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Integrated high temperature gas sensor system based on bulk acoustic wave resonators

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Abstract

A high temperature gas sensor system based on bulk acoustic wave resonators is developed. The system consists of CeO_2 coated langasite resonators with a special electrode design to detect mechanical and conductivity changes in the sensor film. The data acquisition is performed using a specialized compact impedance analyser and a data processing software using methods of computational intelligence. The system is tested in different atmospheres containing mixtures of CO and H_2 and exhibits selectivity to these gases.

Keywords: Langasite; High temperature microbalance; Resonant gas sensor; Impedance analyser

1. Introduction

Due to the increasing relevance of PEM fuel cells highly effective fuel reformers are required. In particular, the formation of CO must be minimized to prevent catalyst poisoning of the PEM fuel cells. An improved reformer performance and the suppression of the unwanted by-product of the reforming process, CO, is expected if already the first reforming step at about 600–700 °C can be monitored and controlled by appropriate sensors. However, for the distinction of CO and H_2 at high temperatures new sensor concepts are demanded.

Aim of the work is the demonstration of the capabilities of a new sensor system to distinct between these two gases at high temperatures. The investigations of other gas mixtures is beyond the scope of this paper. Common metal oxide based conductivity gas sensors show only limited selectivity on H_2 and CO. The influence of these gases on the conductivity is very similar. Optical sensors permit indeed a distinction of H_2 and CO, but high costs prevent an application in small- and medium-scale systems.

The selectivity improvement of metal oxide based sensors, requires additional information about the sensor films. Resonant sensors, e.g., bulk acoustic wave (BAW) resonators, allow the detection of resonance frequency shifts caused by changes in mechanical properties of the sensing layer. For example, density (or mass) and stiffness are determined by gas phase dependent variations of the sensor film stoichiometry. Using this information in addition to the conductivity delivers often orthogonal information about the gas composition.

New high temperature stable piezoelectric materials like langasite ($La_3Ga_5SiO_{14}$) and gallium orthophosphate ($GaPO_4$) enable the development of such improved sensors. These materials can be excited to bulk acoustic waves at temperatures up to 1470 and 900 °C, respectively. At higher temperatures a higher damping of the resonators due to increasing bulk conductivity occurs. This leads to broader resonance spectra, but an exact determination of the resonance frequency is still possible. Further, at temperatures of about 600 °C the stability of langasite is ensured at oxygen partial pressures down to 10^{-20} bar [1]. Therefore, the latter material is suitable for gas sensing applications in reducing atmospheres and can be operated in the first stage of a fuel reformer.

This paper presents a sensor system based on langasite bulk acoustic wave (BAW) resonators. The overall system (Fig. 1)

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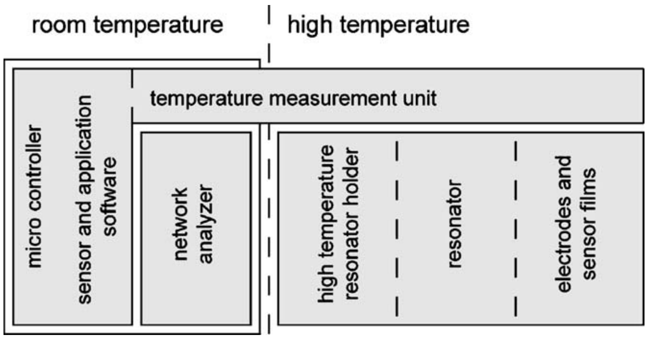

Fig. 1. Sensor system overview.

consists of a high temperature stable piezoelectric resonator coated by a sensor film, an alumina holder, an impedance analyser for data acquisition and a data processing software using methods of computational intelligence for obtaining the present gas concentration.

