Sensitive NO$_2$ detection with surface acoustic wave devices using a cyclic measuring technique

C. Müller, T. Nirmaier, A. Rügemer, M.v.Schickfus
Institut für Angewandte Physik, Universitt Heidelberg
Albert-Ueberle-Str. 3-5, D-69120 Heidelberg, Germany

SUMMARY

The detection of NO$_2$ in ambient air requires sensors that are capable of measuring concentrations in the low ppb range at high resolution. Using a cyclic measuring technique, a resolution below 1 ppb has been attained at NO$_2$ concentrations below 10 ppb with a Surface Acoustic Wave (SAW) sensor. This technique requires that the SAW sensor is first put into a defined initial state by a combination of heating and evacuation, where it is almost totally freed from residual NO$_2$ adsorbates. From this state, NO$_2$ concentration is determined from the temporal change of the SAW attenuation, which is proportional to the NO$_2$ coverage. Advantages of this technique are that previously adsorbed test gas is rapidly removed and that drift of the sensor is eliminated. An increase of the lifetime of the sensor in ambient air was found to be possible by using an ozone filter.
Keywords: *surface acoustic waves, gas sensor, nitrogen dioxide, phthalocyanine*

INTRODUCTION

The concentration of NO$_2$ in the ambient air varies between 0 and 150 ppb in the course of a day. In order to monitor such concentration profiles, NO$_2$ sensors are required that offer high sensitivity at low concentration. Presently, expensive systems based on gas phase chemiluminescence are used for this purpose. Cheap sensors like, e.g., surface acoustic wave (SAW) sensors [1], [2] using phthalocyanines [3], [4] as the sensor film [5], [6], are presently not well suited for this task because they either lack sensitivity or exhibit a drift of the baseline together with a sensor signal that depends on previous expositions to the test gas. Furthermore, times exceeding 30 min are required to reach equilibrium after a concentration change.

Here we present a technique that cycles a SAW sensor between a well defined initial state reached by rapid desorption and exposition to the test gas [7]. Using the initial slope of the sensor signal after applying the test gas, NO$_2$ concentrations down to the ppb range could be detected with a resolution of less than 1 ppb.

Theoretical aspects

In this section we will shortly outline the dynamics of adsorption and desorption of a gas chemically bound by a film which results in a change of the conductivity of the sensitive semiconductor layer. In equilibrium at a given temperature, adsorption rate j_{ads} and desorption rate j_{des} are equal. Then the coverage θ of the film exposed to the test gas of concentration c is described by the Langmuir isotherm

$$\theta = \frac{n}{n_{max}} = \frac{K(T)c}{1 + K(T)c} \quad , \tag{1}$$

where K depends on temperature and material parameters, e.g. the sticking coefficient, n is the density of adsorbed molecules in the film, and n_{max} the density of adsorption sites. Higher temperatures will lead to lower values of K and thus of θ. In the non-equilibrium case, ad- and desorption rates determine the behavior of the sensor. They are given by

$$j_{ads} = H\left(1 - \theta\right) \frac{N_A c}{V_{mol}} \sqrt{\frac{k_B T}{2\pi m_A}} \quad , \tag{2}$$

$$j_{des} = n_{max} \frac{\theta}{\tau_A} e^{-E_{des}/(k_B T)} \quad , \tag{3}$$

where H is the sticking coefficient, and m_A the mass of the gas molecule. The gas molecules are bound to the film with an energy E_{des}, desorption is described by an Arrhenius behaviors with an attempt frequency τ_A^{-1}.

For a step-like change of gas concentration c or of temperature at time t_0, the coverage will asymptotically change from the initial equilibrium θ_i to the final equilibrium θ_f with

$$\theta(t) = \theta_f - \left(\theta_f - \theta_i\right) e^{-(t-t_0)/\tau} \tag{4}$$

with a time constant τ given by

$$\tau^{-1} = \frac{1 + K(T)c}{\tau_A} e^{-E_{des}/(k_B T)} \quad . \tag{5}$$

This equation shows that desorption can be enhanced by increasing the temperature of the device.

For desorption $\theta(t)$ has its largest value at time t_0 and is given by the derivative of Eq. 4. If θ_i is assumed to be 0, the initial rate of change of θ is given by

$$\frac{d\theta(t)}{dt}\bigg|_{t=0} = \theta_f/\tau \quad , \tag{6}$$

which has its largest value immediately after the change at time t_0 and is proportional to the gas concentration c.

