**Introduction**

Trace gas analysis is regarded as increasingly important when it comes to topics like environmental monitoring or improving the efficiency of energy producing or energy consuming processes.

Compared to other methods of quantitative analysis, the concept of Photoacoustic Spectroscopy (PAS) offers the advantage of developing very sensitive multi-component specific detectors without having to meet complex measurement conditions. The concept of miniaturization by using an integrated MEMS sensor element further aims at enhancing the sensitivity and the stability of the system.

**Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)**

The first stage of developing an integrated QEPAS solution of a piezoelectric detector module was to test the overall concept by means of a piezoelectric standard device. For this reason an acoustic micro-resonator (mR) composed of hydrodynamic needles was combined with a quartz tuning fork (QTF), which are usually used as clock generators in electronic watches, in order to take advantage of a double resonance system.

The drawing of the QTF in Fig. 1 visualizes the output of a simulation of its oscillation using the software Comsol Multiphysics. The resonance frequency of the QTF was simulated to be \( f_{\text{res}} = 32744 \, \text{Hz} \), which differs 0.2% from the measured value of \( f_{\text{res}} = 32752 \, \text{Hz} \). All pictures were taken with a digital Keyence VHX-1000D microscope. The central column illustrates the concept of the so-called off-beam QEPAS concept and it shows the QTF being adjusted to a hole, which was cut into the resonator using wire electric discharge machining (wire EDM). The distance between the resonator pipe and the QTF was determined to be \( d = 127 \, \mu\text{m} \).

While Fig. 3 shows the entire experimental setup, i.e. the excited laser beam illuminating the measuring cell, Fig. 2 delivers insight into the internal technology of the QEPAS cell.

**Sensitivity of the System**

Up to the current level of development, traces of nitrogen dioxide (NO2) are used to generate the photoacoustic signal by absorbing the radiation of a diode laser at a wavelength \( \lambda = 450 \, \text{nm} \) with an optical output power of \( P_{\text{out}} = 1.4 \, \text{W} \) being modulated at a frequency of \( f_{\text{mod}} = 32752 \, \text{Hz} \).

Using this setup, a two point measurement at 200 ppm NO2 and without analyte at all was made, respectively. The minimum detectable concentration at SNR = 30 was calculated to be \( C_{\text{min}} = 110 \, \text{pb} \). [1]

**QEPAS → MEMS Detector Module**

Although the overall concept of the MEMS detector module is in accordance with the QEPAS method, the miniaturization towards a micromechanical detector module has several advantages:

- simplified bottom-up illumination of the mR without the need of definite focusing
- improved orientation of mR and cantilever increases the system stability
- cantilever optimization by investigating different materials and geometries

**MEMS Resonator Pipe**

The resonator pipe is made up of two semi-circular-shaped channels etched into a glass wafer, which get bonded on top of one another. In order to realize the radius of the pipe (r = 600 μm), various etching mask materials and parameters had to be investigated. In this regard, masks of different thicknesses made of chromium (Cr), amorphous silicon (a-Si), diamond-like carbon (DLC), silicon carbide (SiC) as well as a stack of a-Si and SIC were studied in terms of their chemical resistance to hydrofluoric acid (HF).

The masking coatings were vapor-deposited either by means of PECVD or e-beam PVD and structured using lithography and reactive ion etching (RIE).

After removing the mask from one of the two substrates, they can be solderically bonded to form the resonator pipe.

**MEMS Cantilever**

In order to translate the acoustic signal into a voltage signal, a cantilever has to be bonded on top of the glass substrate, where there is a slit etched into the pipe. The functional layer of the cantilever is made of piezoelectric lead zirconate titanate (PZT), synthesized using the sol-gel technique with Zr(Oi-C4H9)4, Ti(Oi-C4H9)4 isopropoxide and anhydrous Pb(II) acetate as precursors. [2]

The thickness of the preliminary tested PZT layer is 235 nm and it is meant to reach a target of 1 to 5 μm by multiple spin-on coating steps. The stack of the oxide layer (SiO2), the adhesion promoting titanium layer (Ti) and the bottom electrode made of platinum (Pt) is 471 nm thick, in which the Ti coating is about 10 nm and the Pt coating is about 100 nm, respectively.

Although different parameters (e.g. viscosity of the stock solution, spin-off iterations, temperature ramps and the absolute temperature of the sintering process) already are varied and its influence on the layer quality has been investigated in the course of the PZT layer preparation, the X-ray picture in Fig. 7 (comparable with the X-ray diffraction pattern of PZT, still not being quite rough and partly delaminated from the Pt coating, which has to be further optimized).

The X-ray diffraction was recorded from a powder-like sample obtained by removing the coatings off the wafer. While the other peaks are assigned to Pt and Si, the one at 2θ = 30.8° results from PZT (110),[2]

**Literature**