2. Sensor system description

2.1. Resonator and holder

Langasite BAW resonators coated with a metal oxide sensor film are used as sensing element within the sensor system. The design of the resonators is shown in Fig. 2. Thereby, keyhole shaped platinum electrodes of different diameter are deposited at the front and rear side of each resonator. Layout A represents the situation where the sensor film is deposited on the larger electrode. In particular, it does not exceed the electrode area. Consequently, the platinum electrode fixes the electrode area independently of the sensor film conductivity and the resonance behaviour is solely determined by mechanical properties of the sensor film (microbalance mode). In contrast, layout B is featured by a sensor film deposited on the smaller electrode. The diameter of the sensor film exceeds the platinum electrode and corresponds approximately to that of the larger rear electrode. This configuration leads to sensor film conductivity dependent effective electrode areas (conductivity mode). Electrical and mechanical changes can be determined simultaneously using both electrode layouts. Consequently, a single data acquisition technique can be applied which simplifies the data acquisition and reduces the costs of the sensor system.

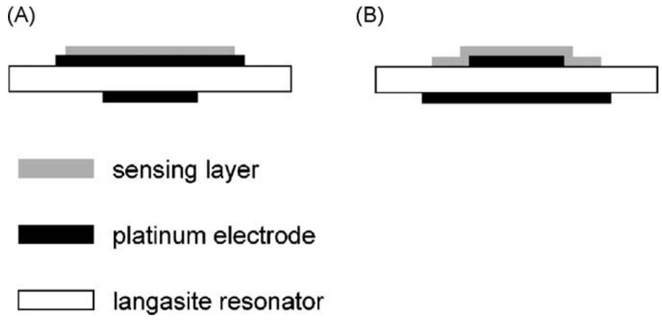

Fig. 2. Cross section of the used electrode and sensor film layout for microbalance (A) and conductivity (B) mode.

In order to set up the resonators in the gas measurement chamber, resonator holders made of alumina are developed. These holders are equipped with conductors for contacting the resonators. On the rear side of the resonator holder a meander type heater structure is deposited which offers the possibility to adjust and control the temperature in the proximity of the resonators. Platinum is chosen as material for the conductors because of its high-temperature stability and its resistance in harsh environments. The platinum conductor paths are prepared using the cost-effective screen-printing technology. A fritless paste (Paste 64120410, Ferro) is chosen. After firing the thickness of the platinum film is about 5 μm and exhibits a good adhesion on the alumina substrate material.

2.2. Data acquisition electronics

In order to characterise the resonance behaviour of the langasite resonators at high temperatures, a measurement device is preferred which provides multiple information such as frequency shift and damping figure. Normally, conventional low coast oscillator circuits cannot fulfil this requirement. In particular, they may fail to excite resonant gas sensors since they are highly damped at high temperature. Considering these limitations, a data acquisition device based on impedance measurements is necessary. For most impedance spectroscopy applications precise commercial impedance analysers are available, covering a broad impedance and frequency range. All these commercial analysers are bulky and costly thus being suited as laboratory devices but not as sensor electronics for industrial applications with requirements of small size and low cost. Therefore, a compact and fast impedance analyser was developed. The device is specially adapted to the frequency range of the resonators and well suited for process control applications.

The developed sensor interface for measuring the complex impedance depending on frequency consists of three main parts (Fig. 3):

(1) a sweep generator to generate the frequency swept sine signal which excites the gas sensor in the vicinity of the fundamental mode (5 MHz) and of the 3rd overtone (15 MHz),

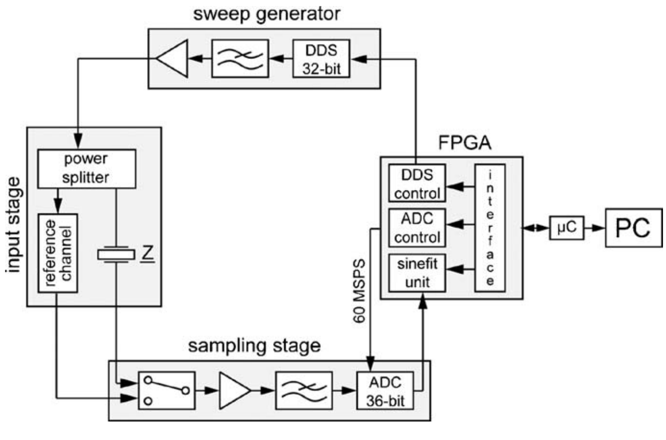

Fig. 3. Sensor electronics for the compact impedance analyser.