Each adsorbed NO_2 molecule forms a new acceptor site, so that the coverage $\theta(t)$ is directly proportional to the conductivity σ [4]:

$$\sigma = \theta\, n_{max}\, e\, \mu\, e^{-E_{act}/(k_B T)} \quad , \tag{7}$$

where e is the elementary charge, μ the mobility, E_{act} the energy for thermal activation (in accordance with [4] we find 0,16 eV). A change in θ therefore leads to a corresponding change in the conductivity slope.

A conducting film on a SAW device causes an attenuation σ which is described by the following equation:

$$\frac{\alpha}{k} = \frac{K^2}{2} \frac{\sigma_s v\, C_S}{\sigma_S^2 + v^2 C_S^2} \quad , \tag{8}$$

with K^2 and C_S the electromechanical coupling factor and capacity per unit length, respectively, k the wavevector of the surface wave, and v the the velocity of the SAW. In our experiments we worked in a region of the above parameters such that the dependence of α goes linear with σ. As described later, we did not use the absolute value of α, but rather the slope $d\alpha/dt$ as the sensor signal. Furthermore, desorption was enhanced by raising the temperature of the device at the end of each measuring cycle.

Experimental

The sensor elements used by us were either inductively coupled [8] or conventionally gold-wire bonded SAW devices. The center frequency was 365 MHz.

As a sensitive layer we used an evaporated 15 nm thick copper phthalocyanine film, initially in the α-modification. By IR-Spectroscopy we found that, at the elevated operating temperature, the sensitive CuPc layer transformed into the β-modification [9], [10]. This process required about half an hour. Therefore all experiments reported here were effectively done with a β-phthalocyanine film. As described above, the sensor signal was the attenuation α of the SAW induced by conductivity changes of the sensor film, which in turn is proportional to the uptake of NO_2 [1]. Attenuation was measured by a network analyzer (Hewlett Packard 8752C) and recorded by a personal computer which also calculated the derivative $d\alpha/dt$.
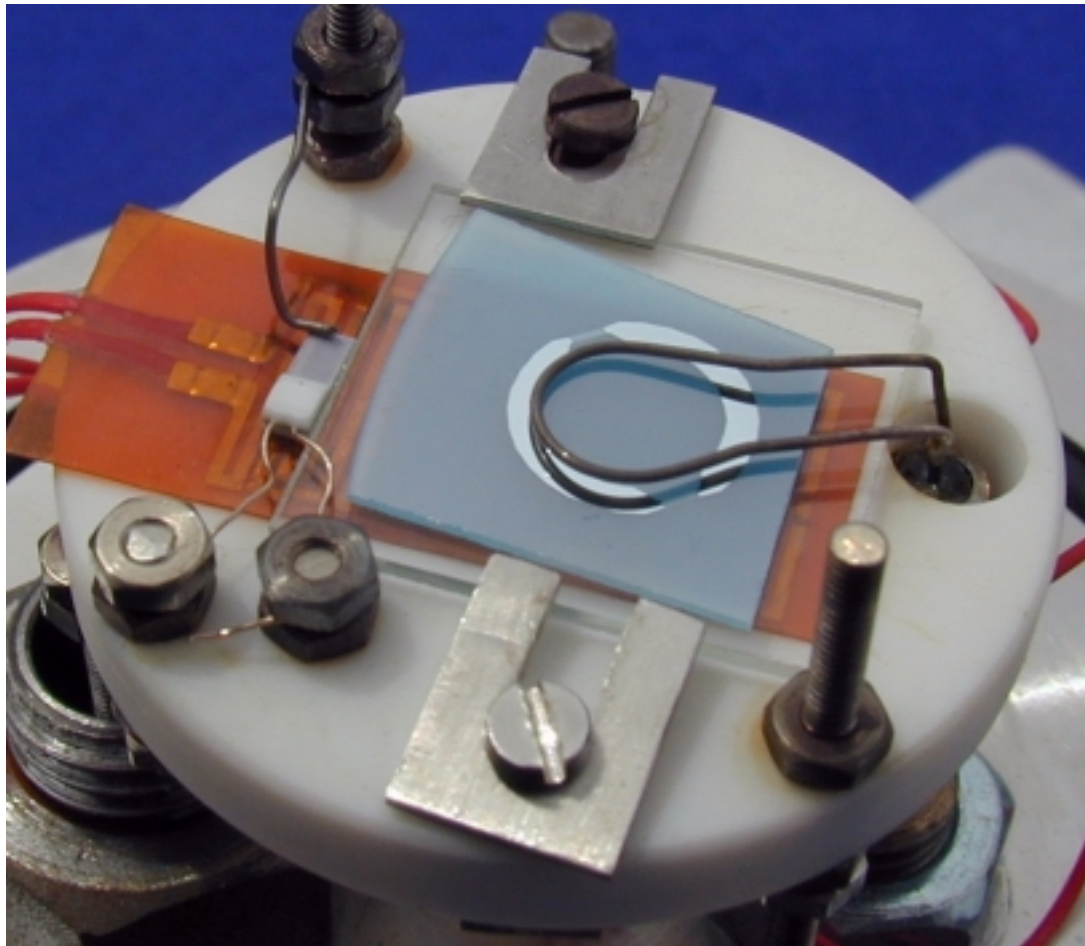
Fig. 1: The experimental setup: In the center one sees the primary coil placed about 1 mm above the coupling loop of the SAW device. The interdigital transducers (IDTs) interrupting the coupling loop on the SAW device can be recognized. The heater is pressed to the baseplate by a glass plate, which also provides a flat support for the sensor device. Part of the heater foil and the platinum resistance thermometer can be seen on the left side of the baseplate.

