A personal sampler for direct mass determination of nano-particles using a resonant cantilever sensor

S. Merzsch[*], T. Salthammer[**], H. S. Wasisto[*], I. Kirsch[**], E. Uhde[**], A. Waag[*] and E. Peiner[*]

[*]Institute of Semiconductor Technology (IHT), Braunschweig University of Technology
Braunschweig, Germany, s.merzsch@tu-braunschweig.de
[**]Fraunhofer WKI, Department of Material Analysis & Indoor Chemistry
Bienroder Weg 54E, 38106 Braunschweig, Germany, tunga.salthammer@wki.fraunhofer.de

ABSTRACT

Work place monitors and personal samplers are demanded to assess the exposure of production workers by engineered airborne nanoparticles. Comparatively complex and costly instrumentation, which is often too large for personal mobile operation, is already available. In this joint research project MEMS-cantilevers of slender geometry providing a large surface-to-volume ratio, driven at resonance by a piezoelectric stack placed below the cantilever, were used for sensing. A mass resolution of 5 ng was observed. The core parts for sampling are matching the specifications for mobile operation. Important considerations for the development were: Low production costs (< 200 Euro), battery lifetime of at least 8 h (one shift), sampler weight below 500 g, sufficient stability against climate changes, rugged design. The personal sampler is validated in environmental test chambers against test aerosols generated from technical nano-particles (SiO_2, carbon, TiO_2, Ag, PTFE).

Keywords: engineered nanoparticles, personal sampler, MEMS, piezoresistive cantilever

1 INTRODUCTION

Nowadays, nanoparticles (NP) are present in many environmental areas and industrial production. Next to manifold expections in relation to achievable technical advantages, there are also discussions about their possible impact on human health.

Monitoring of airborne NPs next to respiration zones of potentially endangered workmen in factories is essential for evaluation of NP concentrations. Uninterrupted job performance can only be realized by a small-sized, lightweight sampler.

Resonant sensors are able to detect very small masses precisely. Thermally excited MEMS resonators have shown mass sensitivities as high as 1.6 kHz/pg [1]. However, those resonators are driven at resonances in the tens of MHz range and a portable analysis is not investigated, yet. Furthermore the resonator is operated in low-pressure condition (~100 mBar).

In this paper, a miniaturized cantilever-based airborne nanoparticle detector (CANTOR) is presented. Electrophoresis is utilized to focus charged particles onto a slender cantilever. Trapped particles increase the mass of the cantilever and cause a shift in the resonant frequency. By measuring the shift, the collected particle mass is calculated.

2 SAMPLER COMPONENTS

The sampling part consists of an aluminum tube with a fan mounted at the outlet part to ensure an airstream through the tube. A slender cantilever is positioned centrally in the stream. Highly negative voltage is applied to the cantilever while the tube wall is at zero potential for sampling.

2.1 Sampler casing

Three parts, made of aluminum, represent the outer tube. They are joined by threads, which guarantees a secure way to connect the parts without endangering the slender cantilever. An outer diameter of 20 mm and a current length of 45 mm entail a reasonably small dimension. Figure 1 presents a CAD model of the sampler. Within subimage 1a, Part I is the inlet. A small channel assures guidance of the aerosol flow to the cantilever. An optional coarse particle filter can be mounted in the inlet channel. It can be applied to prevent the sampling of particles within the µm-range. Part II includes the inner setup to align the cantilever to the aspired sampling position. A fan (MF10A03A, SEPA Europe GmbH) is mounted at the outlet (Part III). This provides a flow of 0.68 l/min of NP-laden air through the tube.

2.2 Inner setup

The assembly inside the tube is fixed by a screw to Part II. An insulating plastic holder assures the separation between negative voltage at the cantilever and the zero potential at the tube. A piezo actuator is fixed on the holder. On top of it, a ceramic printed circuit board provides the necessary connections between the cantilever unit and the evaluation electronics. Bonding wires are connecting the