(2) an input stage to connect the gas sensor with the sensor electronics and
(3) an impedance analyser, which detects the reference signal and the signal of the device under test and calculates the complex sensor impedance $\underline{Z}(\omega)$ at each frequency.

Amplitude and phase of sine signal $\underline{V}_Z$ in Fig. 3 is depending on the complex sensor impedance and thus the complex voltage ratio $\underline{r}(\omega)$ in Eq. (1) is determined on that impedance, too.

$$\underline{r}(\omega) = \frac{\underline{V}_Z(\omega)}{\underline{V}_{\mathrm{ref}}(\omega)} = \frac{|\underline{V}_Z(\omega)|}{|\underline{V}_{\mathrm{ref}}(\omega)|} \mathrm{e}^{j\phi_{\mathrm{V}}} \qquad (1)$$

The wiring of the resonator holder and the properties of the impedance analyser should not influence the result of the measurement. In practice, the electronics parameters (e.g. stray capacitances) are unknown. Thus, a calibration must be done to accurately calculate the complex sensor impedance $\underline{Z}(\omega)$ [2].

The developed sensor electronics is shown schematically in Fig. 4. A Direct-Digital-Synthesizer (DDS) is used to generate the frequency swept sine signal. Its output spectrum contains the fundamental plus aliased signals (images) and therefore a low-pass filter is implemented to suppress the effects of non-harmonic images and other spurious signals.

Based on transmission method the input stage is made up of reference channel with $\underline{V}_{\mathrm{ref}}$ and measuring channel with $\underline{V}_Z$. Attenuators used in both channels decouple the sensor impedance from sensor electronics and realise adaptation to characteristic impedance of connecting cables. The complex impedance is determined using a combination of a Direct-Sampling-Technique (DST) and a sine correlation method. Using the DST, both sine waves $\underline{V}_Z$ and $\underline{V}_{\mathrm{ref}}$ are directly analogue-to-digital converted without extended analogue signal pre-processing. Following, the amplitude $|\underline{V}|$ and phase ω_{V} of the corresponding sampled sine wave are determined using the sine correlation technique determines. This combination of both techniques rejects harmonics and DC-offsets very well, and noise effects are significantly reduced by the selection of appropriate integration times (respectively by the number of samples). A specific Field Programmable Gate Array Logic (FPGA) hardware implementation allows real time digital signal processing for the sine correlation method. With using amplitude and phase for sampled sine wave $\underline{V}_Z(\omega)$ and $\underline{V}_{\mathrm{ref}}(\omega)$ at each frequency, the microcontroller (μC) calculates the complex voltage ratio $\underline{r}(\omega)$ and respectively the complex sensors impedance $\underline{Z}(\omega)$ according to (2).

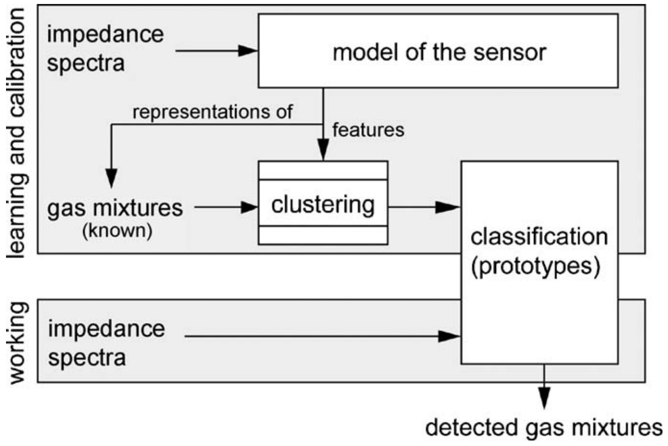

Fig. 4. Data processing scheme.

