point of view of chemical detector technology, it is hard to believe that any other solid-state micro gas sensor technology, than those employed in this study, could improve significantly the sensitivity requirements of the chemical detector in the CWA-TIC detection applications. Actually high sensitivity emphasizes other concerns such as selectivity and accuracy where is definitely still room for improvements. The key solutions and future recommendations in that respect could be development of hybrid sensor modules, sensor operational algorithms and pattern recognition algorithms for the multiparameter detectors. On the other hand, as was pointed out in this work, the sensitive layer microstructure and composition can also improve selectivity and improve reliability in long-term operation.

Nowadays the main markets for safety, security and military devices, like CWA detectors, are more or less outside Europe (*i.e.* USA, Asia, Middle East), but still European manufacturers have strong positions in those markets. From that point of view, it is also recommended that the strong Nordic and European scale expertise shall be maintained if not even strengthened. One obvious way to do it is to allocate public financing to the safety and security research and development, and, furthermore, pointing out the importance of protection against chemicals, whether released in accidents or in terrorist attacks.

The sensor development is time and money consuming. It is also full of risks and requires skillful people. The expertise gained in the frame of this project forms a good basis for any future development project.

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1 Introduction

Due to increased threat of international terrorism, societies need to pay more attention on protecting their citizens. A significant risk is the release of toxic chemicals, either by accident or terrorist act. Therefore fast detection and identification of toxic chemicals is crucial for efficient protection of citizens.

The toxic chemical threats can be classified to two basic types: chemical warfare agents (CWA) and toxic industrial chemicals (TIC) as shown in detail in Table 1. Especially the threat of TICs has been realized in the recent years. That is due to their easy availability due to wide industrial use. Although CWAs are gradually more toxic and thus more dangerous than TICs, the CWA threat is reducing since in 1997 by more than 160 nations ratified the chemical weapons convention (CWC). That convention prohibits the development, production, stockpiling and use of CWAs as well as many of their precursors. Moreover, nations who are members of the Organization for the Prohibition of Chemical Weapons (OPCW) are banned from trading with nations, which did not sign the convention. Nevertheless, well-trained terrorists may still obtain chemical weapons - either by synthesizing themselves or from the nations which do not belong to the OPCW.

TABLE 1. Definitions and examples of the highly toxic chemical agents.

CWA, chemical warfare agent	Nerve agents (e.g. sarin, soman, tabun and VX) Blister agents (e.g. sulfur mustard, lewisite) Choking and blood agents (e.g. phosgene, cyanide)
TIC, toxic industrial chemical	Common toxic chemicals e.g. ammonia, hydrogen cyanide, various inorganic acids, formaldehyde, chlorine Less-common highly toxic chemicals e.g. isocyanates, pesticides Less-toxic highly volatile chemicals e.g. benzene, toluene, acrylonitrile

One of the crucial concerns related to TICs is the wide number of agents. The National Institute of Justice's Guide for the Selection of Chemical Agent and Toxic Industrial Material Detection Equipment for Emergency First Responders provides a list of 98 TICs classified to three levels according to their production volumes, transportation activity, toxicity and volatility. Furthermore, in the case CWAs, OPCW provides 43 chemical groups or specific chemicals in three schedules. All together, the request for number of chemical agents to be detected and identified by CWA-TIC detector raises easily over 150 agents providing an extreme challenge for the detector developers. Fortunately, many suitable sensor and spectrometer technologies have been demonstrated and are also available in the market. Detectors deploy for example ion mobility spectrometers, IR spectrometers, flame photometric detectors, solid-state gas sensors and electrochemical

sensors and their combinations. Basic key figures of these CWA-TIC detectors are detection, identification and quantification performance. Also response time can be considered as a key figure. Other favoured features are the capability of continuous operation, low weight, small size and ease of operation. However, any of the CWA-TIC detectors available in the market today does not meet all the requirements regarding detection and identification performance and other technical challenges. Therefore, there is still significant need for further technology development.

EnviroNics Oy (Mikkeli, Finland) is one of the most recognized CWA-TIC detector developers and manufacturers in the world. The EnviroNics' CWA-TIC detectors can be used as handheld or man-portable equipment or can be installed as stationary detector in buildings or public spaces as illustrated in Fig.1. The main functions of these detectors are early warning and monitoring. The first hand-held size version was brought to market in 2001 and commercialized later using trade names ChemPro®100, ChemPro®FX, MultiIMS and ChemRAE by EnviroNics, Dräger Safety and RAE Systems, respectively. Since then, militaries and first responders have successfully deployed the detector for early warning and the monitoring of chemical threats.



Fig.1. ChemPro®100 handheld chemical detector equipment in the field use and a stationary detector installation (ChemPro®FX) for buildings or public spaces.

The Environics chemical detector concept is based on the multisensor technology platform where key technologies are aspiration-type ion mobility spectrometry (IMS) and semiconductor gas sensors. The first commercial devices based on that concept were brought to market already in early 1990s.

IMS is proven to be an efficient sensor technology for sensitive and selective detection and identification of the most important CWAs, namely nerve agents, but lacks of performance in the case of many TICs as well as few CWAs, such as sulphur mustard. However, evidently the detection and identification performance of the IMS-based detector can be significantly enhanced by combining it with other sensor technologies.

An especially potential sensor technology combination is the combination of IMS and metal oxide semiconductor (MOS) gas sensors. This combination is also employed in the ChemPro detector concept. In the case of metal oxide gas sensors, the detection and identification performance towards mustard gases, cyanides and many TICs can be improved significantly than could be possible by using IMS alone. Evidently, MOS gas sensors have high potential in the application, but the conventional MOS gas sensors possess also significant power requirement (typically 200-1000 mW per sensor) and have lack of sensitivity to many important target agents. However, novel MOS gas sensors fabricated using MEMS technology, i.e. so called micro hot-plate –based MOS gas sensors, are known for their small size and very low power consumption making them very attractive solution to be implemented to the handheld chemical detectors. Furthermore, the sensitive layers in that context are also developed thanks to nanomaterial technology based innovations. The novel sensor materials may facilitate new functionalities also in the field of CWA and TIC detection applications.

Other suitable technologies are field effect (FE) -type gas sensors, that can be operated in lower temperature than MOS sensors and can be designed to be specific to selected group of TICs. Both of these low power novel micro gas sensor technologies have been developed and commercialized by a Swedish company AppliedSensor, predominantly for automotive and other industrial high volume applications. One of the main aims of this project was to implement the existing sensor technology expertise of AppliedSensor in the completely new application area: CWA-TIC detection. In addition to that the advanced microtechnology fabrication and clean-room facilities of the Helsinki University of Technology also have a crucial role in the project by realizing new ideas and designs of the micro hot plate based MOS sensor. That solution, called the Advanced Microsensor, aimed at to higher level of accuracy and reliability than any other micro hot plate –based MOS sensor in the market. That aim was high and the risks to reach it successfully were accordingly also very high.

Furthermore, Helsinki University of Technology role in the project was also to carry out functional, material characterization and sensor phenomena modeling studies to MOS gas sensors. That part of the work aimed at to improve understanding of the basic phenomena and possibly that way give new ideas to improve accuracy and reliability of the new

sensors, either to the advanced microsensor concept or to the commercial MOS sensors in this new application area.

This project was focusing to implement novel micro gas sensors to the IMS-based ChemPro chemical detector concept and this way improve its CWA and TIC detection and identification performance. The technology development of the IMS technology was beyond the scope of the project, although the developed prototype detector also involved several improvements in the existing aspiration-type IMS solution.

2 Chemical detector concept as technology platform

ChemPro[®]100 (EnviroNics Oy, Finland) handheld chemical detector is probably the smallest, the most cost-efficient and the least maintenance-requiring detector concept when compared to a number of integrated sensor technologies. The weight of the detector is only 800 g with the battery and its power consumption is around 2 watts. For chemical sensing, the device uses miniaturized ion mobility spectrometry and semiconductor gas sensors. Furthermore, the high accuracy and self-diagnostics functions of the device are facilitated by integrated humidity, temperature, pressure and mass-flow sensors that can easily compensate for outdoor condition variations and minor malfunctions by utilizing its sophisticated pattern recognition algorithm.

The basic operational principle of ChemPro[®]100 handheld chemical detector is illustrated in Fig.2.

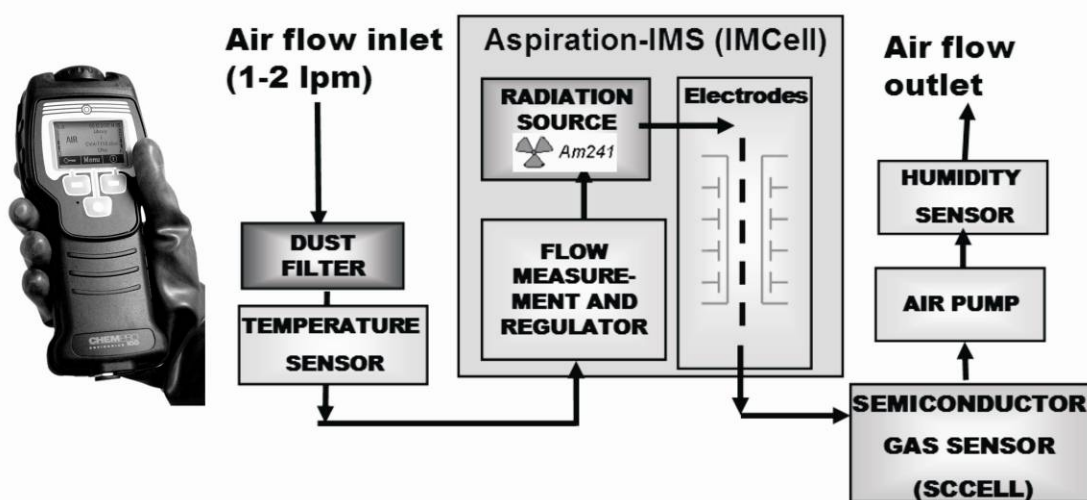


Fig.2. Modular concept and operational principle of the ChemPro[®]100 handheld chemical detector.

The technical concept is a modular flow-through system, based predominantly on the aspiration-type ion mobility spectrometry. In some contexts, the aspiration-IMS is also referred as an open loop IMS in contrary to conventional time-of-flight ion mobility spectrometers. Characteristically, all type of IMS employs atmospheric pressure ionization and analysis of the mobility of formed product ions or ion clusters at ambient temperature with air as carrier [2]. The details of the deployed aspiration-IMS have been given elsewhere [1,3] and shown schematically in Fig.3.

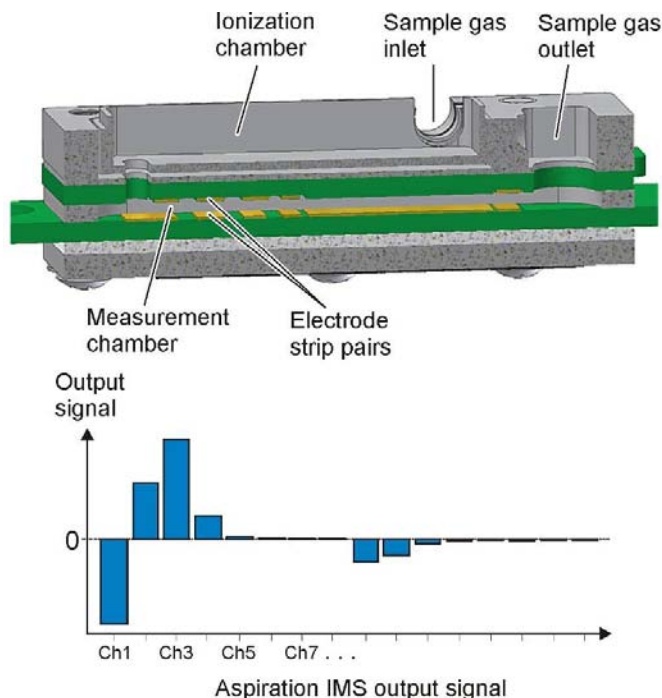


Fig.3. Operational principle of the aspiration-type IMS sensor. After ionization, the product ions travel through an orthogonal electric field in which the ions are deflected to multi-channels located on the collecting electrode. Ions with higher mobility are void to the electrodes much faster than ions with lower mobilities. The output is given in channels containing information of ion mobility and ion polarity. The total number of channels is 16. The general IMS response can be given as a sum of all individual channels [3].

In addition to IMS sensor, ChemPro®100 contains also two thick film -type metal oxide semiconductor gas sensors, consisting of WO_3 and SnO_2 -based gas sensitive layers, designated as SCCell-1 and SCCell-2, respectively. This research focuses to improve detector's CWA and TIC detection and identification performance either by increasing the number of semiconductor gas sensors or replacing these existing ones.

3 Novel microsensors

3.1 MOS sensors

The gas sensing principle of resistive metal-oxide gas sensors is the change of electrical conductivity of the metal-oxide film [4, 5]. The metal-oxide film is kept at high temperature (300 – 400 °C) in order to enhance reactions with gases. This temperature requirement is the basis of surface chemical reactions induced gas sensitivity as well as main reason for the power consumption. The detailed model of the MOS gas sensor transducer principle was developed within the project and presented in the Chapter 5.

Over the last few decades the gas sensors deploying metal oxide semiconductor (MOS) materials for the gas sensors have been created using TiO_2 , WO_3 , SnO_2 and Ga_2O_3 powders and thick-films in particular. The sensor technology originates late 1960s being initially developed in Japan [6]. Actually, in many contexts the sensors are known as Taguchi-sensors or TGS (Taguchi Gas Sensor) referring the original innovator's name. Today, MOS gas sensors are produced in millions of quantities by several sensor manufacturers, located predominantly in Europe and Japan. The MOS gas sensors are typically used in ventilation control, combustible gas leak warning, combustion control and breath alcohol detection applications. The applications of MOS gas sensors in the toxic chemical warning and monitoring are rare and especially the use of MOS gas sensors to detect chemical warfare agents are very rare.

The characteristic feature of the recent state-of-art MOS gas sensors is that they are based on the micro hot plates fabricated using advanced silicon technology [7]. On the other hand, the conventional Taguchi gas sensor is always based on ceramic fabrication processes. Both types of MOS sensors are illustrated in Fig.4. Furthermore, a typical schematic structure of the micro hot plate –based MOS gas sensor is illustrated in Fig.5.

Apparently, micro hot plate platform facilitates several advantages compared to conventional ceramic MOS sensors. They provide faster start-up, faster response, lower power consumption, more accurate temperature control and thus is expected that they provide also more accurate detection and identification characteristics. However, one of the key issues that determine sensitivity and selectivity to gases in both sensor types is the sensor material. In the sensors employed in this study, the sensor materials were either WO_3 or SnO_2 as shown in Table 2. The sensor materials are based on nanotechnology (i.e. material properties in nanometer scale). They can have different microstructures, they can involve different minor additives or catalysts and the preparation and production technologies can vary significantly resulting in major differences in their functionality as a sensor.

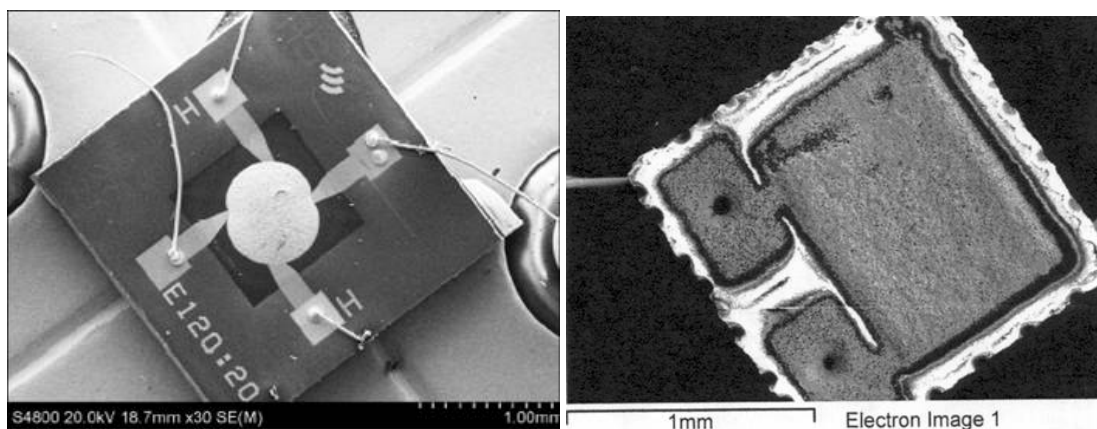


Fig.4. (left) MOS gas sensor based on the micro hot plate platform and (right) MOS gas sensor based on the ceramic platform (*i.e.* SCCell in the ChemPro detector concept).