The device was mounted on a ceramic baseplate (Macor) which, because of its low heat capacity, allowed rapid temperature changes. Onto this plate, a heater foil was pressed by a glass plate, on top of which the sensor device was placed (Fig. 1). Temperature could be controlled to better than ±0.01 °C. For the inductively coupled sensors, the

primary coil was placed above the sensor in order to have a sufficient distance between the inductive coupling structures and the metallic components of the heater placed under the device. The whole setup was contained in a vacuum tight stainless steel measuring cell where the test gas mixture could be applied.

Pre-mixed NO_2 in synthetic air was sucked through the cell by a membrane pump at a rate of 0.75 l/min. The NO_2 concentration applied to the sensor was adjusted by mixing appropriate quantities of synthetic air and the test gas using mass flow controllers (Tylan FC 260). At the gas intake of the measuring cell, a computer controlled magnet valve allowed to evacuate the measuring cell with the membrane pump.
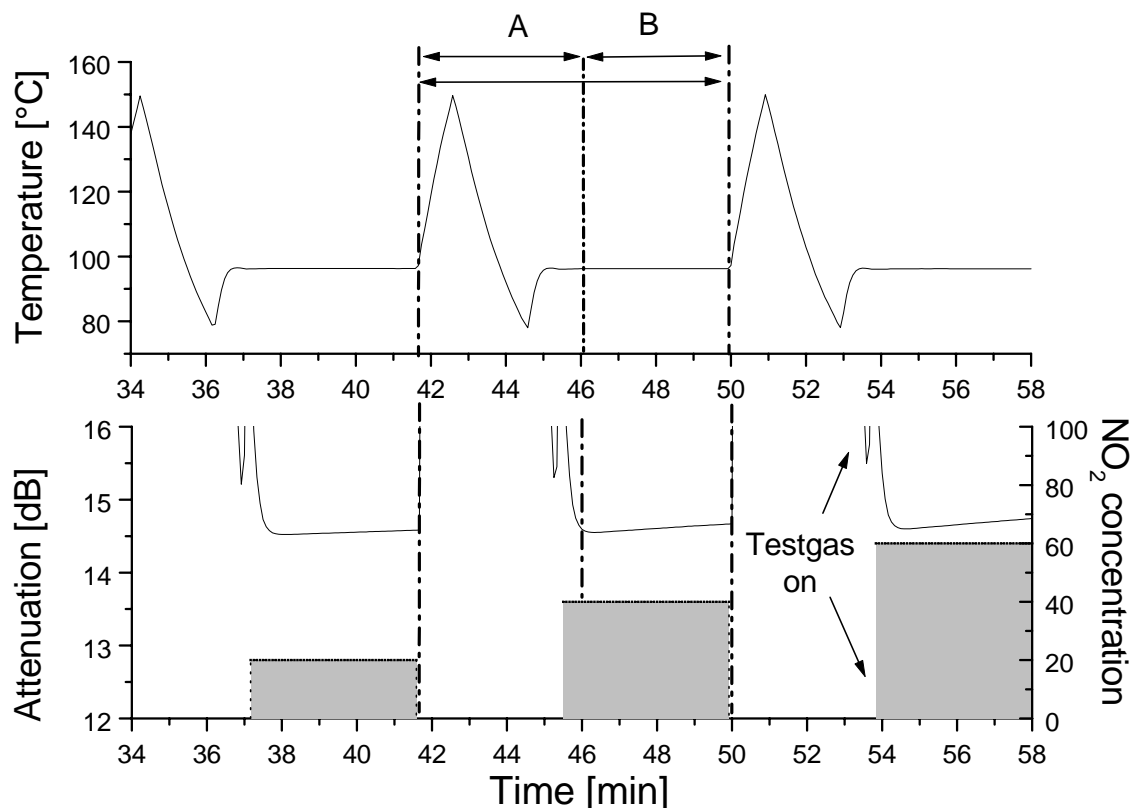