2.3. Data processing

To by-pass the problem of analysing a complex physical model the data processing is performed by methods of computational intelligence, in particular clustering. This also permits an easier evaluation of multidimensional data sets. The applied data processing can be divided into two main parts, the learning/calibration phase and the working phase (Fig. 4). During the learning/calibration phase, a phenomenological model of the resonance behaviour is used to extract significant features from the measured data. Based on known gas concentrations these features are used to classify the data and to assign them to a certain number of clusters. The resulting classification set is used to acquire the unknown gas mixture from the recorded data during the working phase.

The required features for classification are extracted from the impedance spectra of the resonators, which are measured in the vicinity of the resonance frequency. The maximum of the real part of the admittance can be described by a Lorentzian function. The parameters of this function are determined using a non-linear Levenberg–Marquardt fit procedure. The data presented here bases on the evaluation of the peak frequency f and is used as parameter for cluster analysis. A temperature compensation using the 3rd overtone of the resonator, as described in [1], is performed and suppresses effectively temperature dependent fluctuations of the resonance frequency. The temperature compensated frequency f_{tc} is obtained for the resonators operated in the microbalance (f_{MM}) and conductivity (f_{CM}) mode to build a two-dimensional feature vector for clustering.

The process of clustering can be described as the minimization of the cost function J (see Eq. (2)). Every x of N feature vectors has a distance d to a cluster-prototype v of C clusters and belongs to a cluster with a membership value of u_m. Thereby x is a single feature vector and N the total number of feature vectors.

$$J_{\mathrm{q}}(U, V) = \sum_{j=1}^{N}\sum_{c=1}^{C}(u_{j,c})^m d_c^2(x_j, v_c) \to \min_{U,V} \qquad (2)$$

The determined clusters represent features of certain gas mixtures and are obtained during the learning/calibration phase. After that, an unknown gas composition can be acquired by calculating the distance d of a feature measured during the working phase from this cluster-prototype. In Section 4.2 the application of clustering methods is shown at real measurement data.

3. Test procedure

A sensor system equipped with CeO_2 coated resonators is examined at 600 °C. The used resonators are machined using a Czochralski-grown langasite single crystal provided by the Institute of Crystal Growth (Berlin-Adlershof, Germany) [3]. Disks

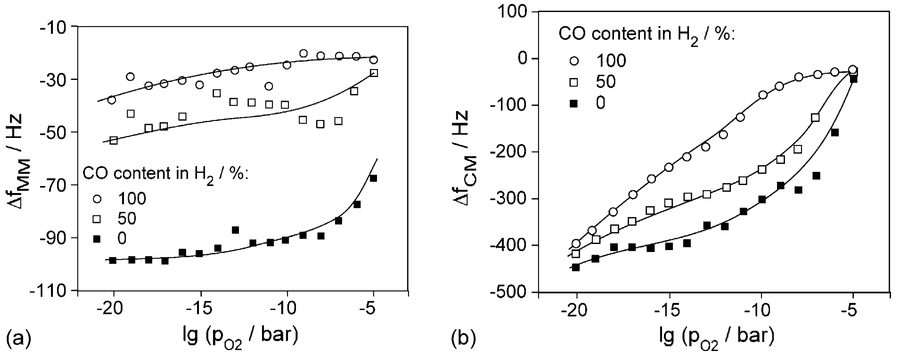

Fig. 5. Temperature compensated resonance frequency of CeO_2-coated resonators in microbalance (a) and conductivity (b) mode at different gas composition containing a 0.25% H_2/CO mixture in argon.

are cut perpendicular to the y-axis and polished subsequently. The thickness of the resonators is 270 μm leading to a resonance frequency of about 5 MHz. The platinum electrodes and the CeO_2 sensor films are deposited on the resonator using pulsed laser deposition (KrF excimer laser, $\lambda = 248$ nm, 200 mJ pulse energy). The sensor film of the resonator operated in microbalance mode is thereby twice as thick (400 nm) as on the resonator operated in the conductivity mode (200 nm) to increase the influence of the mechanical properties on the resonance frequency.