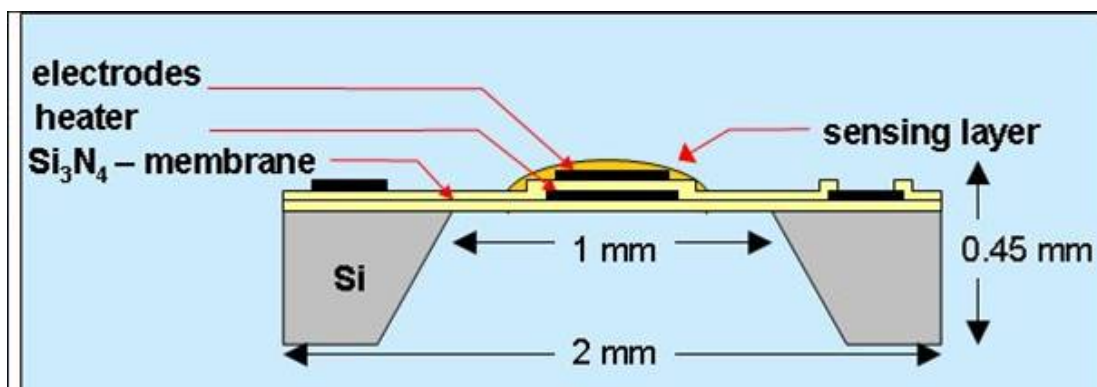


Fig.5. Schematic cross-sectional view of micro hot plate –based MOS gas sensor.

The studies of the project focused to feasibility of micro hot plate –based MOS gas sensors in CWA-TIC detector application. The research is carried out through gas exposure tests and stability studies as well as analyzing and modeling the basic phenomena behind sensor responses by electrical and material characterization methods. Furthermore, the fabrication process of micro hot-plate based MOS sensors is developed, too. That part of the work (carried out in Helsinki University of Technology) had eventually two main functions: (i) to gain knowledge of fabrication related concerns in sensor functionality and (ii) to develop innovative micro hot plate gas sensor to the new level of accuracy, quality and controllability by taking into account specific needs of CWA-TIC detectors and new possibilities provided by advanced nanomaterials and related fabrication technologies.

The comprehensive screening of commercially available MOS gas sensors were carried out in Environics before this project. As a result of those studies three sensor types were selected for further studies. These sensors are designated further on as MOS-1, MOS-2 and MOS-3. In addition, the novel micro hot plate –based MOS gas sensor developed in Helsinki University of Technology is designated as the “Advanced Microsensor”. The summary of the studied MOS gas sensors is presented in Table 2.

TABLE 2. The MOS gas sensors employed in the studies.

Sensor	Metal oxide (base material)	Type
MOS-1	WO ₃ thick film	Micro hot plate
MOS-2	WO ₃ thick film	Micro hot plate
MOS-3	SnO ₂ thick film	Micro hot plate
SCCell-1	WO ₃ thick film	Conventional ceramic
SCCell-2	SnO ₂ thick film	Conventional ceramic
Advanced Microsensor	SnO ₂ thin film	Micro hot plate

3.2 FE sensor

Another type of semiconductor gas sensor employed in the studies was field effect gas sensor. The basis for the sensor is the Field Effect transistor operating in the diode-coupled mode. The gas sensitive properties are achieved by depositing a catalytic metal stack as the gate of the device. The specific catalytic stack layer was developed before this project by AppliedSensor according to specifications provided by Environics. The sensitive layer was designed to be specific and sensitive to hydrogen containing toxic gases, such as NH₃, HCN and H₂S. Thus, the performance expectations of the FE sensors are in improved TIC detection and identification, although high sensitivity to H₂ shall be expected too. The implementation of this novel microsensor to the chemical detector concept was the focus of this project.

The chemical surface reactions of the FE sensor is facilitated by elevated temperature (typically 120-200°C). The dominating chemical reactions that give rise to the sensing properties are as follows: Hydrogen or hydrogen containing gas will adsorb and dissociate into hydrogen atoms on the surface of the catalytic metal stack. The hydrogen atoms will be transported through the metal down to the metal-insulator interface resulting in an effective dipole layer at the interface as illustrated in Fig.6. The effective dipole layer will in turn give rise to a potential drop over the interface, affecting the transistor in the same way as if the gate bias had been changed, i.e. shifting the I-V curve. Hence, the actual sensing part of the device is the metal-insulator interface, which is accessible only to hydrogen atoms and thereby gives excellent selectivity and robustness. The back-reactions include transportation of hydrogen from the interface to the surface

and water formation ($2\text{H} + \text{O} \rightarrow \text{H}_2\text{O}$). The steady-state point between all the reactions is dependant on the actual hydrogen gas concentration in the ambient.

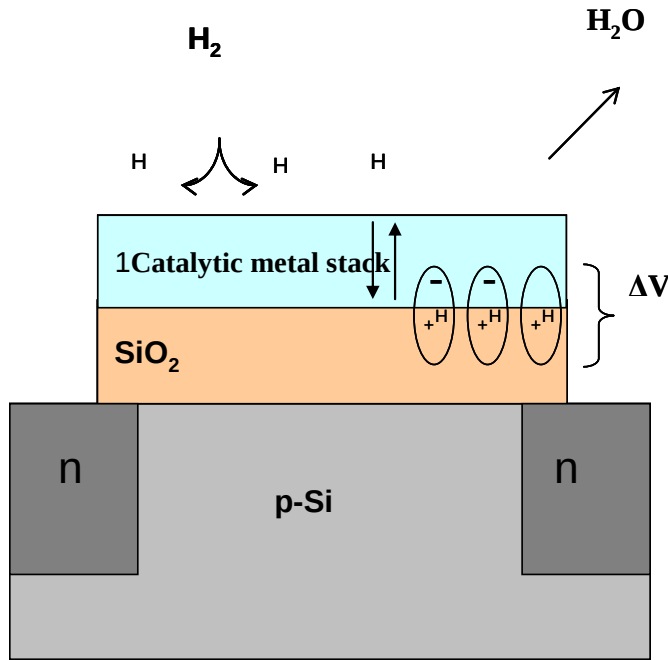


Fig.6. Operational principle of the FE sensor.

3.3 Fabrication of the Advanced Microsensor component

The Advanced Microsensor component was fabricated using silicon processing technologies in the Helsinki University of Technology Micronova clean-room facility. Materials and methods used in fabrication were selected according to equipment availability and contamination control restrictions, resulting in some unconventional innovative solutions.

The sensor platform for the advanced microsensor is designed to provide a resistively heated microhotplate with temperature readout and versatile electrodes for measuring the characteristics and response of the gas sensing layer. Micromachining of the suspended hotplate structure is performed after sensor layer deposition to enable deposition and patterning on a robust substrate without danger of device breakage during processing. Thus, the mechanically sensitive membrane structure is formed immediately prior to chip dicing and packaging. A variety of sensor components can be processed on a single silicon wafer, so the most effective electrode and membrane geometry can be chosen for each completed production run, depending on the properties of the deposited gas sensing material.

Sensor materials

Tin dioxide (SnO_2) was chosen for the basic gas sensitive material for the Advanced Microsensor. It was processed by two different deposition techniques: atomic layer deposition (ALD) and physical vapor deposition (PVD).

ALD is a well established technique for depositing a variety of materials in thin film form with excellent control of film growth. The method comprises exposure of the substrate to two or more alternating source gases, each of which forms a single-molecule layer of material on the substrate surface. The alternating source materials react together to form the deposited material, which in this case was tin dioxide, although many other interesting materials could also be deposited with a similar process.

Sputtering, a form of physical vapor deposition (PVD) method uses a plasma discharge to eject single atoms of source material in a vacuum onto the substrate surface, where they accumulate to form a uniform film. In the semiconductor industry, this is the preferred method for depositing electrically conductive metal layers in integrated circuits. Various methods, such as reactive sputtering (sputtering in a reactive gas atmosphere) and RF (radio frequency) sputtering are used to deposit compound materials including insulators and semiconductors.

Both methods of thin film deposition, ALD and PVD, are generic in the sense that they are not specific to this application (in fact, both are quite novel in this application), demonstrating the versatility of the sensor platform. The same platform could be adapted to other classical and novel materials and deposition methods with little or no modification. For the two deposition methods used here, the fabrication process differs only in how the deposited films are patterned. In the high-temperature ALD process, conventional photolithography and etching must be employed after deposition, whereas the room-temperature PVD method enables easier processing by photolithography prior to deposition, followed by a lift-off process. With some materials, patterning of the sensing layer may not even be necessary, if electrical connections via wire bonding to the contact pads on the sensor device can be made reliably through the sensing layer.

Micromachining and chip dicing

In a typical microhotplate release process, micromachining is performed on the wafer front side. It entails protective layer deposition and patterning prior to etching, and blanket removal of the protective layer after etching. In the present design such extensive processing on the wafer front side is not possible without harming the already deposited gas sensing layer. Therefore the release etch was performed on the back surface of the wafer.

The wafer back side is already protected by a layer of silicon nitride deposited early in the process. This layer is patterned to serve as an etch mask for micromachining. The

wafer front side is protected by ProTEK, a relatively new spin-on etch-resistant material from Brewer Scientific. Furthermore, the wafer is mechanically clamped in an etching jig which exposes only the wafer back side to the etchant. In some samples, a two-stage etch with an extra masking layer of silicon dioxide is performed to leave a silicon island in the middle of the membrane, to improve mechanical stability and temperature uniformity of the microhotplate.

Following the release etch, the wafer is diced into individual component chips. The same ProTEK material covering the wafer front surface serves a dual purpose here, protecting the device from contamination during dicing, as well as increasing the mechanical strength of the membrane. The fragile membranes have been found to easily withstand the stresses imposed during wafer dicing, when the ProTEK layer is employed. Following dicing, the ProTEK layer is removed from individual components by a solvent treatment.

Fabrication process

The basic fabrication process of the Advanced Microsensor component is shown schematically in the Figure 7.

Variations on the process have been performed where the SnO_2 film is deposited by PVD instead of ALD, and patterned by lift-off. The general process flow remains essentially the same. Devices without the buried electrode have been processed omitting step (c), and such devices have also been made with platinum metallization in the heater layer. Instead of etching, platinum has been patterned by lift-off, and the following insulating film has been CVD-deposited silicon nitride, but apart from the material differences the process remains again unchanged.

Formation of the silicon island by two-stage timed etching in KOH utilizing a removable silicon dioxide etch mask is simple to implement, but highly critical in the etching step, and produces varying results. An improved version of a future process flow is also proposed in the figure: prior to the first oxidation and nitride deposition steps, a heavy dose of boron is diffused into the wafer surface where the silicon island is to be. Thermally grown and patterned silicon dioxide is used as a mask during the diffusion step. After removal of the oxide mask, processing continues from oxidation and nitride deposition (i) and then follows an identical process flow as before. During patterning of the wafer back side, no oxide island is left in the etching holes (j). After deposition and patterning of the SnO_2 film, the release etch to form the hotplate is performed in a single step. Due to the selectivity of KOH between lightly doped silicon and highly boron-doped silicon, an island defined by the boron diffusion step is left underneath the hotplate membrane (k). This process involves an extra mask level to define the boron diffusion, but has one less mask in patterning the wafer backside. While extra cleaning, oxidation and annealing steps are required in the boron diffusion, the final bulk etching step is greatly simplified and will likely produce greatly improved results in terms of repeatability.

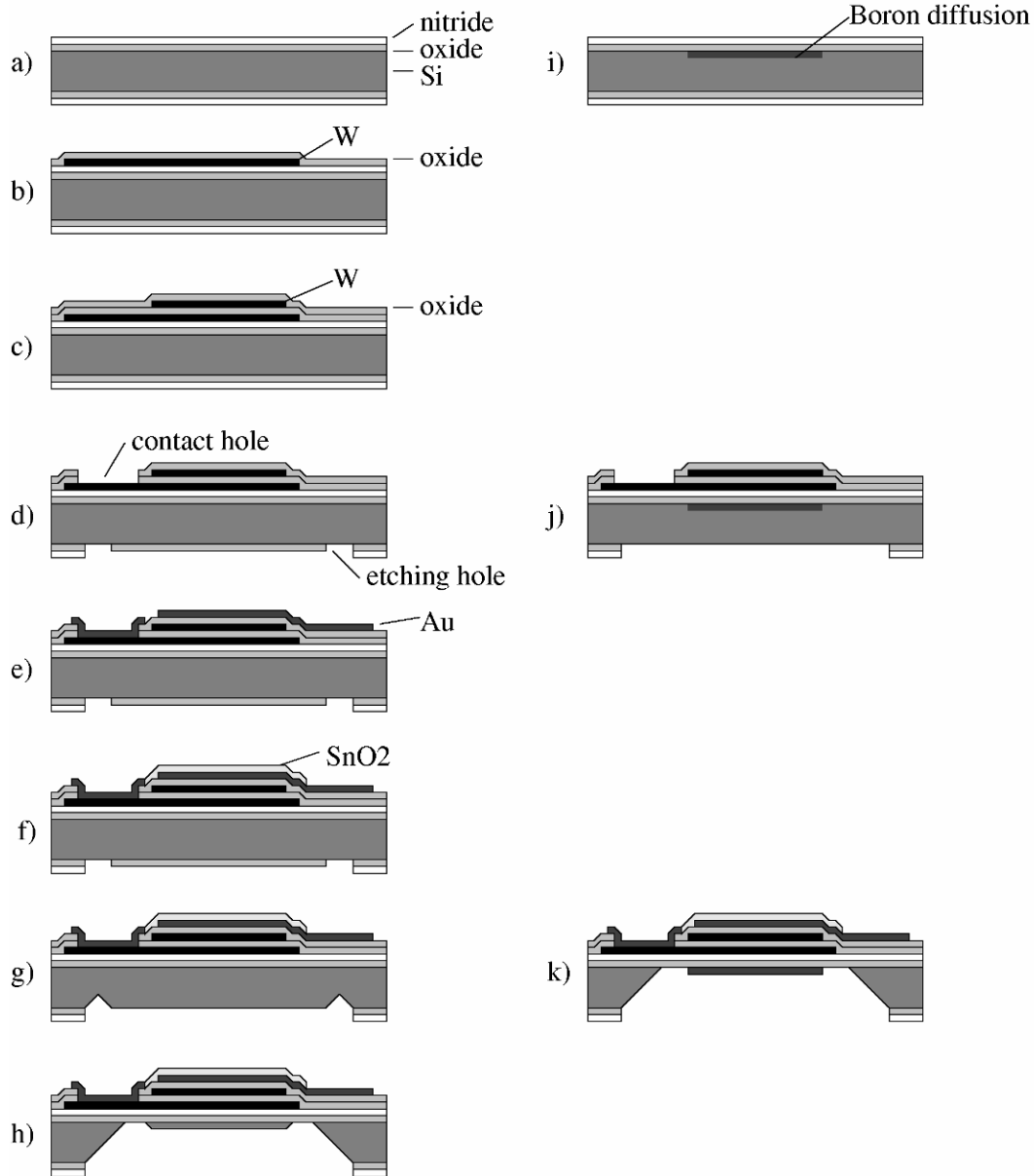


Fig.7. Schematic of the Advanced Microsensor fabrication process.

The steps illustrated in Fig.7 are as follows:

- ⊗ Wafer selection, cleaning, thermal oxidation, CVD of silicon nitride (a)
- ⊗ Sputtering of tungsten heater film, lithography and plasma etching of tungsten
- ⊗ PECVD deposition of insulating silicon dioxide film (b)
- ⊗ Thermal annealing of PECVD deposited oxide
- ⊗ Sputtering of tungsten buried electrode film, lithography and plasma etching
- ⊗ PECVD deposition of insulating silicon dioxide film (c)
- ⊗ Thermal annealing of PECVD deposited oxide
- ⊗ Lithography and wet etching of contact holes to heater and buried electrode
- ⊗ Back-side lithography and patterning of etch-mask for microhotplate (d)

- ⌘ Sputtering, lithography and etching of gold electrodes and contacts (e)
- ⌘ Deposition of SnO₂ film by ALD, lithography and wet etching (f)
- ⌘ Wet etching of wafer backside by KOH, removal of mask oxide (g)
- ⌘ Timed wet etching of wafer backside by KOH (h)

3.4 Design of electronics and packaging

The novel microsensors were deployed in the studies in three basic concepts:

- MOS3+FE sensor hybrid component
- MOS1+MOS2 sensor hybrid component
- Advanced Microsensor component

Of those, the completely new packaging and electronics solutions were needed to be designed for MOS3+FE component as well as for the Advanced Microsensor component. The partners participating to design and fabrication of the sensor package and electronics solutions were predominantly the industrial parties of the project, namely Environics, AppliedSensor and Kitron Microelectronics.