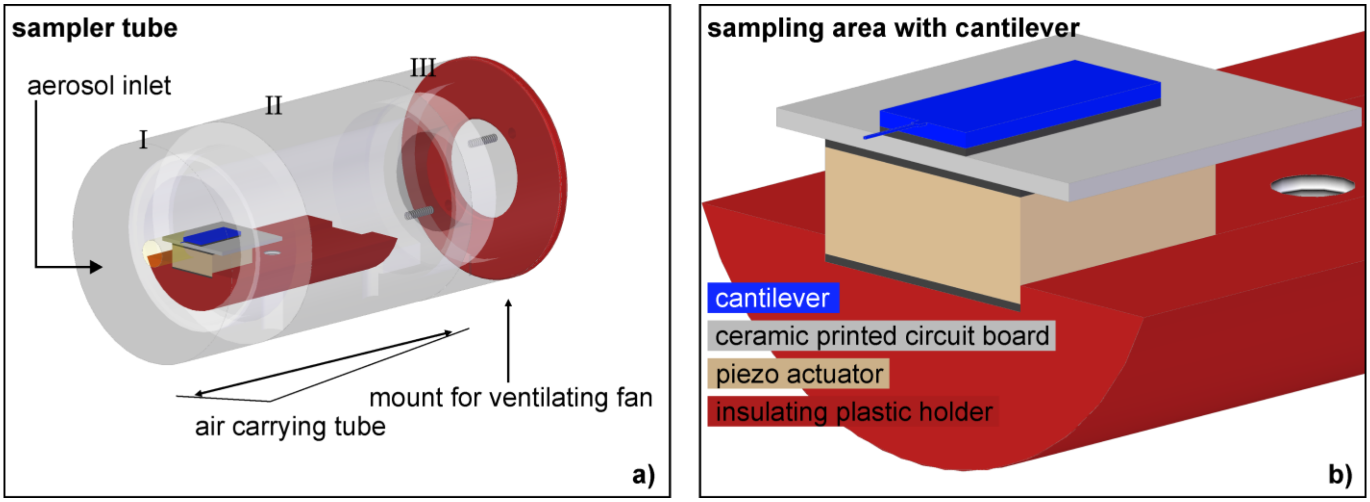

Figure 1 CAD for the sampling tube a) and a magnification of the cantilever and surrounding area b)

board to the piezoresistors at the cantilever, which is centered onto the board by two-sided glue strip.

2.3 Cantilever fabrication

In order to produce low-cost sensors, silicon is used as a base material due to its excellent micromachining capability. The cantilevers are made by a standard MEMS process. Conventional lithography and cryogenic reactive ion etching (RIE) enhanced by an inductively coupled plasma (ICP) built the shape of the cantilevers. The complete micromachining process including steps of photolithography, diffusion/implantation and etching for fabrication of the sensors has been published elsewhere [2]. The resonator includes an integrated full Wheatstone bridge by piezoresistors in a square geometry. Those resistors are placed at the anchor point between cantilever and bulky silicon to achieve a strong signal response. By strain-to-resistivity change, the cantilever deflection is readable. The differential output voltage ΔU_{out} has a relation to the supply voltage U_{in} applied at the Wheatstone bridge and the nominally identical unstrained resitances R as follows.

$$\Delta U_{out} = \frac{\Delta R}{R} U_{in} \tag{1}$$

The output ΔU_{out} will be at maxima values for a resonant actuation.

2.4 Active sampling by electrostatic field

A battery pack ($U_0 = 3.8$ V) drives the fan and a portable DC/DC converter. It provides an electrode voltage of $U_1 = 481$ V. The negative electrode is connected to the cantilever, while the tube is grounded. The resulting electrostatic field E forces positively charged NPs in the direction of the cantilever. Assuming a cylindrical shape for the cantilever, the electric field E in dependence on the distance r between the electrodes within the small inlet-channel is given by

$$E(r) = U_1 / \left[r \cdot \ln(r_o / r_i) \right], \tag{2}$$

where $r_i = 15$ µm is the radius of the cantilever and $r_o = 1.25$ mm is the radius of the inlet-channel. Figure 2 shows the corresponding dependence in case of positioning the cantilever inside the channel. Charged NPs are encountered by a drastically rising electric field while approaching the sensor.

2.5 Signal analysis

For further processing of ΔU_{out} an electric circuit based on a phase lock loop (PLL) is used. It ensures the ability to achieve online-monitoring of the resonant frequency. A first circuit achieved a frequency stability Δf of 1.4 Hz for more than 20 min. This implies a frequency resolution of $\Delta f / f_0 = 156$ ppm for a resonant frequency at 9 kHz. It