Fig. 2: Three adsorption/desorption cycles. Top: Temperature profile of the sensor. Bottom: Sensor signal (SAW attenuation) and test gas concentration. Desorption (A) and adsorption phases (B) are indicated for one cycle. The slope in phase B differs for the three NO_2 concentrations.

Cyclic desorption was accomplished in the following way:
A: Heating of the sensor from the operating temperature (usually around 100 °C) to the desorption temperature (≈ 150°C) substantially enhances desorption (Eq. 5). When the desorption temperature is reached, heating is stopped and the sensor reaches the operating temperature again. Simultaneous evacuation of the measuring cell strongly reduces the partial pressure of the test gas ($j_{ads} \approx 0$), without the necessity of purging with pure air. In this region of the measuring cycle the sensor signal is erratic.
B: The desorption phase, lasting about 4 minutes, is followed by an adsorption phase (Eq. 6) at normal operating temperature during which the test gas is guided through the measuring cell.
For three measuring cycles the variation of the temperature and of the attenuation

of the device are shown in Fig. 2. During phase A, large attenuation changes are associated with the strong and rapid changes of the device temperature and of the test gas flow. For example the last peak before the adsorption phase is caused by the onset of the gas flow in the previously evacuated measuring cell. In the adsorption phase B, the attenuation change with gas concentration can be recognized at the scale used in Fig. 2. Fig. 3 shows the slope of the attenuation signal detected in phase B together with the corresponding test gas concentration. NO_2 concentration increases in equal steps from 11 to 15 ppb and decreases again. At a NO_2 concentration of 15 ppb the attenuation slope is about $3.7 \cdot 10^{-2}$ dB/min.

It can easily be seen that the detection limit is below 1 ppb. Therefore the cyclic method is suited for the monitoring of NO_2 in ambient air.