3.4.1 MOS3+FE dual sensor

The most advanced solutions for packaging and electronics were eventually developed for MOS3+FE component relying predominantly on the expertise of AppliedSensor.

The MOS3+FE sensor component is a basically dual sensor device with one FE sensor and one MOS3 sensor on the same header. In all solutions the field-effect sensor components are mounted on a thermal insulating Pyrex glass carrier according to Figure 8. The glass carrier construction, consisting of four pillars, together with the low thermal conductivity of Pyrex work together in order to minimize the heat dissipation, and thereby the power consumption of the device. The MEMS design of the MOS3 sensor provides the same feature but in a chip integrated manner.

A feasible cost-efficient package, especially for the testing purposes was a TO header. The concept of the dual sensor device is illustrated in Fig 9.

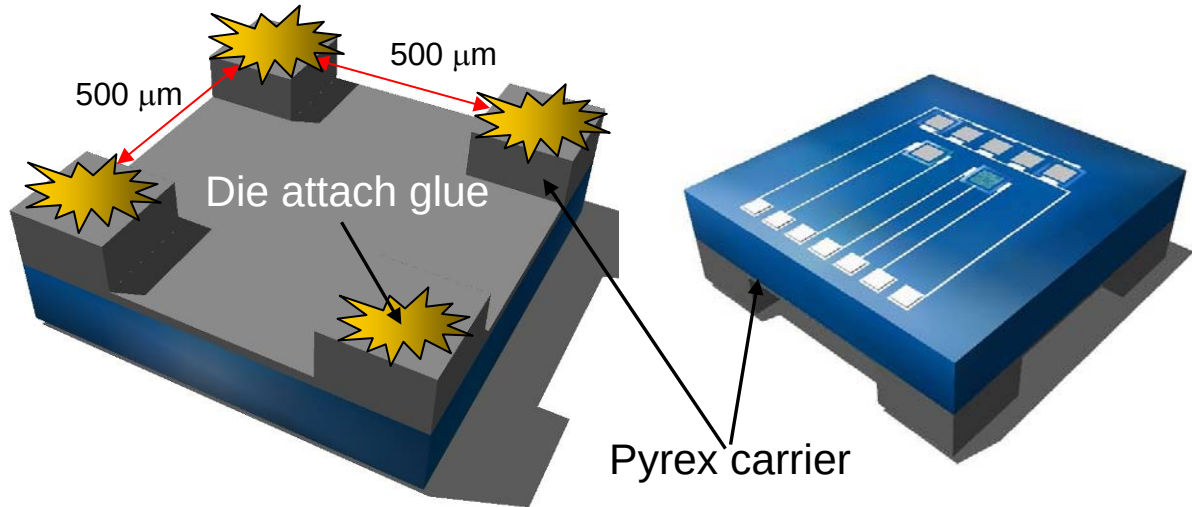


Figure 8: Thermal insulation of FE sensor component using micro-machined Pyrex glass carrier.

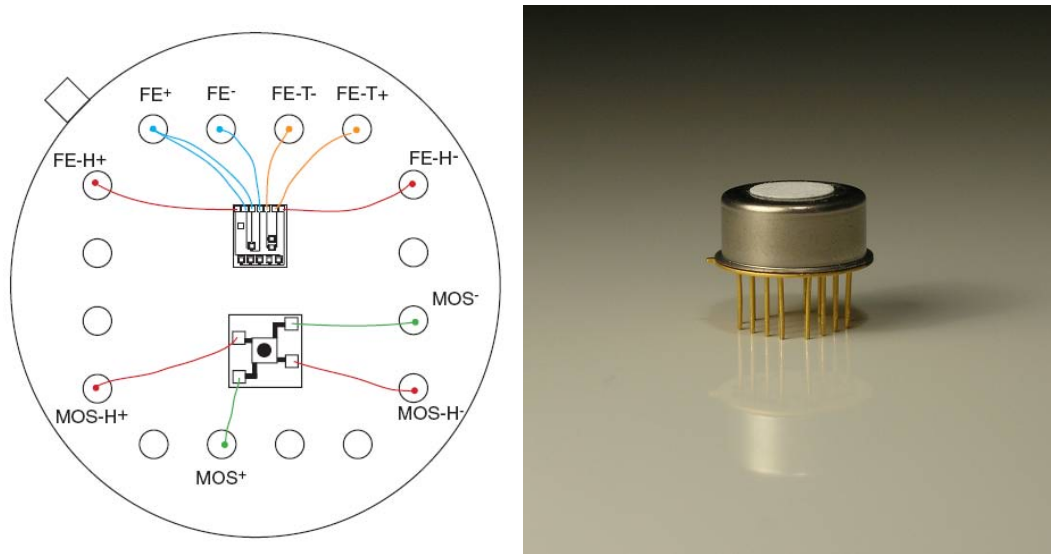


Figure 9: Top view of the schematic bond pattern of the MOS3 and FE sensors (left) and final sensor component (right).

An alternative, yet more advanced solution to MOS3+FE dual sensor was designed and prototyped as well. In that case, the basis of design is the sensor module with integrated chip-on-board mounted sensor chips with special mechanics to facilitate the assembly of sensor board to the detector's gas flow line.

The MOS3+FE sensor module design comprises electronic components used for sensor measurement and storage of individual ID- and calibration data. The prototype of the sensor module is shown in Fig 10.

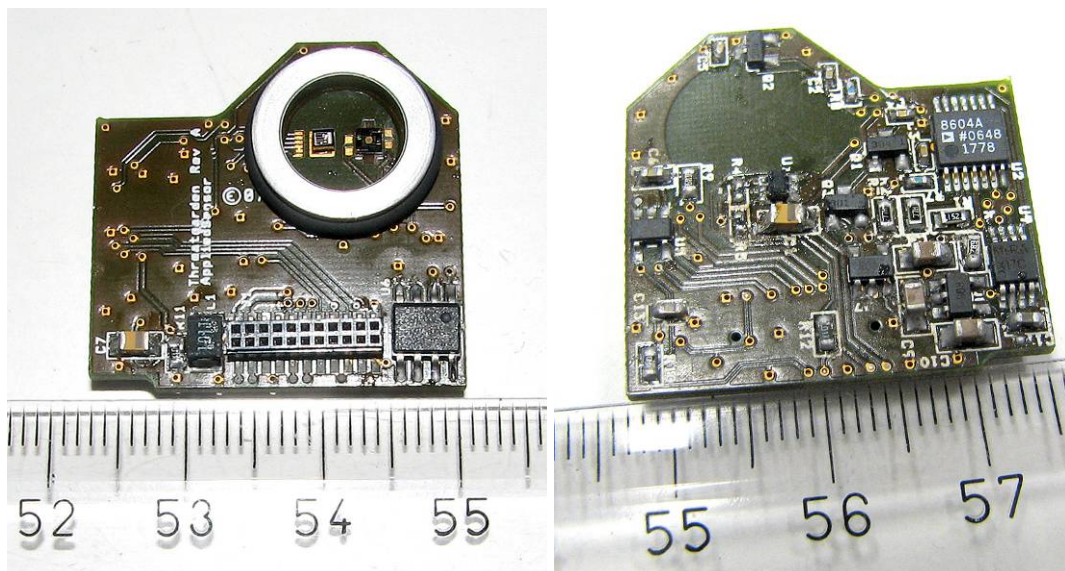


Figure 10. MOS3+FE dual sensor module prototype (top view, left and bottom view, right).

The main advantage of module concept is its independency on other electronics of the detector. That should facilitate easy maintenance in the end-use as well as further sensor development with minimum changes in the basic detector concept. Furthermore, such module sensor solution could be especially suitable to independent application or fixed detector system installation.

3.4.2 Advanced Microsensor

The Advanced Microsensor design had two size options: $500\ \mu\text{m} \times 500\ \mu\text{m}$ and $1000\ \mu\text{m} \times 1000\ \mu\text{m}$. The linewidth of the electrodes was $30\ \mu\text{m}$ in the smaller and $60\ \mu\text{m}$ in the larger design. Furthermore, there were two options for the electrode configuration in the Advanced Microsensor design: the single and dual configuration. The contacts of the single configuration are shown in Fig.11.

The advanced microsensor package was chip-on-board type solution, similar kind as was developed for the MOS3+FE sensor module. The package and sensor test board was developed by Kitron Microelectronics. Figure 12 illustrates the solution in detail.

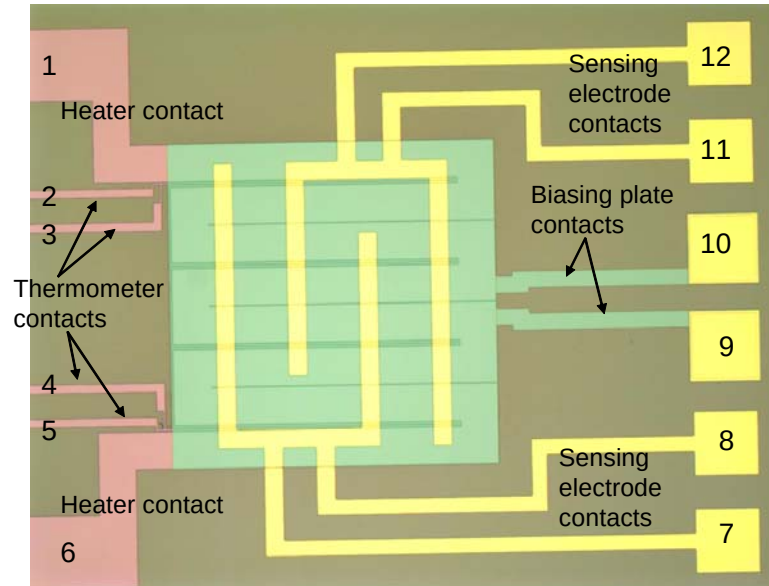


Figure 11. Top view of one of the chip design types of the Advanced Microsensor. The contacts and the contact pad numbers are indicated.

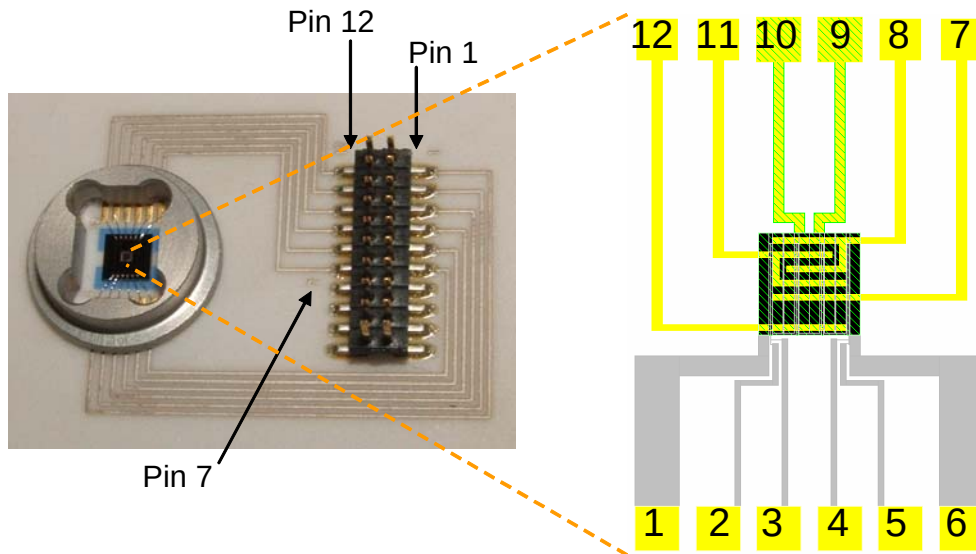


Figure 12. The Advanced Microsensor test board and pin order that corresponds the bond pads shown in Fig.11.

3.5 Detector prototype and other test set-ups

The functional testing of the gas sensors requires also well-established measurement and control electronics (as well as calibration procedures, if found necessary) as well as test set-up to interface sensor to the controlled atmosphere and vapor generation systems. The simplest way to do the sensor tests is to construct special test benches where electronics design can be replaced by commercial tools dedicated to signal generation and processing and accurate power control. That approach was implemented in the Advanced Microsensor studies as well as for the quality control test procedures of the MOS3+FE dual sensors.

However, within the frame of project, novel electronics solution to the ChemPro detector concept was developed in Environics, too. That approach facilitated to study sensor functionality in the system level and thus closer to the final application.

3.5.1 Microsensor implementation to the detector concept

The two new sensor boards: 1) MOS3+FE and 2) MOS1+MOS2 were implemented to ChemPro detector concept as illustrated in Figs 13 and 14.

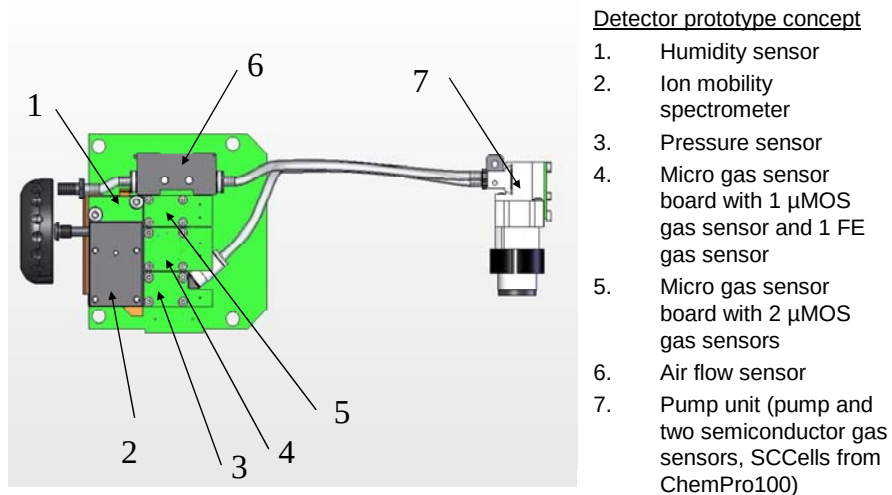


Fig. 13. The detector prototype is a new design for the ChemPro®100 detector implementing new sensor boards (4 and 5).

Novel microsenors assembled in the Detector Prototype

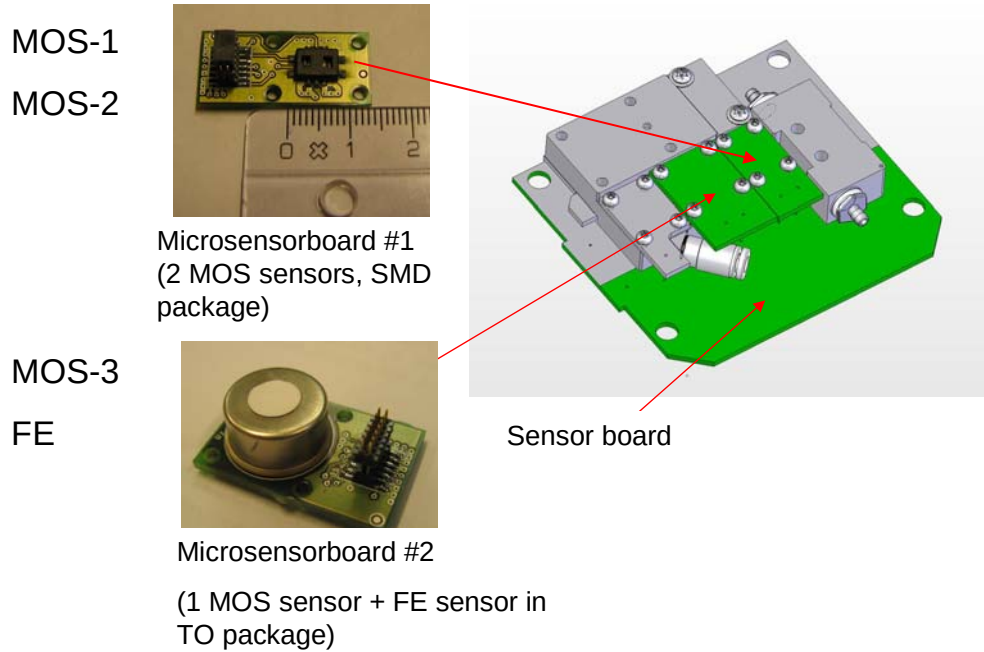


Fig 14. Photographs and assembly of new micro gas sensors to the detector prototype.