The measurements are realized using a gas tight furnace, where gas mixtures of argon containing 0.25% CO or H_2 or a mixture of these gases can be supplied. A constant oxygen partial pressure is adjusted by adding oxygen to the gas mixture using a zirconia oxygen ion pump (ZIROX GmbH, Germany). Thereby, the oxygen partial pressure ranges from 10^{-4} to 10^{-20} bar at gas flow rates of 20 cm^3 min^{-1}.

4. Results

4.1. CeO_2 sensor films

Fig. 5 shows the dependence of the temperature compensated resonance frequency f_{tc} from the oxygen partial pressure for different gas mixtures. The resonators operated in different modes (microbalance and conductivity mode) exhibit different curve progressions. Furthermore, both resonators show a different behaviour to a given gas mixture, which can be ascribed to different effects taking place in the electrical and mechanical properties of the sensing layer. The variation of the frequency in conductivity mode is thereby significant larger than in the microbalance mode.

The frequency shift of the resonator operated in the conductivity mode is caused by a change of the effective electrode diameter due to changes in sensor film conductivity [4]. At high p_{O_2}, the sensor film is insulating and an excitation of the resonator only takes place at the platinum electrodes. At low p_{O_2}, the conductivity of the sensor film increases and the CeO_2 film acts like an additional electrode area for excitation. Since mass sensitivity has a Gaussian distribution and the mass load on the resonator is non-uniform, the broadening of the excitaded area leads to an increase of the mass sensitivity in the area of the platinum electrode. Therefore, the platinum electrode appears to be heavier and leads to a frequency shift of the resonator.

The existence and determination of two different effects within sensor film leads to a significant improvement of the sensor selectivity and enables a distinction of H_2 and CO at high temperatures. Considering the standard deviation of the frequency measurements of about 2.5 Hz and a frequency change of 150 Hz between the mixtures containing CO and H_2, a sensor sensitivity of 1.7% can be expected using CeO_2 sensor films.

Previous measurements using TiO_2 sensor films [4] showed gas sensitivity between $p_{O_2} = 10^{-20}$–10^{-15} bar, only. In contrast CeO_2 is applicable at higher oxygen partial pressures up to $p_{O_2} = 10^{-5}$ bar and offers therefore a larger application range.

4.2. Data evaluation

The data processing methods described above are applied to the obtained data sets. In order to test a promising feature space, the temperature compensated and normalized frequencies are ploted versus each other. As seen in Fig. 6, these parameters lead to a promising feature set, which can be used for clustering. Well-defined groups representing different gas mixtures can be distinguished.

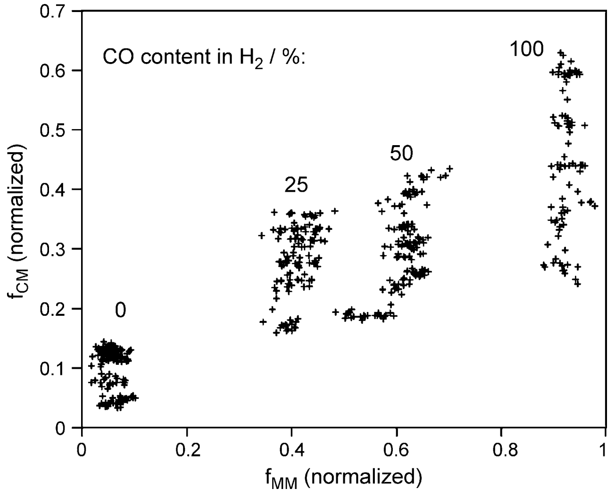

Fig. 6. Temperature compensated and normalized frequencies of microbalance and conductivity mode.