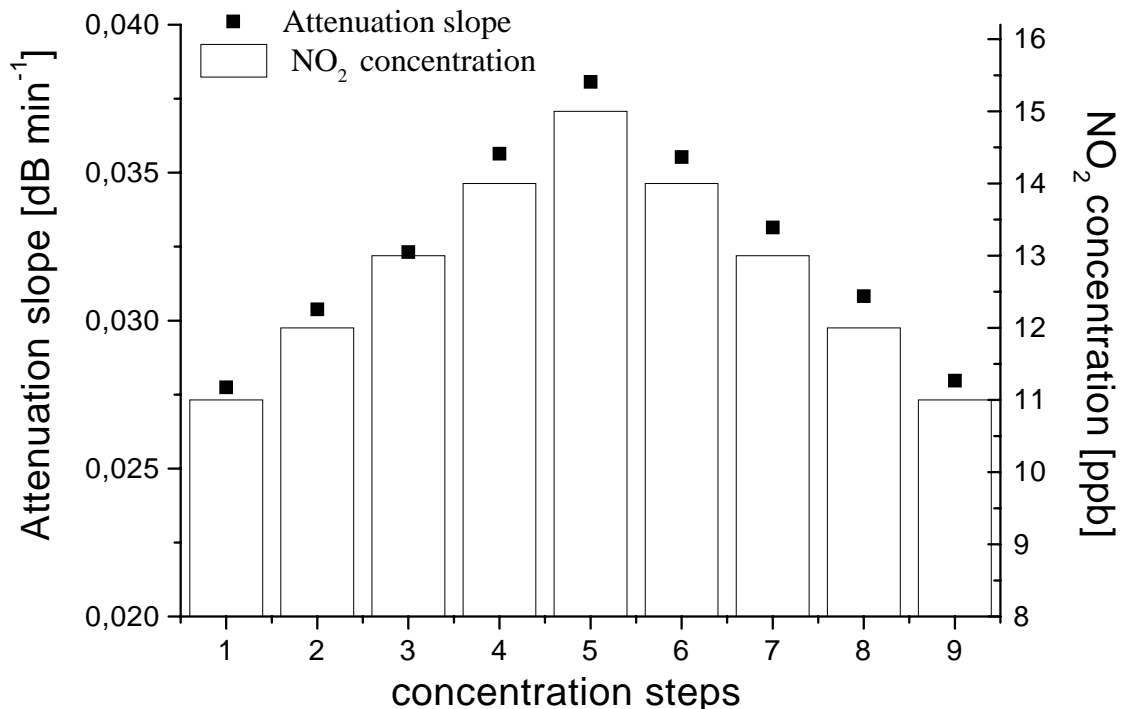Fig. 3: Detection of NO_2 concentrations in the range from 11 to 15 ppb. Concentration was varied in steps of 1 ppb. The detected level is indicated by squares, the applied NO_2 concentration by solid lines.

To test our method under realistic conditions, we measured the NO_2 concentration of ambient air for 15 h and compared the result with the measurements taken with an apparatus based on gas phase chemiluminescence (Bendix BE 8101) which was located in an environmental monitoring station at a major intersection in Heidelberg, 3 km from our experiment. The chemiluminescence apparatus gave a 30 min average of the NO_2 concentration in the ambient air. Fig 4 shows the good equivalence between the two measuring techniques. The data rate of our experiment was around three times higher than that of the chemiluminescence apparatus. Deviations between the measured NO_2 concentrations can be explained by the distance of the two measurement sites and by differences in the local environment (traffic load etc.).

For long-time experiments with ambient air we found that the sensitivity of the sensor
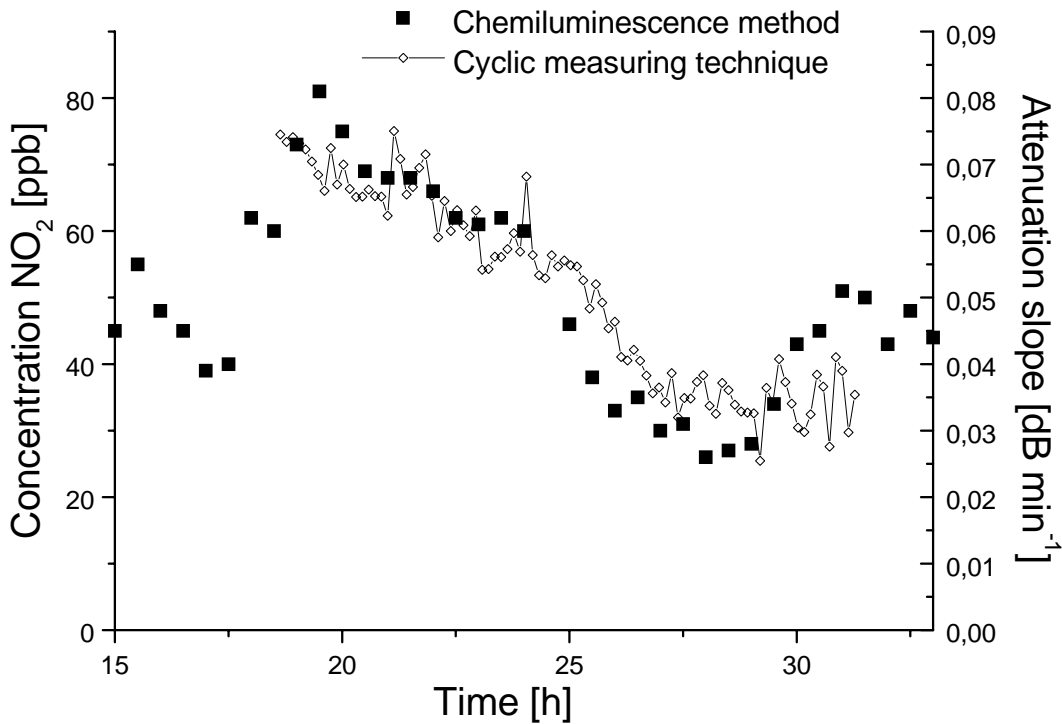
Fig. 4: Comparison of NO₂ concentration measured with a commercial system based on chemiluminescence in an environmental monitoring station with data taken simultaneously with the SAW sensor using the cyclic measuring technique. The agreement between the two data sets is remarkable.