3.5.2 Microsensor test benches

Another form of test set-up were gas blocks designed for testing sensor boards. This kind of test set-ups were deployed in AppliedSensor to develop quality control procedures for sensor deliveries as well as for basic research in TKK and Environics. An example of the test system is shown in Figs.15 and 16.

Within the frame of project, slightly different test benches with especially different electronics interface solutions, were deployed for all three basic concepts of microsenors:

- MOS3+FE sensor hybrid component
- MOS1+MOS2 sensor hybrid component
- Advanced Microsensor component

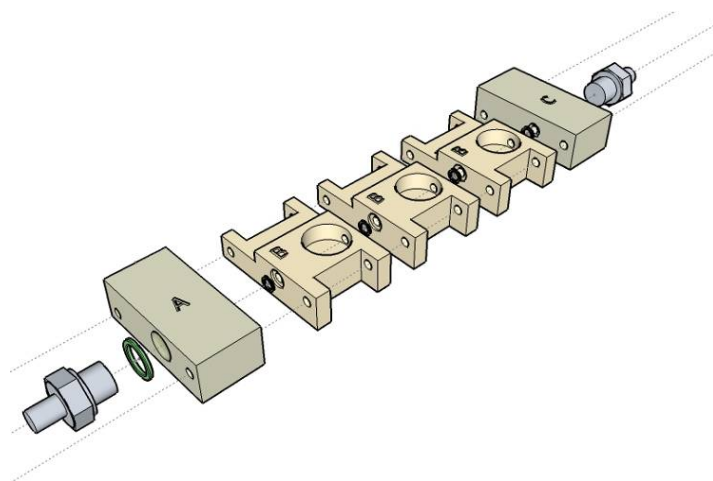


Fig. 15. Mechanical design of a test bench with special gas block and appropriate air flow channel interface. The gas block has been manufactured in Teflon material.

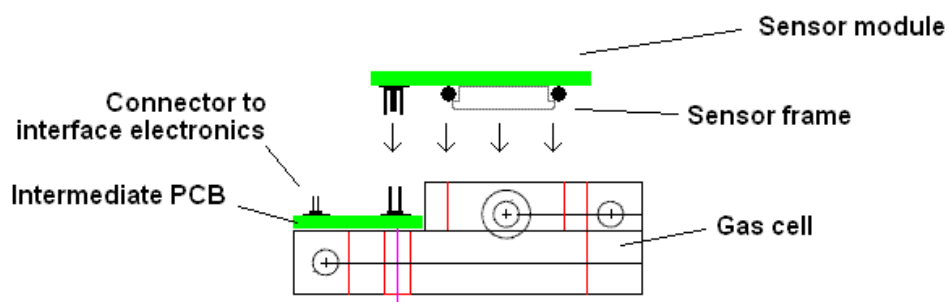


Fig. 16. A single gas block viewed from the side and the connection of the sensor board to the flow channel.

4 Functional studies

Sensor functionality testing protocols for CWA and TIC tests are demanding and requires sophisticated chemical laboratory environments with knowledge of generation of vapors, instrumental methods of chemical analysis and high level safety management.

Experienced laboratory for testing of detectors and sensors against various toxic agents is NBC Division of Swedish Defence Research Agency, FOI. The most demanding CWA tests were carried out there. Furthermore, less-demanding CWA tests (e.g. simulant agents) and TIC tests were carried out in Environics and in Helsinki University of Technology. The key point in sensor functionality is that sensor should possess sensitivity to target agents (i.e. CWAs and TICs) in all outdoor conditions where main concerns are variations in humidity and temperature. Other important tests are selectivity studies against interferences (i.e. less toxic agents) including environmental gases. Also sensor stability (i.e. sensitivity remains similar over pro-longed time), drift, response time and proper recovery are important aspects as well.

The CWA agents are semivolatile compounds and characteristically liquids in room temperature. On the other hand, TICs and interferences are highly volatile liquids, if not gases, in the room temperature. In order to generate liquid phase compound to the vapor phase, a special vapor generation system (VGS) is needed. An example of the VGS is presented in Fig. 17 where basic principle is to evaporate liquid agent into humidity controlled clean air. The evaporation method can vary, in this example it is syringe and syringe pump driven system, but also diffusion or permeation systems can be employed.

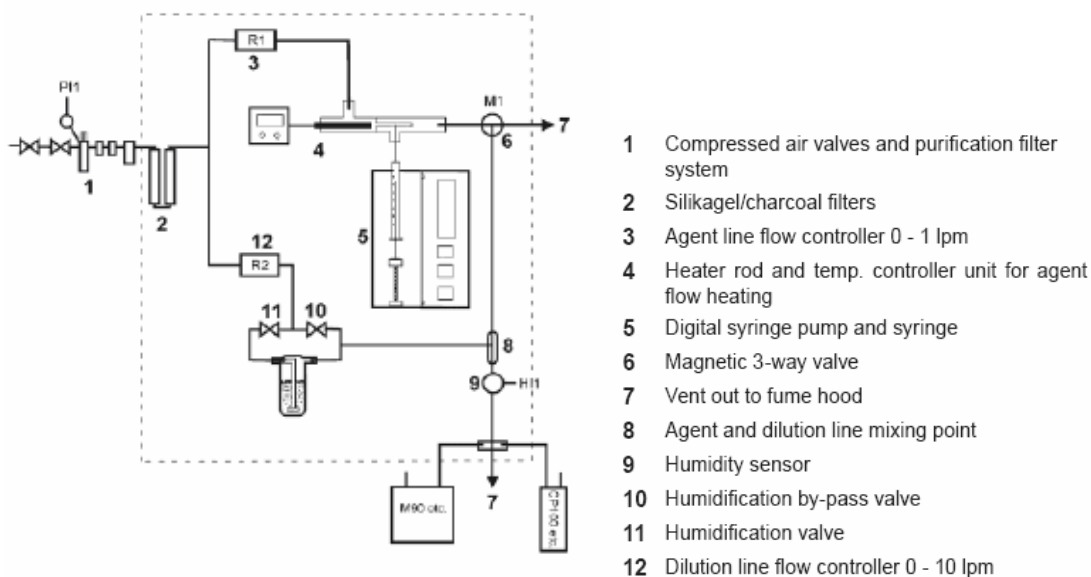


Fig. 17. Schematic presentation of the vapor generation system.

The comprehensive CWA tests were carried out in FOI, Swedish Defense Research Agency, Umeå, Sweden for the detector prototypes. The vapor generation system of FOI was employing a heat controlled diffusion chamber as an evaporation method (contrary to syringe driven system shown in Fig.17). The concentration determination method in FOI was on-line method to monitor agent concentration directly on the vapor generation system by applying precisely calibrated FPD (Flame Photometry Detector). Agent purity control relied predominantly on the synthesis product quality where over 99% purity was typical and determined using independent methods such as NMR (nuclear magnetic resonance) and GC-MS (gas chromatography-mass spectrometry).

The set-up for mounting the detectors to the vapor generation system in FOI is presented in Fig.18. Two parallel detector units were deployed simultaneously. In the case of hot and cold temperature tests, a special climate chamber was deployed by placing detectors inside the chamber.



Fig.18. Two ChemPro units mounted on the agent generation test system and a climate control chamber for cold and hot temperature tests.

Typically a gas exposure test protocol contained 15-30 min conditioning, 1 min exposure and full recovery. The exposure results are typically presented as sensor response vs. time curve to each test point. Since the detector is multisensor device it provides simultaneous response-time curve to all implemented sensors. The data for IMS is presented as a sum of all 16 channel output in picoamps (i.e. current created by product ions) while MOS gas sensor output is obtained as ratio R_s/R_0 , where R_s is sensor resistance in each time point and R_0 is the sensor resistance in the beginning of the exposure. Furthermore, for FE sensor the response is voltage difference V_s-V_0 , accordingly to MOS sensors.

4.1 CWA tests to the detector prototype

All together 7 detector prototype units were employed in about 4 months test period in FOI covering eventually 513 exposures to the CW agents including most of the organophosphonate nerve agents as well as blister agents. As expected, IMS response to all nerve agents is dominating and selective while MOS gas sensors responses is generally less intensive and FE sensor responses practically negligible.

Good responses of MOS sensors was obtained in the case of sulfur mustard (HD, bis(2-chloroethyl)sulfide) where especially three of the MOS gas sensors gave good response. Same MOS sensors, namely MOS-1, MOS-2 and SCCell-1 gave also significant responses to low concentration of VX nerve gas. Common to these three MOS gas sensors is that they are based on WO_3 metal oxide while the other two (MOS-3 and SCCell-2) were based on SnO_2 . This result indicates that WO_3 -based MOS gas sensors are particularly suitable for detection of sulphur-containing CWAs such as HD and also VX.

Further focus was paid to MOS sensor detection performance to VX nerve gas [8] since VX can be synthesized in several forms, *i.e.* especially forms known as VX and Russian VX (RVX) (Fig. 19). Furthermore, VX purity can vary significantly due to by-products and residuals of the synthesis and especially due to degradation products. One of the most prominent degradation products for VX is 2-diisopropylamino ethanethiol (VX-thiol) as shown in Fig.19. Accordingly, RVX dissociates to RVX-thiol. The volatility of the VX-thiol is higher than VX and therefore the quality of VX vapor decreases drastically when the degradation in the liquid phase proceeds. The amount of degradation products can depend also significantly on the thermal effects in the vapor generation system as well as storage temperature and period.

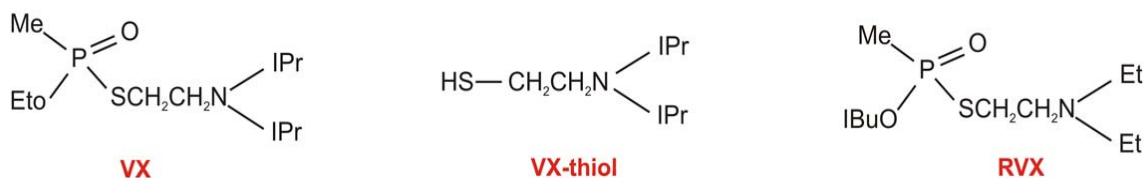


Fig. 19. Various forms and degradation products of VX nerve gas.

In order to study the sensor responses to the variable forms of VX, a special evaporation method was applied in FOI to produce extra pure VX and RVX vapors. In that method, the agents are generated by letting filtered air pass through a fused silica column coated with the agent as described in Ref [9]. The results of MOS gas sensors responses to the different forms of VX are shown in Fig.20.

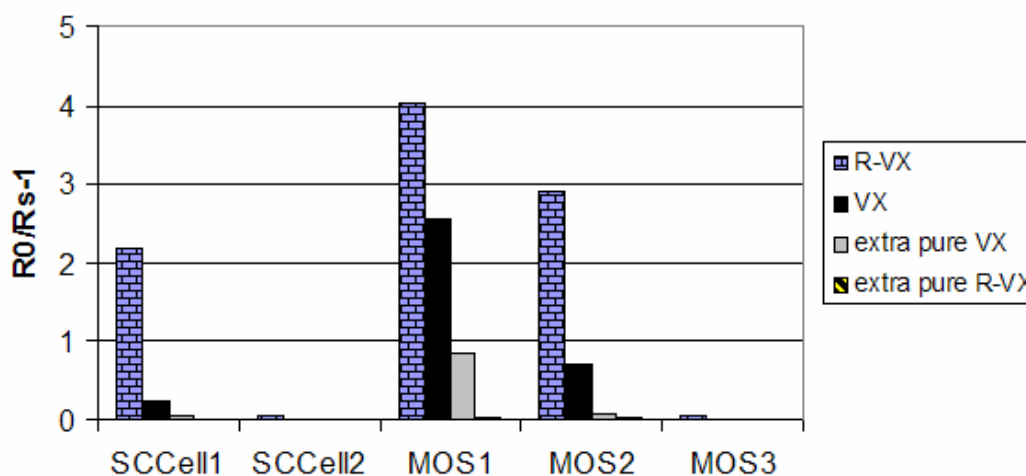


Fig. 20. MOS gas sensors responses for the different forms of VX in 0.1 mg/m^3 at 25°C and 50% RH.

The MOS gas sensor responses are not significantly dependent on whether the form is VX or RVX, but rather the purity of VX, namely, the higher the purity the less seems to be the sensor response. The results indicate that MOS gas sensor response is more or less related to VX degradation products such as VX- and RVX-thiols.

4.2 Introduction to TIC and interferent tests

The typical health effecting exposure limits for various chemicals actually does not ever classify the chemicals to TICs or interferents (not even CWAs), but provides simply lists of chemicals with different concentration limits for specified chemicals with specified health effect. Apparently, different chemicals have a health effect in different concentrations as given in Table 3. If the chemical has serious influence on human health or life already in extremely low concentration, the chemical may be classified as CWA. However, if the chemical has very minor health effect although the concentration is high, the chemical may be considered in many contexts as an interferent. Most of the chemicals between these two extremes could be classified to the TIC category.

The Protective Action Criteria (PAC) for chemical releases is recently developed list of chemical exposure limit values for emergency response planning applications [10]. Key components of the PAC are the Temporary Emergency Exposure Limits (TEELs) given in three levels as follows:

TEEL-0: The threshold concentration below which most people will experience no appreciable risk of health effects.

TEEL-1: The maximum concentration in air below which it is believed nearly all individuals could be exposed without experiencing other than mild transient adverse health effects or perceiving a clearly defined objectionable odor.

TEEL-2: The maximum concentration in air below which it is believed nearly all individuals could be exposed without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action.

TEEL-3: The maximum concentration in air below which it is believed nearly all individuals could be exposed without experiencing or developing life-threatening health effects.

The TEEL-values are predominantly based on the chemical exposure limit values given in Acute Exposure Guideline Level (AEGL) values published by the U.S. Environmental Protection Agency (EPA) and Emergency Response Planning Guideline (ERPG) values produced by the American Industrial Hygiene Association (AIHA). Furthermore, the methodology for the derivation of TEELs is based on hierarchies of the existing and commonly available exposure limits. These include the Occupational Safety and Health Administration (OSHA) and the American Conference on Industrial Hygienists (ACGIH) Short Term Exposure Limits and Ceiling Limits (*i.e.* acronyms such as, PEL-STEL, TLV-STEL, PEL-C, and TLV-C), as well as Immediately Dangerous to Life or Health (IDLH) -values. The IDLH values are given by the National Institute for Occupational Safety and Health (NIOSH) as respirator selection criteria and were first developed in the mid 1970's. OSHA defines an IDLH as follows [11]:

IDLH: “An atmospheric concentration of any toxic, corrosive or asphyxiant substance that poses an immediate threat to life or would cause irreversible or delayed adverse health effects or would interfere with an individual's ability to escape from a dangerous atmosphere.”

Furthermore, in very high concentrations of combustible and highly volatile chemicals the main health affecting concern may be eventually their explosive limit. There are two explosive limits for any gas or vapor, the lower explosive limit (LEL) and the upper explosive limit (UEL). At concentrations in air below the LEL there is not enough fuel to continue an explosion; at concentrations above the UEL the fuel has displaced so much air that there is not enough oxygen to begin a reaction. Concentrations of explosive gases are often given in terms of percent of lower explosive limit (%LEL).

TABLE 3. List of the TEEL (Temporary Emergency Exposure Limits) -values, IDLH (Immediately Dangerous to life or health)-values and LEL (lower explosion limit) -values for the selected chemicals [10, 11].