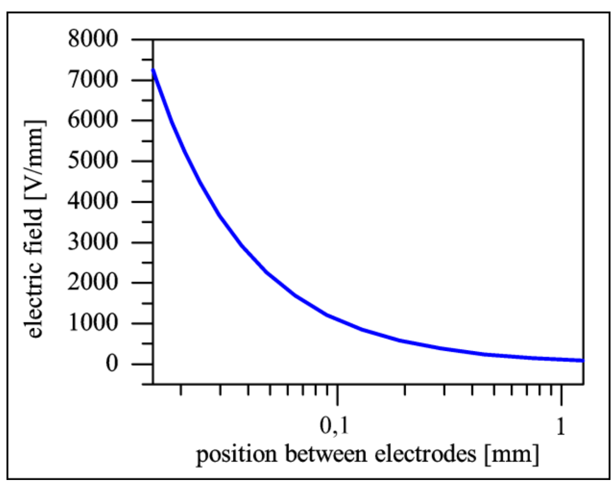

Figure 2 Electric field between the inlet of the aluminum tube and the silicon cantilever

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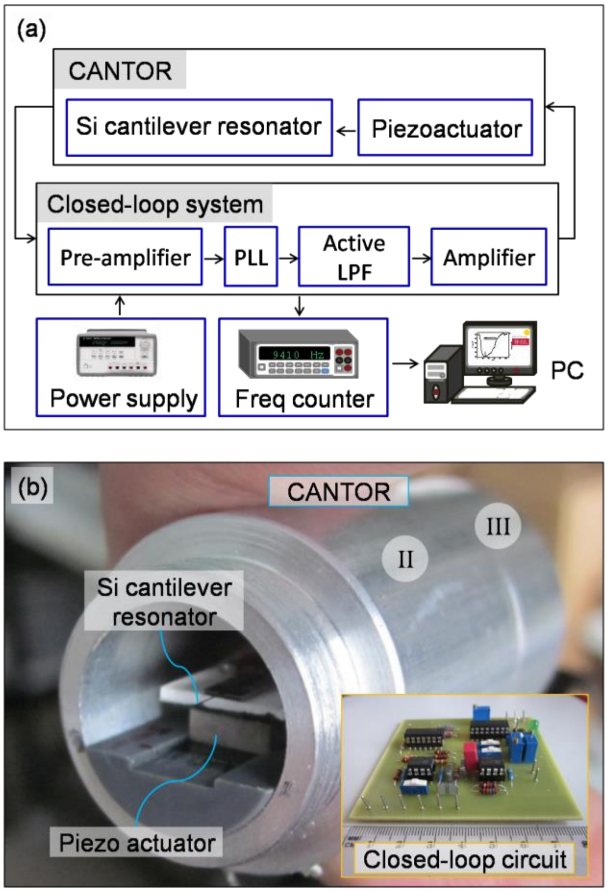

Figure 3 Schematic of the online measurement setup (a) and a photography of the CANTOR inner part including an inset showing the recent PLL circuit

furthermore determines the mass resolution to be in the tens of a nanogram. A more advanced version of the circuit is already able to resolve a hundreth of a nanogram by a frequency stability of 0.01 - 0.02 Hz. Figure 3 contains the schematic of the measurement setup. The PLL input is a preamplified version of ΔU_{out}. It retraces the resonant frequency and emits it. After a low pass filter, the signal is adjusted to operate the piezo actuator. This continual circular flow is monitored by a frequency counter and subsequently analyzed by a PC.

2.6 Particle filtration

Particles in the micrometer range have an immense impact to the resonant frequency shift while they accumulate at the cantilever. A membrane filter is a simple method to separate size fractions of particles from each other. Commercially available grids for transmission electron microscopy consist of regulary arranged holes down to diameters of 0.6 µm. Those grids are very fragile, which hinders the usability in a significant way. By ICP-RIE, we built silicon grids from bulk material. Filters are produced by processing two-inch wafers. Figure 4 shows a cut through an example and a complete filter in the inset.

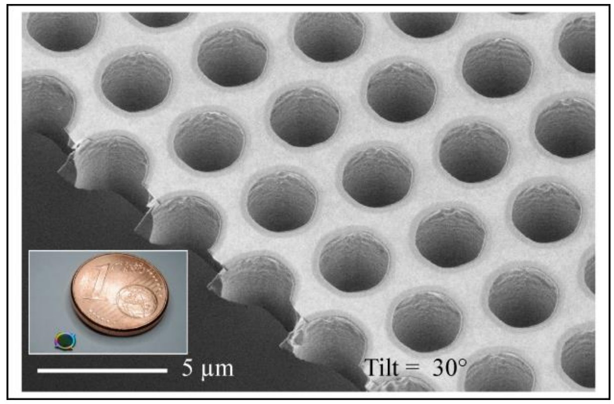

Figure 4 Cut through a filter element with hole diameters of 2.5 µm and a membrane thickness of 4 µm

Hole diameters of 2.5 µm are arranged in a hexagonal close packing. The thickness of the silicon membrane after deep etching of approx. 290 µm is about 4 µm. Those grids allow separation of µm-sized particles from NPs. As mentioned before, it can optionally be integrated in the inlet of CANTOR for size-preselection. The process sequence has already been published elsewhere [3].