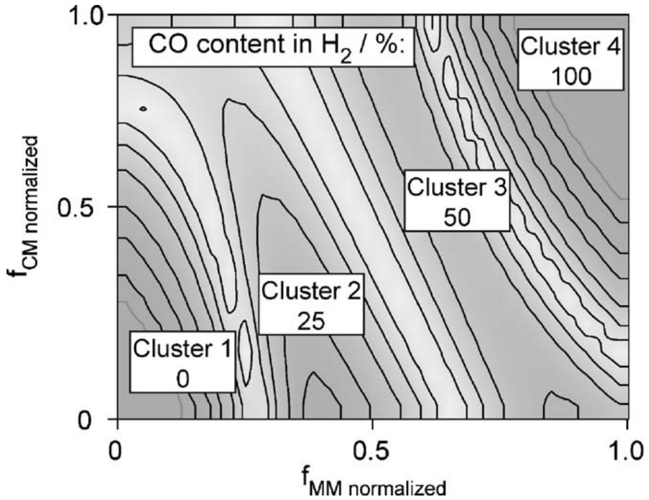

Fig. 7. Contour of cluster's membership values.

To find groups of different CO/H_2-ratios the first aim is to find prototypes for a known number of clusters based on the known gas compositions.

Several clustering methods where tested. The most promising algorithm is the Gath–Geva (GG) method [5]. The other investigated algorithms such as fuzzy-*c*-means (FCM) and the Gustafson–Kessel (GK) method [6] do not allow an accurate description of the given data sets. The FCM method is restricted to circular clusters whereas GK allows after all the detection of elliptic and rotated clusters. The applied GG algorithm, which takes in spite of the other algorithm also cluster size and density in consideration is more suitable for evaluation of data sets containing a large number of data points.

Fig. 7 shows the contour of the clustering results. It is obvious that the GG algorithm allows a good separation of the different gas compositions. The contour lines give information about the probability of a data point belonging to a certain cluster. Depending on the metrical distance between signal and prototype vector further quantitative information will be performed.

5. Conclusion and outlook

A gas sensor for high temperature applications is presented. The sensor system consists of a high temperature microbalance measuring changes in conductivity and mechanical properties of metal oxide sensor films, a low cost impedance analyser for data acquisition and a data processing software using methods of computational intelligence to obtain information about the present gas composition. CeO_2 coated langasite resonators permit a distinction of H_2 and CO at high temperatures. A classification of the obtained data using the Gath–Geva cluster algorithm provides well-defined cluster prototypes for different gas mixtures. Therefore, it is suitable for the presented application example.

Future sensor films will be prepared by screen-printing. Due to the increased surface area and the higher film thickness sensitivity improvements are expected. The sensitivity and cross-sensitivities of the sensor will be tested with respect to other gases like NO_x and SO_2. So far resonators coated with CeO_2 and TiO_2 sensor films are used. Other metal oxide sensor films open new application fields such as the monitoring of combustion processes directly within the combustion chamber. The latter is desired for an improved process control and emission reduction.

In order to reduce the size and the costs a further integration of the sensor system is necessary. The next step in this direction will be the implementation of the data processing software into the micro controller already used for data acquisition.

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Biographies

Denny Richter graduated in physical technology in 2003 at the University of Applied Sciences Merseburg. Currently, he is member of the Department of Physics, Metallurgy and Materials Science of the Clausthal University of Technology. His work focuses on the development of gas sensor applications based on high temperature piezoelectric materials.

Holger Fritze received his diploma degree in physics in 1992 from Technical University of Dresden and the PhD in 1996 from Technical University of Clausthal. After a 15 month postdoc at Massachusetts Institute of Technology, he joint again the Faculty of Natural and Materials Sciences of the Technical University of Clausthal in 1999. Since March 2006 he is a faculty member at the University of Applied Studies and Research, Wernigerode. His research is devoted to high temperature piezoelectric materials with special emphasis to the correlation of defect chemistry and electro-mechanical properties as well as high temperature sensor applications.

Thomas Schneider has been a member of the Sensors and Micro Systems Group at the Otto-von-Guericke-University since 2003 when he graduated at the Department of Electrical Engineering. He is involved with the development of sensor electronics for resonant and capacitive sensors. Currently, he is concentrating on the development of new sensor electronics for a high temperature gas sensor based on langasite resonators.