Chemical Name							
	UNITS	TEEL-0	TEEL-1	TEEL-2	TEEL-3	LEL	IDLH
Acetic acid	ppm	5	5	35	250	40000	50
Acetone	ppm	200	200	3200	5700	21500	2500 (LEL)
Acrylonitrile	ppm	2	10	35	75	30000	85
Alcohols, C6-C12 (N.O.S.)	mg/m ³	10	30	50	250		
Ammonia	ppm	25	30	160	1100	150000	300
Arsine	ppm	0.05	0.05	0.17	0.5	51000	3
Benzene	ppm	1	50	150	1000	12000	500
Bis(2-chloroethyl)sulfide; (HD;sulfur mustard)	ppm	0.0035	0.01	0.02	0.32		
Butane	ppm	800	2400	4000	19000	16000	
Butyl acetate, n-	ppm	5	5	200	3000	14000	1700 (LEL)
Carbon monoxide	ppm	50	83	83	330	120000	1200
Chlorine	ppm	0.5	0.5	2	20		10
Cyanide (-CN)	mg/m ³	5	5	5	25		25
Cyanogen	ppm	10	10	10	15	66000	
Cyanogen chloride	ppm	0.3	0.3	0.4	4		
Diborane	ppm	0.1	0.15	1	3.7	8000	15
Diesel fuels	mg/m ³	100	100	500	500	13000	
Ethyl alcohol; (ethanol)	ppm	1000	3000	3300	3300	33000	3300 (LEL)
Ethyl dimethylamido-cyanophosphate; (Tabun; GA)	ppm	0.00013	0.0004	0.0053	0.039		
Ethylene oxide; (Oxirane)	ppm	1	5	45	200	30000	800
Fluorine	ppm	0.1	1.7	5	13		25
Formaldehyde	ppm	0.3	1	10	25	70000	20
Gasoline	ppm	300	500	500	1500	13000	
Hexane	ppm	50	150	250	1100	10000	1100 (LEL)
Hydrogen chloride; (Hydrochloric acid)	ppm	0.5	1.8	22	100		50
Hydrogen cyanide; (Hydrocyanic acid)	ppm	2	2	7.1	15	56000	50
Hydrogen fluoride; (Hydrofluoric acid)	ppm	1	1	24	44		30
Hydrogen peroxide	ppm	1	10	50	100		75
Hydrogen sulfide	ppm	0.51	0.51	27	50	40000	100
Isopropyl alcohol	ppm	400	400	2000	2000	20000	2000 (LEL)

TABLE 3. continues.

Chemical Name	UNITS	TEEL-0	TEEL-1	TEEL-2	TEEL-3	LEL	IDLH
Jet fuels (JP-5 and JP-8)	mg/m ³	100	290	500	500		
Kerosene	mg/m ³	100	100	400	400	6000	
Methane	ppm	1000	3000	5000	25000	50000	
Methyl cyclohexylfluorophosphonate; (GF)	ppm	0.00006	0.0002	0.0025	0.018		
Mineral oil, petroleum distillates	mg/m ³	40	125	500	500		
Nitric acid WFNA; (White Fuming)	ppm	0.53	0.53	24	92		25
Nitric oxide	ppm	0.50	0.50	12.5	20		100
Nitrogen dioxide	ppm	0.50	0.50	12.5	20		20
Ozone	ppm	0.1	0.1	1	5		5
Phosgene	ppm	0.10	0.10	0.30	0.75		2
Phosphine	ppm	0.3	1.0	2.0	3.6	17900	50
Phosphorus trichloride	ppm	0.5	0.62	2.0	5.6		25
Soman; (3,3-Dimethyl-2-butyl methylphosphonofluoridate, GD)	ppm	0.00003	0.00018	0.0022	0.017		
Sulfur dioxide	ppm	0.20	0.20	0.75	27		100
Sulfur trioxide	mg/m ³	0.6	2	10	30		
Sulfuric acid	mg/m ³	1	2	10	30		15
Toluene	ppm	200	200	510	2900	11000	500

4.3 TIC tests to the detector prototype

TIC tests were carried out with similar vapor generation system as was applied in CWA tests. However, several TICs are gases (*e.g.* HCN, phosgene and chlorine), and in those cases the source was pre-mixed agent – synthetic air mixture in a gas cylinder. The agent concentration was in those cases controlled by clean air dilution method and in addition in some cases determined using independent method such as Dräger tubes. It is worth pointing out that some TICs, like HCN and phosgene, are also classified to CWA. The results of sensor response curves to 5 selected TICs are shown in Fig.21.

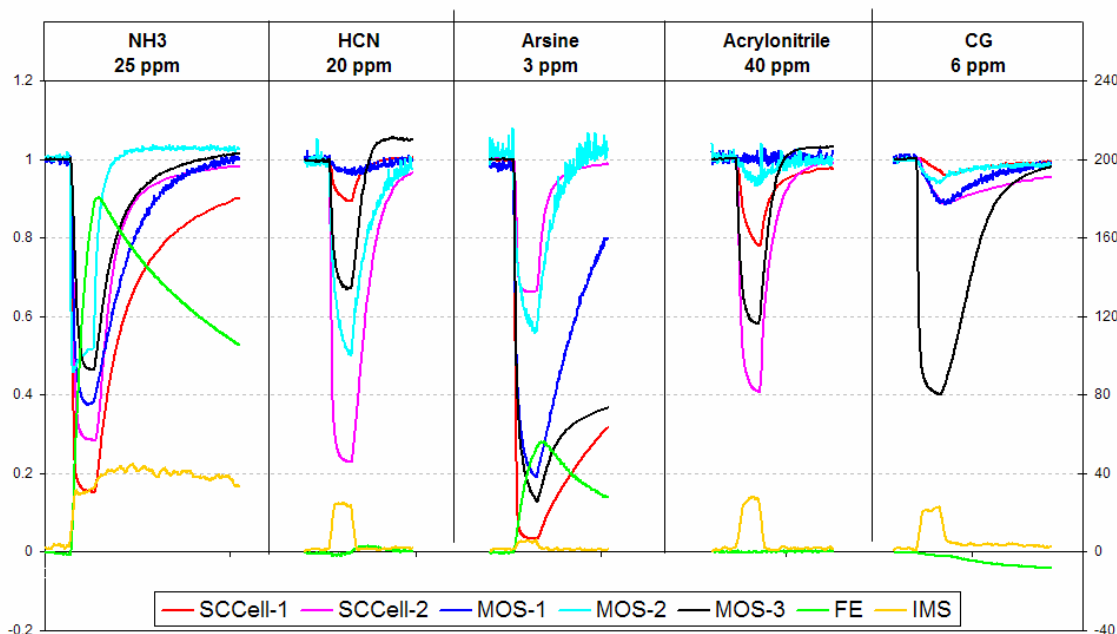


Fig. 21. Sensor response curves to NH_3 25 ppm, HCN 20 ppm, arsine (AsH_3) 3 ppm, acrylonitrile 40 ppm and phosgene (COCl_2) 6 ppm at 25°C and 50% RH.

Although FE sensor did not respond to any of the CWAs, its response to some TICs, such as ammonia (NH_3) and arsine (AsH_3) in Fig.21 was significant and very selective. Furthermore, the high sensitivity of MOS-3 to phosgene is also notable and extraordinary when compared to other implemented sensors. Also SCCell-2 shows good sensitivity and selectivity to HCN and acrylonitrile, the two compounds that could be classified to cyanogenic substances. In general, IMS response to TICs is far from the intensity obtained with nerve agents. Therefore, the MOS gas sensors have crucial role to provide sensitive output in the detector towards many TICs.

4.4 Tests against interferences

The Table 3 summarized exposure limits to several chemicals. Practically all chemicals in some concentration are hazardous, and from that point of view there should not be any interferences at all, but just different concentration requirements. However, in many end-user specific occasion the CWA-TIC detector should not be influenced (*i.e.* no false positive or no false negative) by a list of interferences. Typical features of those interference chemicals are their high TEEL concentration limits and/or missing IDLH value or the IDLH value is at least defined through lower explosion limit (LEL)-value. By stating that, the typical interferences are common solvents, like volatile alcohols (e.g. ethanol and isopropyl alcohol) as well as acetone, also hydrocarbons commonly present in fuels, petroleum distillates and petroleum gases, such methane, butane, hexane, toluene may be

considered as interferences. Another group of interferences is in some cases the environmental gases where typical sources are due to human activities such as exhaust gases. However, many of the environmental gases are also classified to TICs (such as SO_2 , NO , NO_2 , O_3 and CO), and therefore the sensor's detection capability is often good than bad property. Furthermore, also H_2O and CO_2 content in air, and especially their sudden variations, are in many occasions considered as interference. In the ChemPro – concept, the outdoor humidity and temperature effects to the sensor responses have been made acceptable and controllable by taken into account in the pattern recognition algorithm. This is facilitated by comprehensive test protocols to support library and algorithm development as well as by implementing specific humidity and temperature sensors to the detector.

The interferent rejection is an important part of CWA-TIC detector performance. Unfortunately, there is no test standard available and thus interferent test protocols can vary significantly. The test can be performed in the field with appropriate interferent sources in simulated operational conditions or the test can be performed in the laboratory by employing controlled vapor generation methods (same kind of systems as used in this study for CWA and TIC vapor generation). In the latter case, both false positive and false negative tests can be carried out and the test is definitely more repeatable than the field test.

Some interferent test results are shown in Fig. 22. In those cases, the laboratory test set-up for the vapor generation was employed.

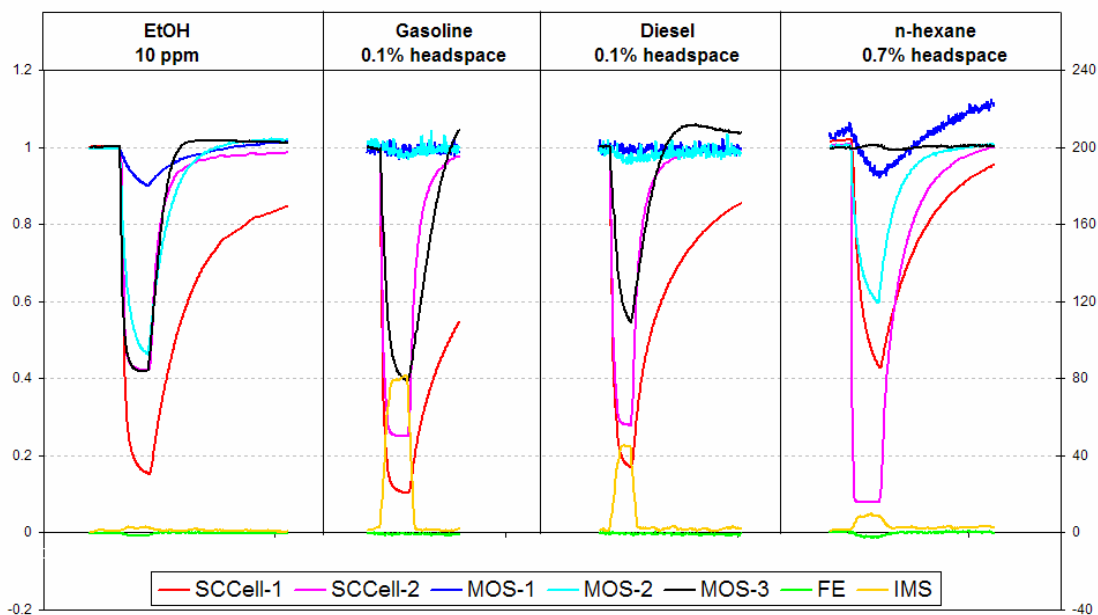


Fig. 22. Sensor response curves to interferent vapors: ethanol 10 ppm as well as headspace diluted gasoline (0.1% of the headspace concentration), diesel (0.1%) and hexane (0.7%) at 25C and 50% RH.

Contrary to the TIC and CWA tests, in some cases (Fig.22) so called headspace dilution method was deployed to generate controlled concentration. In that method, the volatile liquid source is kept in a sealed container in room temperature and the steady-state headspace is brought to the vapor generation system and diluted by clean air to given fraction.

The results of the interferent tests emphasizes one of the main concerns related to MOS gas sensors, namely their high sensitivity to wide range of chemical vapors and gases including interferents. However, the interferent tests show that two of the new sensors, MOS-1 and FE, possess significant improvement in the selectivity and thus interferent rejection capability when compared to other MOS gas sensors. MOS-1 showed earlier extraordinary high sensitivity to CWAs like HD and VX, and now also extraordinary low sensitivity to common interferents indicating excellent selectivity. Furthermore, although FE sensor possessed good sensitivity to some TICs in concentration below IDLH, its sensitivity to interferents is practically negligible.

4.4.1 Integrated calorimetric transducer to improve interferent rejection

As can be derived from the Fig.22, some of the MOS sensors (i.e. SCCells and MOS-2 and MOS-3) showed high sensitivity to combustible interferents. On the other hand, the highest hazardous level (TEEL-3 or IDLH) as given in the Table 3 indicates that in many contexts the interferent-type volatile organic chemicals shall be detected in around 10% LEL concentration. Typical employed sensors to selectively detect and quantify %LEL concentrations are based on the calorimetric transducer principle. These sensors are also known as catalytic sensors or pellistors. The basic phenomena of the calorimetric transducer is the catalyst assisted combustion reactions on the surface of the metal oxide which leads to temperature change in the microscopic sensor and become detected by the temperature sensing and control circuitry. Actually, micro hot plate –based sensors have been actively developed to be operated as calorimetric transducer. Therefore, this study focused to evaluate whether the new micro hot plate MOS gas sensors could be employed to provide simultaneous calorimetric output with the conventional semiconductor resistor-type output. Technically, the calorimetric output can be obtained by keeping the sensor temperature constant and when combustion reaction increases the sensor heat, the heater power and voltage are reduced accordingly. The calorimetric output is thus the heater voltage. The Fig. 23 shows MOS sensors and, accordingly, MOS sensor heater responses to high concentration of hexane vapor.

The calorimetric output is most sensitive in the case MOS-3. Practically, other two, MOS-1 and MOS-2, do not give any calorimetric response, even though MOS-2 sensor response to hexane vapor is as high as for MOS-3. However, regarding the possibility to employ calorimetric output to indicate interferent vapors already in low concentrations (e.g. <100ppm), the sensitivity of MOS-3 is neither good enough. In spite of that, the

integrated calorimetric output of MOS-3 should be useful in some customer specific applications to provide early warning of the potential explosion limit.

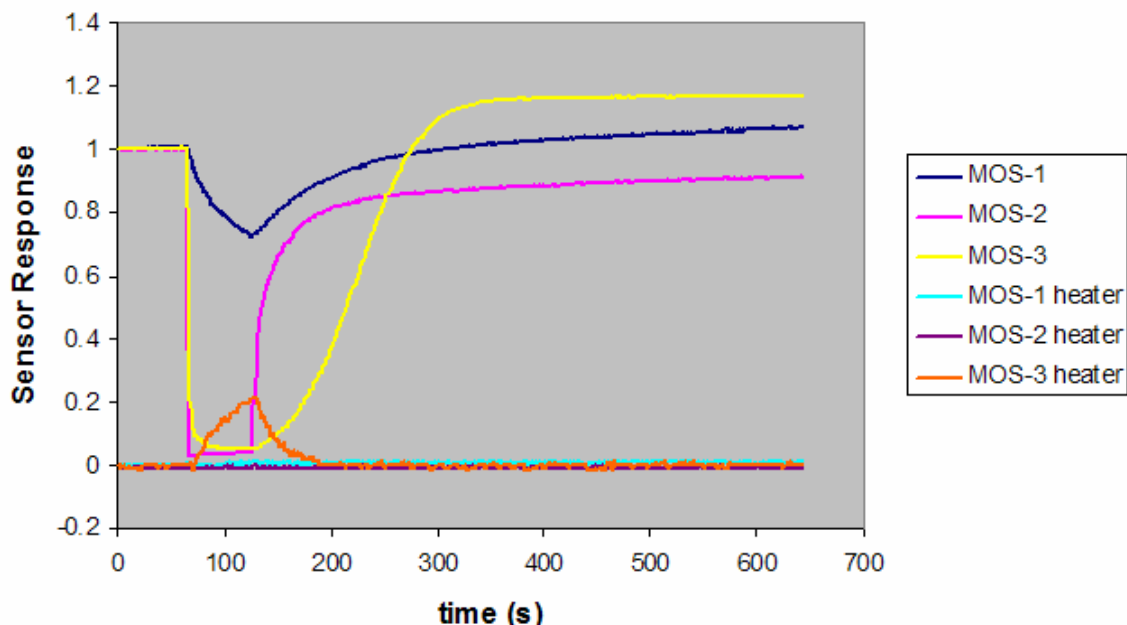


Fig. 23. MOS sensor and MOS sensor heater responses to 8000 mg/m³ hexane vapor exposure (2270 ppm, 23% LEL) at 50% RH and 25C.

4.5 Long-term stability studies

After defining the sensitivity and selectivity properties of the new micro gas sensors, a long-term stability study was carried out. The stability study focused to evaluate whether the sensors can keep their main sensitivity features against CWAs and TICs. The identified target agents for the stability test were as follows:

- MOS-1 and MOS-2: Bis(2-chloroethyl)sulfide; (HD; Sulfur mustard) 2 mg/m³, [for practical reasons simulated by CEPS (chloro ethyl phenyl sulfide) 2 mg/m³]
- MOS-3: Phosgene 6 ppm
- FE: Ammonia 25 ppm

The test was carried out with 3-5 parallel detector prototypes for about 2 months by exposing sensors time to time to target agents. The results are shown in Fig.24.