decreased. At the same time the blue colour of the sensitive CuPc layer got less intensive and finally disappeared. In experiments with synthetic air this effect was not observed.

As the air humidity was one obvious difference in the two experiments, we did some experiments with moistened synthetic air. The result was negative. As a second difference to synthetic air, there is a small amount of ozone in ambient air. Experiments with an ozonizer showed that ozone does lower the sensitivity of the sensor and simultaneously weakens the blue colour of the CuPc layer. Therefore a filter had to be found which is able to remove ozone with a catalytic reaction while not affecting the NO_2 concentration in the air. We tested a number of materials and found MnO_2 imbedded in a fiberglass matrix to have the best filter properties [11]: Nearly 70% of the NO_2 was let through.

The efficiency of the filter was tested by passing a flow of ambient air over two CuPc-coated sensors for one week at $\approx 200°C$. The flow to one of the sensors was led through the ozone filter, the other was not. At the end of the measuring period the colour of the sensor exposed to unfiltered air had bleached considerably, wheras that of the other had not changed. After this promising result, the prolongation of the lifetime of the sensor will be tested again in the measuring cell in a long time experiment with ambient air.

Conclusion

We have presented a cyclic measuring technique for rapid high resolution NO_2 measurements using copper phthalocyanine as the sensor film. Basic features are an enhancement of the desorption rate by shortly raising the device temperature and by simultaneously evacuating the measuring cell. For the determination of the NO_2 concentration, the initial slope of the SAW attenuation was used. This technique avoids problems with drift of the sensor and the long response and recovery times normally observed with phthalocyanine coatings.

For NO_2 concentration measurements at levels comparable to those in ambient air (20–150 ppb) we achieved high resolution (better than 1 ppb) with negligible baseline drift. Data points were taken in eight-minute intervals. The suitability of our setup for monitoring the NO_2 concentration in ambient air was verified in a comparison with a commercial system based on chemiluminescence in an environmental monitoring station. An increase the lifetime of the sensor in ambient air was found to be possible by using an ozone filter which was tested in preliminary experiments.

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Biographies

C. Müller was born in 1969 in Ingolstadt, Germany. He studied in Bayreuth, Germany, St. Andrews, Scotland, and received his Diploma degree in physics from the Ruprecht-Karls-Universität in Heidelberg, Germany in 1997. After working in the field of detector development for high energy particles in Heidelberg and Geneva, his current research interest focuses on SAW sensor applications for environmental monitoring.

T. Nirmaier was born in 1971 in Ludwigshafen am Rhein, Germany. He studied physics in Heidelberg, Germany and at Santiago de Compostela, Spain. In 1999 he obtained his Diploma degree in physics from the Ruprecht-Karls-Universität in Heidelberg, Germany. Currently he is working at the STN ATLAS Elektronik GmbH in Bremen at the Development of Passive Ranging Sonar Systems.

A. Rügemer was born in 1970 in Munich, Germany. She obained her Engineer of Physics degree from the Munich Engineering Scholl in 1994, and her PhD in Physics in 1998 at the Ruprecht-KarlsUniversität in Heidelberg. Currently she is working at the semiconductor facility of Siemens in Munich.

M. v. Schickfus received his Diploma degree in physics from the Technische Universität München, Germany in 1974 and his Ph.D. from the Universität Konstanz in 1977. Since 1983 he is working at the Institut für Angewandte Physik of the Ruprecht-Karls-Universität in Heidelberg. After many years of research in low-temperature physics he started the SAW sensor project in 1987. Research activities are focused on the development of new devices for liquid- and gas-phase SAW sensors.