Peter Hauptmann is Professor at the Sensor and Micro Systems Group at the Otto-von-Guericke-University. He acts as Board Member of the Institute for Automation and Communication (ifak) as well as consultant to industrial and governmental organisations in Germany and abroad. From 1968 to 1985 he worked at the Technical College Leuna-Merseburg as a Lecturer and Senior Lecturer. In 1973 he received his PhD degree from the Technical College Leuna-Merseburg for a thesis about polymer physics. He has extensive experience in ultrasonic sensors and ultrasonic systems, resonant chemical, biological and mechanical sensors, sensor modelling, micro sensors, new sensor materials, sensor interface electronics, industrial sensor applications and is author and co-author more than 300 papers and several successful technology-transfer projects.

Norman Bauersfeld has been a member of the laboratory of Microcontroller and Applications of the Computational Intelligence at the University of Applied Sciences and Studies Wernigerode since 2000, when he graduated at the Department of Automation Control and Computer Science. He is involved in the evaluation of sensor data of resonant and capacitive sensors and the development of evaluation software and applications based on methods of the computational intelligence. Currently, he is concentrating on the development of sensor evaluation software for a high temperature gas sensor and its implementation in a specialized microcontroller platform.

Klaus-Dietrich Kramer received his diploma degree in information technology in 1987 from Technical University of Dresden and the PhD in 1997 from Technical University of Ilmenau. Since 1993 he is at the faculty of Automation and Computer Science at the University of Applied Studies and Research, Wernigerode, since 1998 as Professor of Microprocessorsystems and Computational Intelligence (CI). His research fields are applications of Microprocessors, Microcontrollers and Digital Signal Processors and CI-based Real Time Systems.

Maximilian Fleischer was born in Munich on May 7, 1961. He received his doctoral degree in Physics from the Technical University in Munich in 1992. Since then he is in the employ of the Corporate R&D of Siemens AG working on the development and application of new types of gas sensors. In 1998 he received the doctor habil. from the Technical University of Budapest for scientific work about gas/metaloxide interactions. As Senior Principal Engineer he is currently responsible for the Competence Field Chemical Sensors that includes gas sensors, biological sensors as well as physico-chemical sensors. The work of his group resulted in more than 150 scientific publications and more than 130 patent families. The latter resulted in the Siemens award "inventor of year" in 2003. The knowledge about MEMS chemical sensor technologies resulted in the industrialisation of two new sensor technologies pushed forward by his group as well as various sensor applications. He has been engaged in various national and European research projects, mainly as project coordinator and guides collaborations with German and European Universities. He is acting as expert for various entities, referee for various journals and member scientific comities of international organisations, as well as in the recruiting of new scientists for his organisation.

Kerstin Wiesner was born in Munich, Germany in 1970. She graduated in Chemistry in 1994 and received her doctoral degree from the Technical University of Munich in 1998. She then proceeded to work as a postdoctoral researcher in a joint research project for the Ludwig-Maximilians-University, Munich and Siemens. Since 2001 she has been an employee in the department of Corporate Technology of Siemens AG. Her current research interests are the development and application of new types of gas sensors based on semiconducting metal oxides and bulk acoustic wave resonators.

Günther Karle was born on 9.3.1961 in Mannheim. He finished his study in chemical engineering at the Technical University Clausthal in1993 as a graduated engineer. After final degree he started as an employee in research at the Federal Agriculture Research Centre (FAL) located in Braunschweig/Völkenrode until 2000. Since 2001 he is an employee of the PSFU where he is responsible for research and development, environmental technology and as well for education and working protection.

Andreas Schubert was born on 22.02.1952 in Wernigerode. After an education in grinding technology he studied mechanical engineering at the Fachhochschule Magdeburg. Since 1992 he is general manager of the PSFU GmbH as well as of the Alternative Energiesysteme GmbH. Since 2004 he is also a teaching representative for manufacturing technology at the University of Applied Studies and Research, Wernigerode.