The results indicate that MOS-1 and MOS-2 can keep well their high sensitivity to sulfur mustard simulant, CEPS. Also FE sensor maintains its sensitivity to ammonia (although not shown in Fig.24). However, among new micro gas sensors, MOS-3 has most

significant issues in long-term stability. Especially in higher operational temperature (65mW) the response to phosgene disappears fast (practically less than 100 hours). The situation is significantly improved by lower operational temperature (45mW).

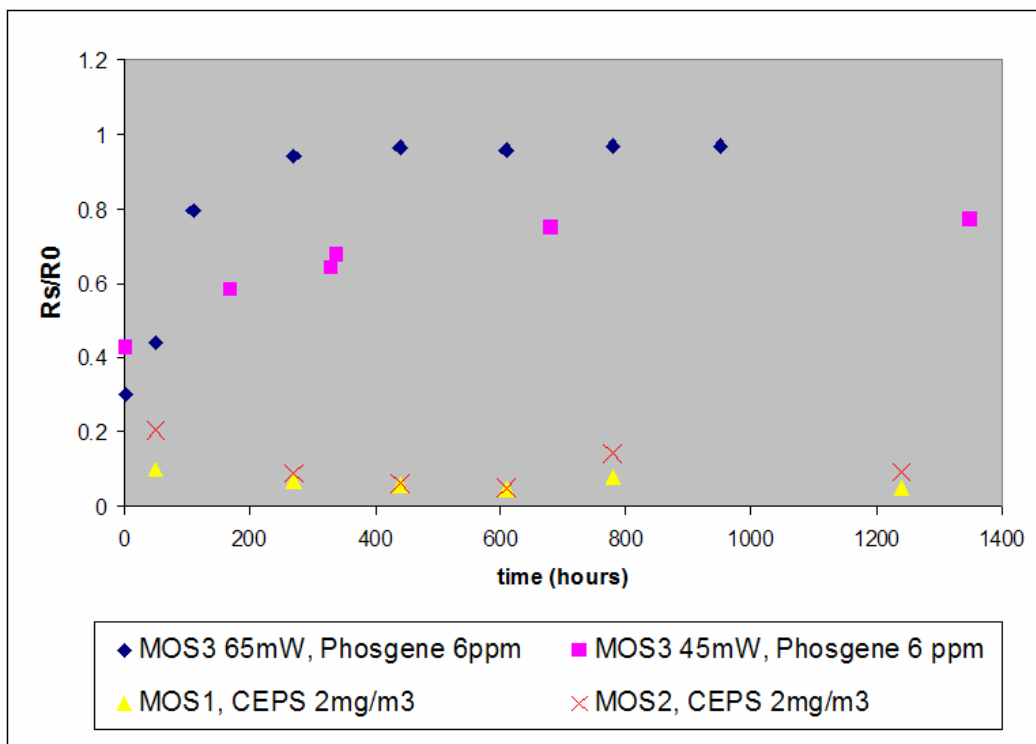


Fig. 24. Long-term stability of the new MOS sensors to their target agents. The data points are averages of 3-5 parallel sensors. The graph shows also the stability of MOS-3 response to phosgene in two different operational temperature (heater power: 45 mW and 65 mW).

The result indicates that in some MOS gas sensors (like MOS-3 in this study), the long-term operational stability may be limited, but that is definitely not a general concern (like it is not for MOS-1 and MOS-2 in this study). Although long-time stability is always advantageous property for any sensor, regarding the CWA-TIC detector in the end-use application, the in-built self-diagnostics and regular maintenance guidance may be sufficient in many contexts.

Furthermore, another form of sensor stability requirement is the stability against long-time storage. In that point of view, MOS gas sensors are generally outstanding compared to many other gas sensor technologies [3], since the main concerns are generally only related to their use and high operational temperature.

4.6 Functional studies with the Advanced Microsensor

The Advanced Microsensor component was developed and fabricated in the clean room facilities of the Helsinki University of Technology. All together, 10 wafer variations, 29 fully processed wafers containing 40 different chip-types were fabricated.

Generally, the main concern of the Advanced Microsensor was its poor fabrication process yield and reproducibility as well as in many occasions observed poor long-term stability in the high operational temperature. However, successful functional studies were carried out, too.

4.6.1 Thermal characteristics of the Advanced Microsensor

In order to measure the temperature of the Advanced Microsensors the resistance of the thermometer was calibrated in the temperature range 20 – 100 °C using a regular thermometer and a Fluke 111 multimeter. In the tests the sensors were kept at the operation temperature of 300 °C in laboratory air or connected to the vapor generation system (air flow through the sensor at 0.2 l/min). The resistances of the thermometer, heater, and sensing layer were recorded during the operation. An estimate of the temperature of the sensor was calculated from the measured thermometer resistance using the calibration data. The measurement DC voltage across the thermometer and the sensing layer was 500 mV and 100 mV, respectively. Keithley 236 and 237 source-measure units were used in the measurements.

The temperature coefficient of the thermometer resistance is 5.7 – 5.8 1/(10⁴ K) to in all sensors. The value of the resistance at 20 °C varies more and depends on the size of the sensor (The Advanced Microsensor design had two size options: 500 µm x 500 µm and 1000 µm x 1000 µm.) The characteristic values of the heaters of the sensors measured in the operation test are listed in Table 4.

TABLE 4. Values of the heaters of the Advanced Microsensors measured in the operation test during heating.

	Sensor area: 1000x1000	Sensor area: 500x500
Heater resistance (Ω)	200	250
Required voltage in order to reach ~300°C (V)	6	4,5
Corresponding heating current (mA)	30	18
Corresponding heating power (mW)	179	81

4.6.2 Sensor material influences on the sensitivity and selectivity

The sensitive layer on the Advanced Microsensor was 20-50 nm thick SnO_2 , deposited in two ways: by ALD (Atomic Layer Deposition) and PVD (physical vapor deposition). The sensor layer was on the top of the micro hot plate structure and patterned as illustrated in Fig. 25. Furthermore, the results of gas sensitivity studies of these different sensor materials are shown in Figs. 26 and 27 as well as in Table 5. The Table 5 shows also for comparison SCCell-2 (thick film type SnO_2 -based MOS sensor) response to similar gas sensitivity tests.

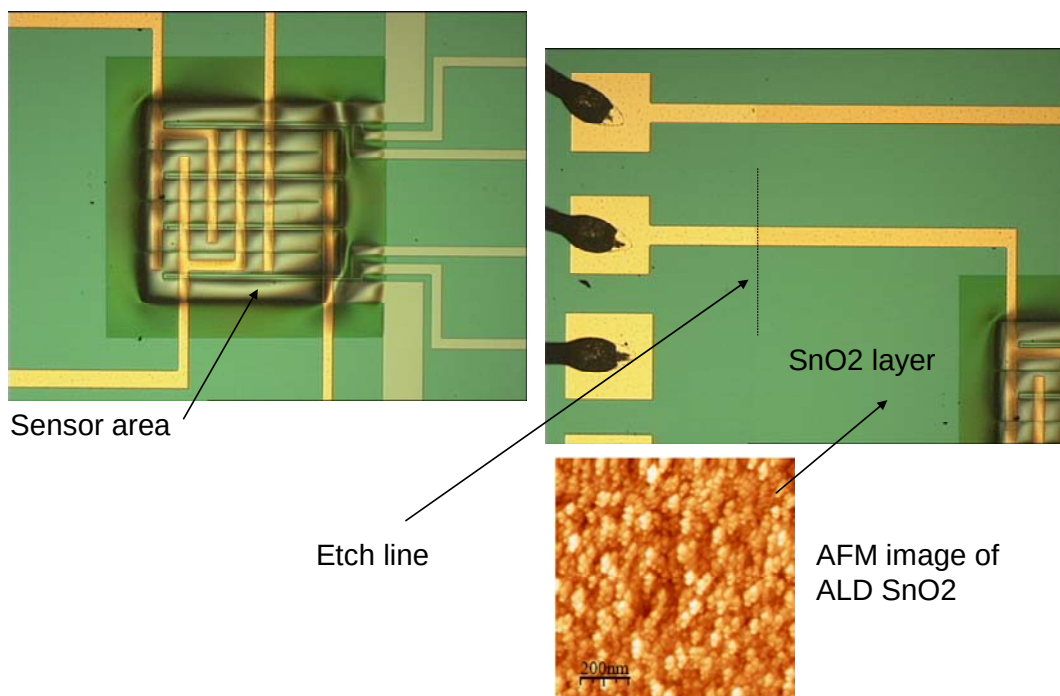


Fig. 25. Top view of the Advanced Microsensor (sensor area 500x500 μm) illustrating the SnO_2 gas sensitive layer. The SnO_2 layer was patterned to leave contact pads free of SnO_2 , but still covering all sensor area.

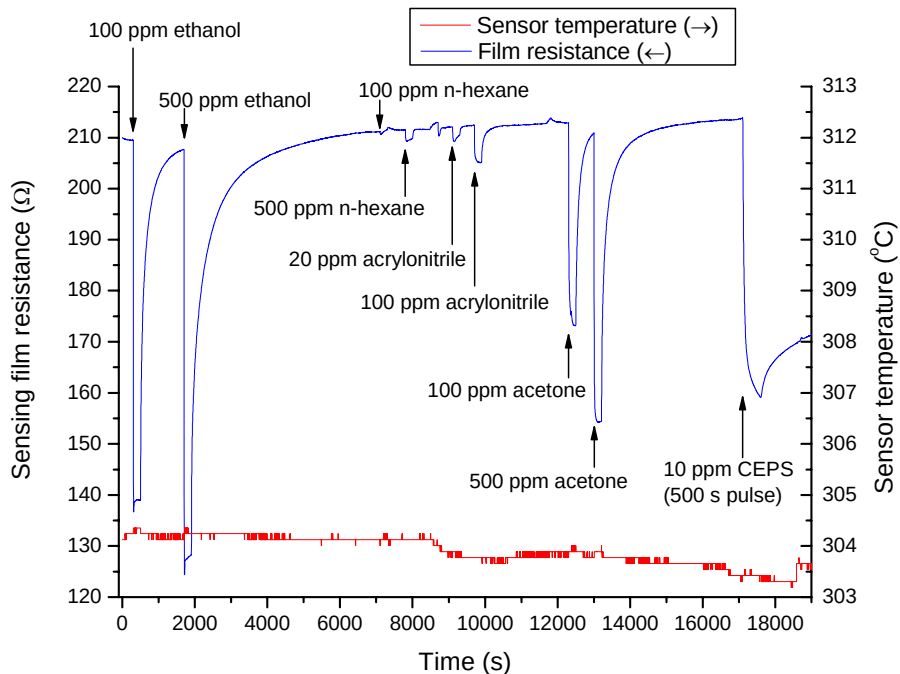


Figure 26. Temperature and sensing film resistance of the Advanced Microsensor with ALD SnO_2 layer during the gas sensitivity test. The humidity is 32 %RH. The length of the all gas pulses except the CEPS pulse is 200 s at 25°C and RH 32%.

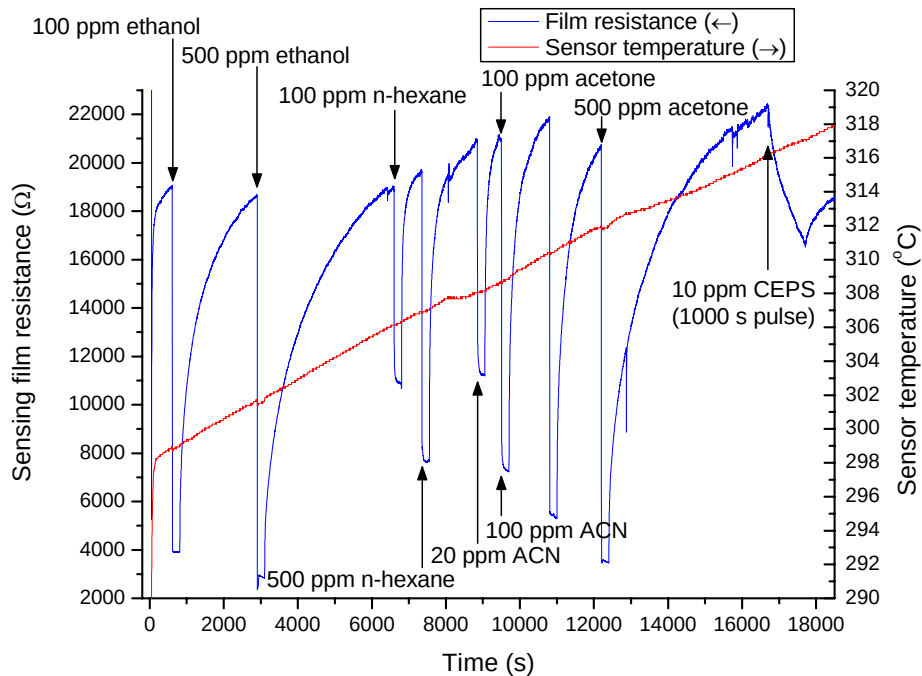


Figure 27. Temperature and sensing film resistance of the Advanced Microsensor with PVD SnO_2 layer during the gas sensitivity test. The humidity is 32 %RH. The length of the all gas pulses except the CEPS pulse is 200 s at 25°C and RH 32%.

TABLE 5. Sensitivities of the sensors with ALD and PVD films to various gases.

Sample	Advanced Microsensor ALD SnO ₂	Advanced Microsensor PVD SnO ₂	SCCell-2 MOS sensor SnO ₂ thick film
Ethanol			
100 ppm	1,5	4,8	6.6
500 ppm	1,6	6,7	
N-hexane			
100 ppm	1,0	1,7	8
500 ppm	1,0	2,5	
Acrylonitrile (ACN)			
10 ppm			2
20 ppm	1,0	1,8	
40 ppm			2.5
100 ppm	1,0	2,9	
Acetone			
100 ppm	1,2	4,1	3.3
500 ppm	1,4	6,2	4.5
2-chloroethylphenyl sulfide (CEPS)			
10 ppm	1,3	1,3	
Bis(2-chloroethyl)sulfide; (HD; Sulfur mustard)			
8 ppm			1.9

The sensitivity characteristics of the Advanced Microsensors depend significantly on the applied SnO₂ material. The sensitivity in general increases in the order: thick film > PVD thin film > ALD thin film. Probably the highest difference between types of SnO₂ films is the high sensitivity of hexane vapor, where conventional thick-film showed clearly highest sensitivity. The reason may be the catalyst additives, such as Pd or Pt that are often added to thick film pastes in order to increase sensitivity to combustible gases.

However, although none of the SnO₂-based sensor show as good sensitivity to sulfur mustard (or its simulant, CEPS) as WO₃-based sensors did, it is interesting to realize that selectivity is clearly best towards this agent when ALD SnO₂ was applied. Furthermore, when comparing the gas response curves of PVD and ALD SnO₂ -based Advanced Microsensors against the highly volatile species, the recovery and baseline stability are much better in the case of ALD SnO₂ than PVD SnO₂. However, the difference in the

response and recovery behaviour of these two sensitive layer types is not significantly different in the case of sulfur mustard exposure.

The main difference between ALD deposited films and PVD deposited films is most likely in their microstructure, where PVD films tend to be more porous and fragile than the dense ALD films. On the other hand, the differences between the exposed chemicals are in their volatility and molecular size, where ethanol, hexane and acrylonitrile exhibit order of magnitude higher volatility than sulfur mustard or CEPS. Therefore, all these results may indicate that diffusion of volatile species into the film microstructure plays more significant role in the case of PVD films while in the case of ALD, the gas-solid interaction is predominantly occurring in the surface of the film.

4.6.3 Conclusions of the Advanced Microsensor studies

In the test it was demonstrated that the Advanced Microsensor samples can perform stable operation without failures. The required heating powers of the sensor prototypes are low: less than 180 mW for large and less than 90 mW for the small sensor to reach about 300°C operational temperature. However, this means that the power consumption of the Advanced Microsensor is higher than in the case of other studied micro hot plate sensors, namely MOS-1, MOS-2 and MOS-3 where heater power were typically in a range 45-65 mW for similar temperature range.

Furthermore, gas sensitivities of the ALD and PVD processed SnO₂ coatings to ethanol, n-hexane, acrylonitrile, acetone, and 2-chloroethylphenyl sulfide (CEPS) were demonstrated. The results were compared to conventional thick film SnO₂-based sensor. The gas sensitivity characteristics between PVD and thick film sensor are quite similar, but ALD SnO₂ possessed differences and interesting possibilities especially in means of selectivity, baseline stability and recovery speed. It should also be expected that proper metal oxide fabrication process can provide new possibilities to tailor MOS gas sensors towards better selectivity against selected CWA and TIC target agents.