3 CANTILEVER RECYCLING

3.1 Recycling procedure

By trapping particles, the resonant frequency is lowered. To enhance operating life of a sensor, brushing up by removing attached NPs is necessary. Volumetric forces are overwhelmed by surface forces in the regime of nanometer-sized particles. Therefore, especially smallest particles are hard to detach them mechanically from surfaces. An efficient repeatable method is based on a coating. By covering of the active sampling area previously to the sampling by a resist. In this case NPs can not directly touch the silicon surface. Therefore attractive surface forces refer dominantly to the coating layer. In case of photoresist, the layer is solvable in acetone. AZ5214 E and its thinner PGMEA (1:9 vol.) were utilized for layer preparation. The thinning was important for keeping the detection limit as high as possible. After a thermal curing, the preparation was finished. A NP-laden cantilever with assisting coating is immersed in a mixture of acetone and deionized water (3:1 vol.) to slow down the reactivity. Furthermore ultrasonic agitation is supporting the cleaning. For the whole period of dissolution, NPs are even not able to touch the silicon, but will be separated from the sacrificial layer and get uniformly distributed in the mixture.

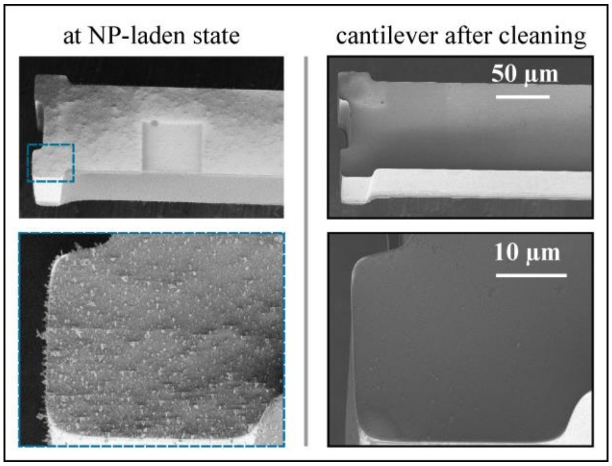

Figure 5 Cantilever covered by a resist film and carbon NPs (left) and after lift off cleaning (right part)

3.2 Recycling results

A verification of the cleaning efficiency was done using a CANTOR setup. The resonant frequency lowers according to [4]

$$\frac{\Delta f_n}{f_n} \approx \frac{m_{add}}{2m_{cant}}, \quad (3)$$

where m_{add} is the additional mass by coating and subsequent sampling, m_{cant} is the mass of the bare cantilever, Δf_n is the value for the frequency shift in resonance and the original frequency is given by f_n. For a bare silicon cantilever (l = 2.75 mm, w = 0.1 mm, t = 50 µm, m_{cant} = 32.04 µg), the resonant frequency for the first out-of-plane mode was found at 9365.35 Hz. After coating, the frequency drops about 77.53 Hz. Assuming a homogeneous covering at the cantilever, which agrees to SEM inspection, the added mass by resist is approx. 530 ng. The test aerosol was prepared in a 1m³ glass chamber with continuous ventiliation (air exchange rate 0.72 h^{-1}, 23 °C). Carbon nanoparticles (< 50 nm, Sigma-Aldrich) were dispersed in BuOH/water and introduced into the chamber using a BGI 6-jet atomizer at 0.5 bar with subsequent dryer. Chamber concentration was monitored by FMPS (TSI 3091) and found to be around 40,000 particles/cm³ on average. The stable test atmosphere was maintained for one hour, the actual measurement took place over 15 minutes.

The final frequency after sampling was 9280.54 Hz. According to the previous result, 49.81 ng of particles were collected onto the surface while sampling. Referring to the NP concentration inside the chamber, the sampling efficiency was ~6.4 %. After cleaning by the introduced process, the resonant frequency had been shifted upwards. The new value f_{clean} = 9365.03 Hz is stable at a level only 34 ppm lower than the original frequency. The cleaning efficiency has also been examined by scanning electron microscopy. Examples for the cantilevers free end are given in Figure 5. The left part contains two magnifications for the cantilever in the laden state. After cleaning, the silicon surface appears to be clean.

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