4.7 Summary of the functional studies

The Table 6 summarizes the key properties of all novel micro gas sensors according to performed studies. Several of them, like MOS-1, MOS-3 and FE a distinct functionality can be identified, especially when implementing them to the ChemPro chemical detector concept. Furthermore, the Advanced Microsensor concept gives also a good future basis for developing new gas sensor functionalities against any target agent.

TABLE 6. Summary of the detection and identification characteristics of novel micro gas sensors.

Sensor type	Detection and identification performance
MOS-1 WO ₃ -based MOS micro gas sensor	Organosulfur specific sensor Excellent sensitivity to mustard gases, organic sulfides and toxic thiols. Highest sensitivity to nerve agents, especially VX, among semiconductor gas sensors. Very good selectivity – low response to highly volatile organic interferents.
MOS-2 WO ₃ -based MOS micro gas sensor	Generic- TIC and VOC sensor Fast response, fast recovery and low drift. Useful in diagnostics and concentration monitoring. Highly sensitive, although not specific to any gas.
MOS-3 SnO ₂ –based MOS micro gas sensor	Phosgene sensitive sensor Integrated calorimetric transducer option Highest sensitivity and selectivity to phosgene among semiconductor gas sensors. Concerns: drift and selectivity. At 65 mW heater power integrated calorimetric transducer provides ca. 20% LEL response.
FE FE sensor with special catalytic stack layer developed for wide TIC detection	TIC specific sensor Good and specific response to IDLH levels of NH ₃ , PH ₃ , B ₂ H ₆ and AsH ₃ . Negligible response to alcohol or hydrocarbons (<i>i.e.</i> common intereferents).
Advanced Microsensor SnO ₂ -based MOS micro gas sensor	Functionality can be tailored by developing the gas sensitive materials and measurement principles

5 Modeling of the MOS gas sensors

In this section a general model of response of resistive metal-oxide gas sensors is presented. It can be used for all resistive metal-oxide gas sensors with granular n -type semiconductor sensing film. Only oxygen O^- ions and a very simple reducing gas reaction is considered. However, they are enough to understand the most of the responses observed experimentally.

The model consists of two parts: the conduction model and the surface state model. The conduction model describes the conduction of electrons in a grain-structured semiconductor. The surface state model describes the adsorbed ions on the surfaces of the grains. The models are coupled. The conduction model defines the electron density on the surface of the grains which controls the surface ion density in the surface state model. The ion or the static charge density in the grain boundary in turn controls the electron density in the conduction model.

Usually the grain-structured metal oxide materials are n -type semiconductors where all the donors are ionized. Thus the electron density in the bulk region, or inside the grains, is constant and equal to the donor density N_d (per unit volume). Two grains of the metal-oxide semiconductor material is illustrated in Fig. 28. The grain boundary and the energy bands are shown. The existence of surface states (see below) gives rise to electric charge on the surfaces of the grains. This produces the surface potential, which bends the energy bands near the grain boundary. For the conduction electrons the surface potential is a potential barrier, which limits their movement considerably. The band bending gives rise to the depletion of conduction electrons near the surfaces of the grains. The charge on the surfaces of the grains is presented by the grain-boundary charge density N_B (per unit area).

The surface states are localized energy levels in the forbidden band gap. Free electrons of the grain-structured film can be trapped on the surfaces of the grains or grain boundaries in two kinds of surface states: intrinsic and extrinsic surface states [12]. The trapping process is illustrated in Fig. 28. The intrinsic states are composed of the states which are created by the existence of the surface itself and the states which are created by surface impurities, doping, and surface defects [12, 14]. The extrinsic states surface states are created by adsorbed gas atoms or molecules at the surface [12]. The existence of the surface states gives rise to electronic trapping processes. If the electron is trapped in an adsorbed atom or molecule (extrinsic state) creating an ion, this process is called ionization. In this work only the extrinsic surface states are considered.

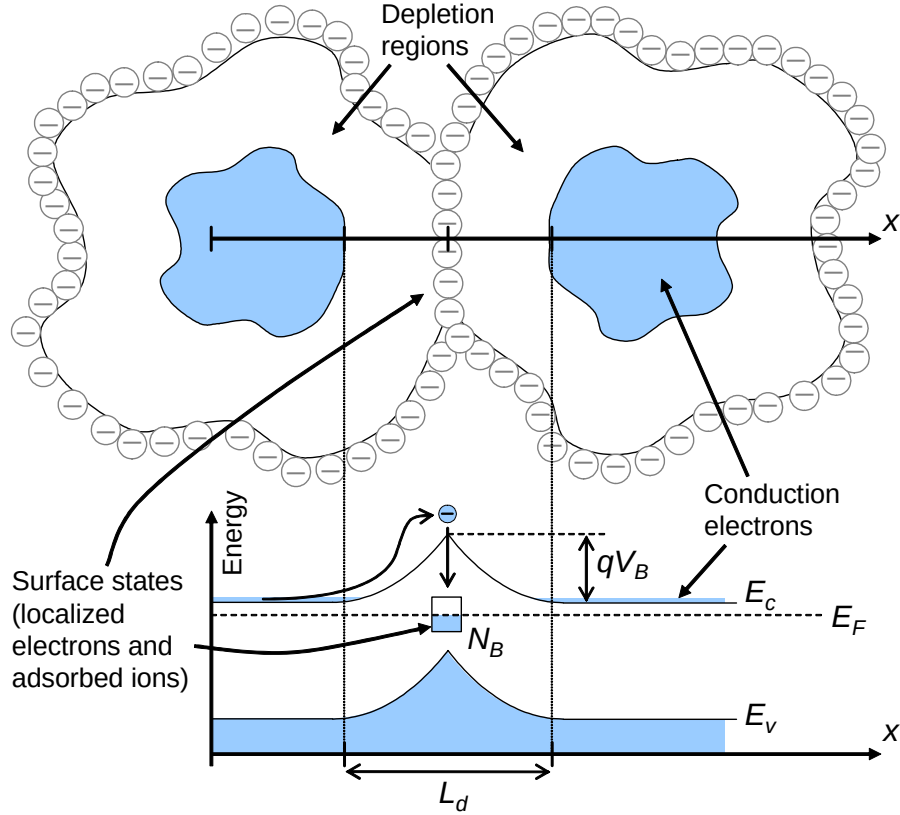


Figure 28. A schematic picture of the grain boundary and the energy bands of the metal-oxide semiconductor material [13]. A trapping of a conduction electron is illustrated. The grain boundary is at $x = 0$. The total width of the depletion region in the grains is L_d . E_c is the bottom of the conduction band, E_v the top of the valence band, E_F the Fermi level, q the electron charge, and V_B the grain-boundary potential barrier, respectively.

5.1 Conduction model

The electric current flowing through the grain-boundary region can be calculated using the drift-diffusion theory and the depletion region approximation [4, 15, 16]. In the derivation it is assumed that the height of the potential barrier V_B is much larger than the thermal voltage $k_B T/q$. The potential barrier V_B is given by [4, 15, 16]

$$V_B = \frac{qN_B^2}{8\epsilon N_d}, \quad (1)$$

where q is the electron charge, N_d the donor density, and ϵ the permittivity of the material, respectively.

When the bias voltage or the DC voltage across the grain-boundary region is low, the DC or AC conductance of the grain-boundary region or the potential barrier has the proportionality [4, 15, 16]

$$G_{barr} \propto \sqrt{V_B} \exp\left(-\frac{qV_B}{k_B T}\right), \quad (2)$$

where k_B is Boltzmann's constant and T the absolute temperature, respectively. Eq. (2) is also valid for the conductance of the whole grain-structured film. Conductance G is the inverse of resistance R , i.e. $G = 1/R$.

In steady-state the density of electrons at the grain-boundary is given by [13]

$$n_B = N_d \exp\left(-\frac{qV_B}{k_B T}\right) \cosh\left(\frac{qU}{2k_B T N_{barr}}\right), \quad (3)$$

where U is the bias voltage, and N_{barr} the number of grain boundaries or potential barriers, respectively.

5.2 Surface state model

In typical operating temperatures of resistive metal-oxide gas sensors, 300 – 400 °C, oxygen is chemisorbed dissociatively and the atomic oxygen O^- ion is the dominant oxygen species on the surface [4, 12, 17–20] The oxygen chemisorption reaction can be written as [21, 22]



where S denotes an adsorption site and k_c and k_{-c} are the forward and reverse rate constants for oxygen chemisorption, respectively. In the case of dominant O^- ions the oxygen ionization, or electron extrinsic surface state trapping, reaction can be written as [21, 22]



where k_i and k_{-i} are the rate constants for oxygen ionization, or electron extrinsic surface state trapping and releasing, respectively. The rate constants k_c , k_{-c} , k_i , and k_{-i} depend exponentially on the temperature. Here it is assumed that the temperature is constant.

In the simplest form the effect of the reducing gas R on the sensing film is given by an irreversible reaction [21, 22]



where the reducing gas R reacts with the preadsorbed oxygen ions O^- and leaves the surface as RO. k_r is the rate coefficient of the reaction between the reducing gas R and the preadsorbed oxygen ions. Reactions (b) and (c) correspond to the rate equation [21, 22]

$$\frac{dN_B}{dt} = k_i n_B N_O - (k_{-i} + k_r [\text{R}]) N_B = k_i n_B (N_O^{\text{tot}} - N_B) - (k_{-i} + k_r [\text{R}]) N_B , \quad (\text{4})$$

where $N_O = [\text{O}_{\text{ads}}]$ the density of the neutral adsorbed oxygen on, $N_B = [\text{O}_{\text{ads}}^-]$ the density of ionized oxygen adatoms or the density of the occupied extrinsic surface states on the grain boundary, $[\text{R}]$ the concentration of the reducing gas, and n_B is the electron density on the grain boundary, respectively. The total density of the adsorbed oxygen or the total density of extrinsic states is given by $N_O^{\text{tot}} = [\text{O}_{\text{ads}}] + [\text{O}_{\text{ads}}^-] = N_O + N_B$. Usually the chemisorption reaction is fast, hence only the ionization rate equation, Eq. (4), is needed [12, 21, 22]. In this work it is assumed this is the case.

In the steady state the chemisorption and the ionization processes have been stabilized.

Setting $\frac{dN_B}{dt} = 0$ in Eq. (4) gives the density of oxygen ions in the steady state [13]

$$N_B = \frac{n_B N_O^{\text{tot}}}{\alpha_i (1 + \alpha_R) + n_B} , \quad (\text{5})$$

where

$$\alpha_i = \frac{k_{-i}}{k_i} , \quad (\text{6})$$

and

$$\alpha_R = \frac{k_r [\text{R}]}{k_{-i}} . \quad (\text{7})$$

The parameter α_R is the ratio between the emission and ion removal rates. Without applied voltage in the absence of a reducing gas, $[R] = 0$ and $\alpha_R = 0$, the steady-state density of the oxygen ions is (cf. Eq. (6)) [13]

$$N_B^0 = \frac{n_B^0 N_O^{tot0}}{\alpha_i + n_B^0}, \quad (8)$$

where n_B^0 is the steady-state grain-boundary electron density and N_O^{tot0} the total density of adsorbed oxygen in clean air and without applied voltage, respectively. The electron density n_B^0 is given by (cf. Eq. (3))

$$n_B^0 = N_d \exp\left(-\frac{qV_B^0}{k_B T}\right), \quad (9)$$

where V_B^0 is the grain-boundary potential corresponding to N_B^0 (see Eq. (1)). Solving the ratio of the rate constants from Eq. (8) gives

$$\alpha_i = \left(\frac{N_O^{tot0}}{N_B^0} - 1\right) n_B^0 = \left(\frac{1}{\beta} - 1\right) n_B^0, \quad (10)$$

where ionization or extrinsic state occupancy ratio is given by

$$\beta_i = \frac{N_B^0}{N_O^{tot0}}. \quad (11)$$

β_i is also defined by the energy difference between the trap or ion level and the Fermi level. Substituting Eq. (10) into Eq. (5) gives a formula for the steady-state density of oxygen ions normalized in respect to N_B^0 [13]

$$\frac{N_B}{N_B^0} = \frac{N_O^{tot}}{N_O^{tot0}} \cdot \frac{\frac{n_B}{n_B^0}}{1 + \alpha_R + \beta_i \left(\frac{n_B}{n_B^0} - 1 - \alpha_R\right)}. \quad (12)$$

Assuming that the reducing gas does not affect the total density of adsorbed oxygen, Eq. (12) reduces to [13]

$$\frac{N_B}{N_B^0} = \frac{\frac{n_B}{n_B^0}}{1 + \alpha_R + \beta_i \left(\frac{n_B}{n_B^0} - 1 - \alpha_R\right)}. \quad (13)$$

If the total density of oxygen atoms is equal to the total density of surface states [S] on the grain boundary, [S] must be much smaller than the surface atom density in order to fulfill the Weisz limitation, which states that with reasonable values of the parameters in Eq. (1) the ratio between the ion density N_B and the surface atomic density must be less than 1 % [23]. This would mean that oxygen can adsorb only on a few possible sites on the surface.

5.3 Combining the models

In order to represent the gas sensor responses in the simplest form, the formulas are normalized to the case where the sensing film is in the steady state without the applied bias voltage in clean air. This case is denoted by 0-superscripts. By using the definitions

$$\nu = \frac{N_B}{N_B^0} \quad (14)$$

and

$$\nu_{tot} = \frac{N_O^{tot}}{N_O^{tot0}}, \quad (15)$$

and Eqs. (6), (10), and (11), Eq. (4) can be rewritten in the form

$$\frac{d\nu}{dt} = k_{-i} \left\{ \frac{n_B}{n_B^0} \cdot \frac{\nu_{tot} - \beta_i \nu}{1 - \beta_i} - \nu(1 + \alpha_R) \right\}. \quad (16)$$

Assuming that the total density of adsorbed oxygen is constant, $\nu_{tot} = 1$, and plugging in Eqs. (3) and (9) into Eq. (16) gives

$$\frac{d\nu}{dt} = k_{-i} \left\{ \exp \left[-\frac{qV_B^0}{k_B T} (\nu^2 - 1) \right] \cosh \left(\frac{qU}{2k_B T N_{barr}} \right) \cdot \frac{1 - \beta_i \nu}{1 - \beta_i} - \nu(1 + \alpha_R) \right\}. \quad (17)$$

Eqs. (14) and (2) give for the conductance of the film

$$\frac{G_{barr}}{G_{barr}^0} = \frac{\sqrt{V_B} \exp \left(-\frac{qV_B}{k_B T} \right)}{\sqrt{V_B^0} \exp \left(-\frac{qV_B^0}{k_B T} \right)} = \nu \exp \left[-\frac{qV_B^0}{k_B T} (\nu^2 - 1) \right], \quad (18)$$

where G_{barr}^0 is the conductance of the film in clean air. Eq. (18) is valid for DC and AC with low values of the bias voltage U , i.e. in the linear regime. In the nonlinear regime,

with high values of the bias voltage U , the dynamical behavior of the conduction across grain-boundary is more complex, and exotic effects such as negative capacitance arise [24].

5.4 Evaluation of the combined model

A typical response of a resistive metal-oxide gas sensor is shown in Fig. 29. The response is divided into 5 parts depending on the state of the sensing film:

1. Initialization. When the temperature of the sensing film reaches the operation temperature, the surface is quickly filled with chemisorbed oxygen atoms. The ionization of oxygen adatoms (i.e. electron trapping) begins. First the conductance and the surface electrons density are high due to low density of ions on the surface.
2. After the initialization ionization or trapping process has reached steady state.
3. The introduction of reducing gas quickly removes many of the O^- ions from the surface. The conductance is quickly increased due to the decreased surface charge density.
4. When the ion removal rate together with the trap emission rate is equal to the ionization or trapping rate, equilibrium is reached. The conductance and the surface electrons density are high due to low density of ions on the surface.
5. Recovery. This part of response is very similar to the initialization. First the conductance and the surface electrons density are high due to low density of ions on the surface.

In general the response characteristics are described by the fast removal of the adsorbed oxygen ions by the reducing gas and slow accumulation by the ionization (i.e. electron trapping) process.

Various simulation results are shown in Figs. 30 – 32. In Fig. 30 the ion or extrinsic state occupancy β_i is varied. With equal k_{-i} the higher values of β_i result in longer initialization and recovery times. In Figs. 31 and 32 the parameter α_R , which is proportional to the density of the reducing gas, is varied. The general behavior is that the both the response and recovery times depend on α_R . Thus with low concentration of reducing gas the response time is long, but the recovery time is short. With high concentration of reducing gas the response time is very short, but the recovery time is long.

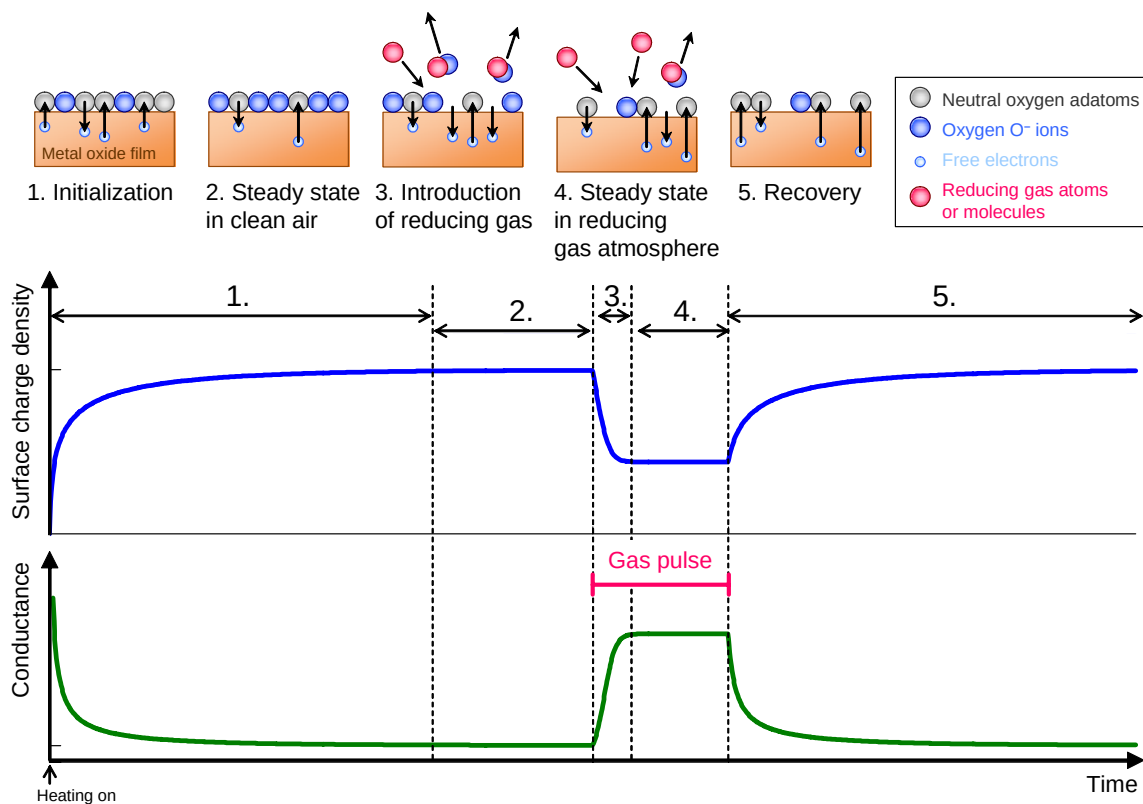


Figure 29. Illustration of a typical response of a resistive metal-oxide gas sensor. The surface charge density on the sensing film and conductance of the film are plotted. In the beginning the heater of the sensor is switched on. Conductance is inverse of resistance, $G = 1/R$.

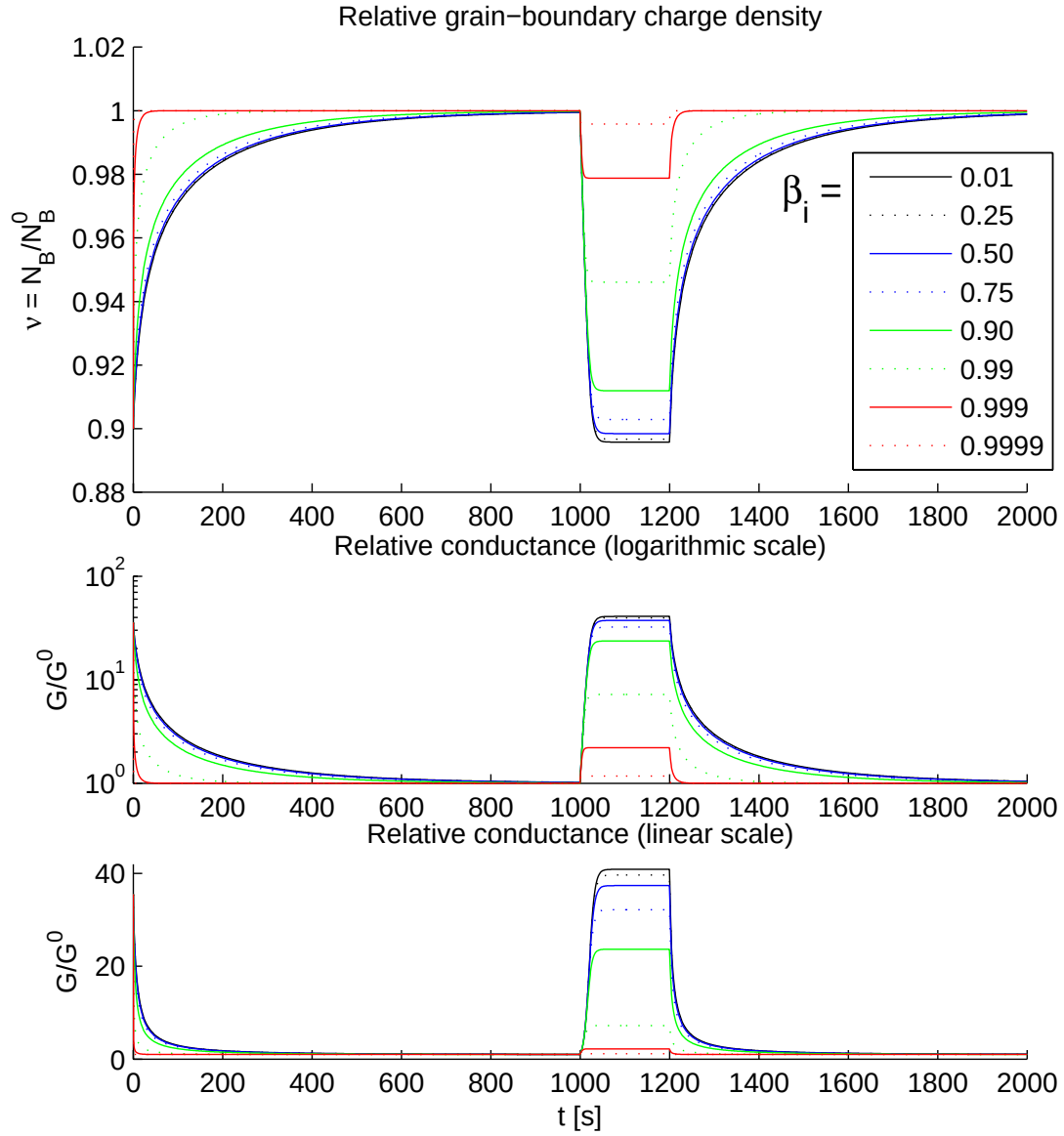


Figure 30. Plot of gas sensor response with various values of the ion ratio β_i using Eq. (17), $V_B^0 = 1$ V, $U = 0$ V, $T = 600$ K, $k_i = 10^{-4}$ s $^{-1}$, and $\alpha_R = 50$. The first part of the response simulates the initialization response because the states are partially empty ($v(t = 0) = 0.9$). The 200 s long gas pulse begins at $t = 1000$ s. The ratio of conductances G/G_0 was calculated using Eq. (18).

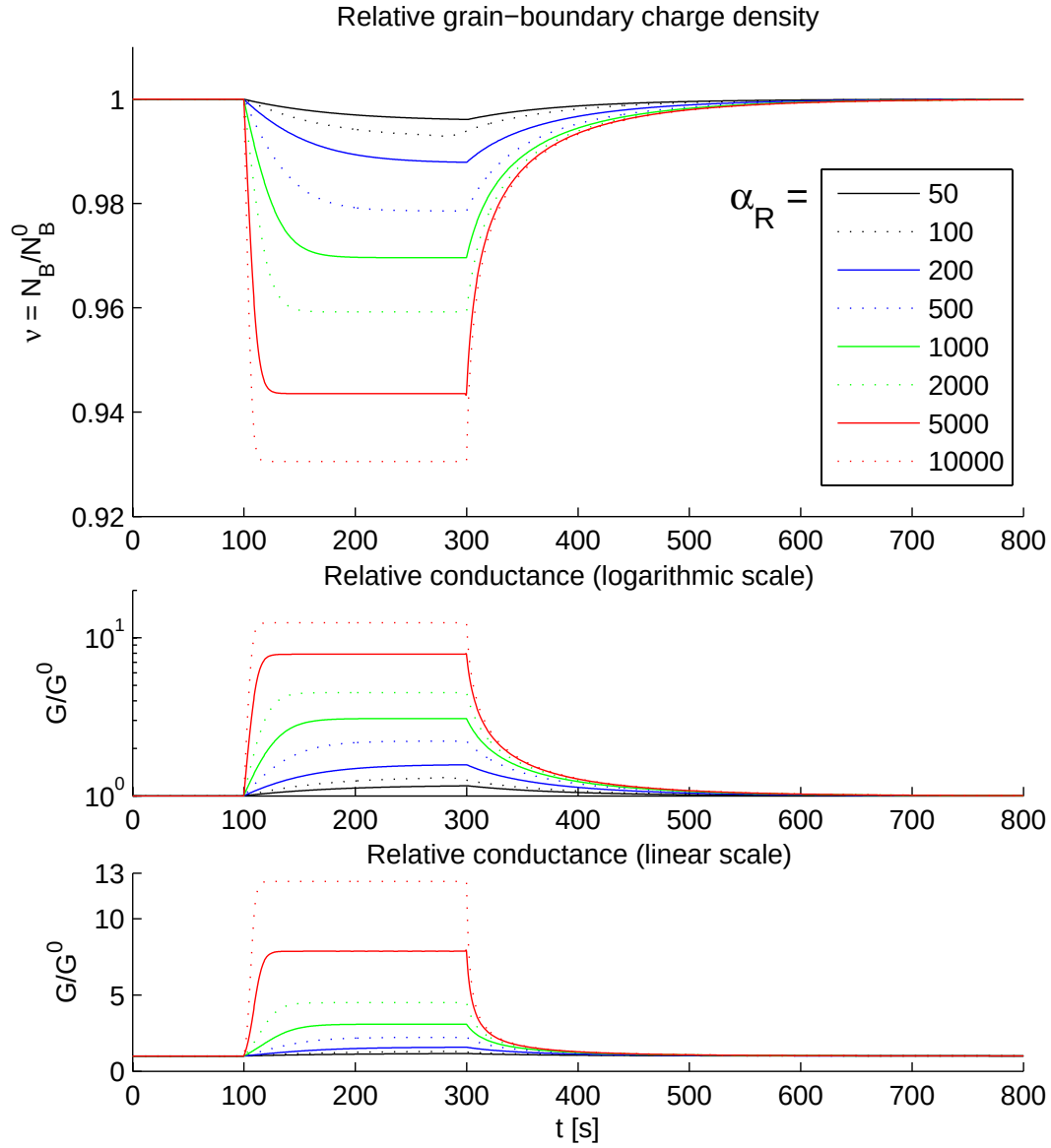


Figure 31. Plot of gas sensor response with various values of α_R using Eq. (17), $V_B^0 = 1$ V, $U = 0$ V, $T = 600$ K, $k_{-i} = 10^{-6} \text{ s}^{-1}$, and $\beta_i = 99.99$ %. α_R is proportional the concentration of the reducing gas. The 200 s long gas pulse begins at $t = 100$ s. The ratio of conductances G/G_0 was calculated using Eq. (18).

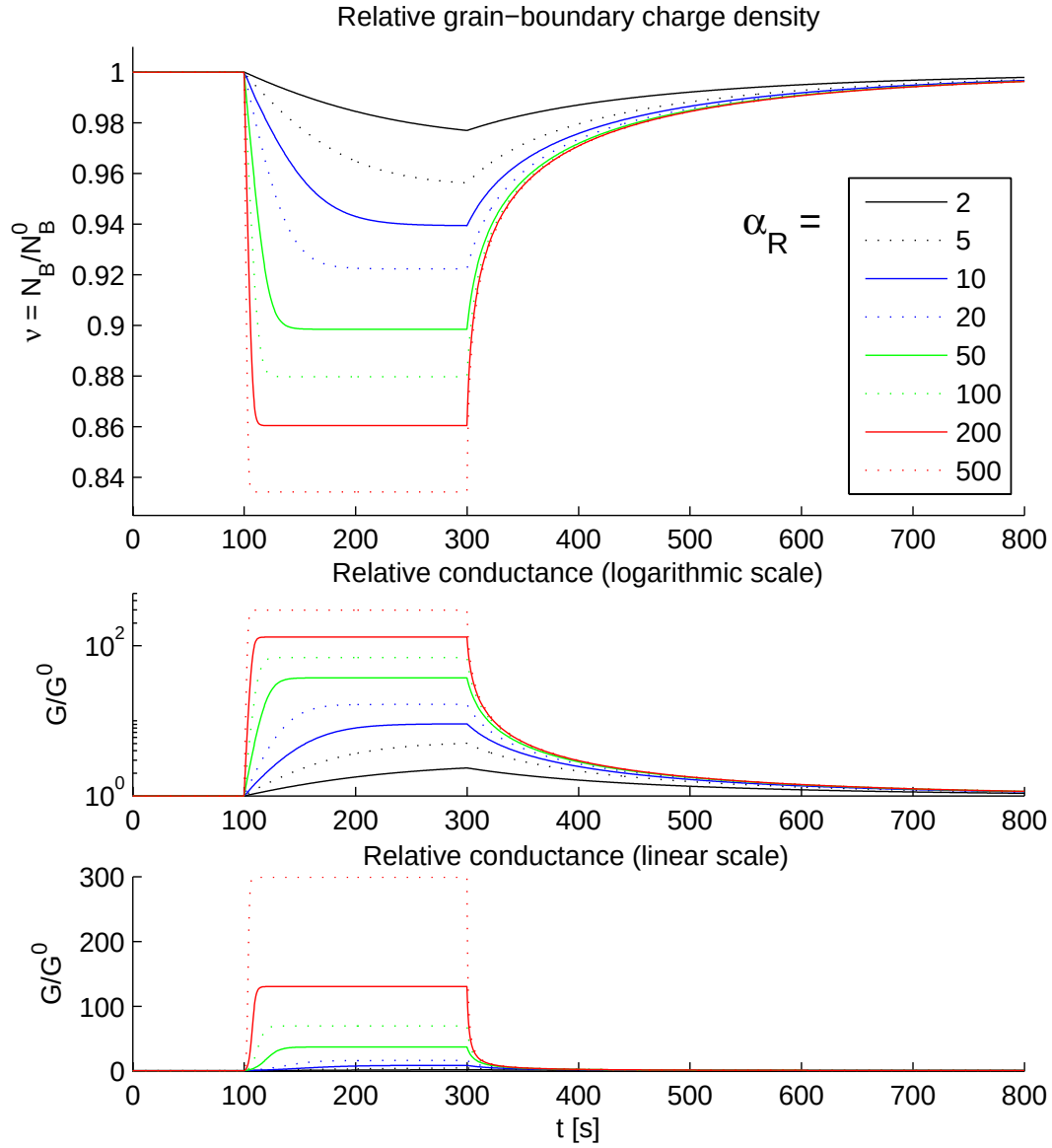


Figure 32. Plot of gas sensor response with various values of α_R using Eq. (17), $V_B^0 = 1$ V, $U = 0$ V, $T = 600$ K, $k_{-i} = 10^{-4}$ s $^{-1}$, and $\beta_i = 50$ %. α_R is proportional the concentration of the reducing gas. The 200 s long gas pulse begins at $t = 100$ s. The ratio of conductances G/G_0 was calculated using Eq. (18).

5.5 Conclusion of the modeling part

By comparing the model results to experimental curves obtained in MOS gas sensors' functional studies, the results show that the response curves are very similar to the ones observed experimentally. This indicates that the approach to employ combined surface state and conduction model is good basis in many occasions to explain the sensor behaviour and its transducer mechanism.

However, in some experiments the conductance behaves in the opposite manner after the first drop during the gas pulse and sometimes the recovery curve can have second order features. The oxygen chemisorption model, does not explain these features, indicating that there is still room to improve the model by taking into account more complexity such as details of the chemical surface reaction mechanisms as well as influences of common air constituents, such as water vapor.

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