Mass measurements based on nanomechanical devices: differential measurements

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Abstract. In the last few years, there has been a strong interest in implementing nanomechanical devices as mass sensors. Regarding this application, an important question to address is to know to what extent the observed frequency shift is exclusively due to the targeted mass loading. For this purpose, we present a device, a polysilicon double cantilever, with an innovative design that allows the direct determination of the measurement uncertainty. Two almost identical nanomechanical resonators are simultaneously operated: one serves as sensor and the other as reference. In this way, rapid and reliable measurements in air are made possible. In first experimental measurements, some masses in the order of 300 fg, locally deposited by focused ion beam, have been measured with an uncertainty of 30 fg. These results are corroborated by the determination of the deposits size based on SEM images.

1. Introduction
Nano/micromechanical structures operated in static or dynamic (resonant) mode are potentially extremely versatile sensors. Very diverse signal domains like magnetic, thermal, electrical, chemical, mechanical, etc... can be transduced with the same mechanical structure. In the late 90s, different authors [1] pioneered the development of micromechanical-based multi-sensors taking advantage of scanning probes with nanoscale tip apex. Since then, diverse sensors based on nano/microstructures have been reported. In resonant devices, electrical, magnetic or thermal energy is converted into mechanical energy by exciting one resonant mode. The resulting displacement is then converted back directly (using for instance capacitive or piezoresistive detection schemes) or indirectly (for example optical transducing schemes) into an electrical signal.

Nano/micromechanical resonators offer outstanding perspectives to measure ultra-small amounts of mass deposited on them [2]. In comparison to the traditional and commercially available quartz crystal microbalance (QCM, widely used for example to monitor the deposition of thin layers in the semiconductor industry), nanomechanical resonators may offer drastic advantages in terms of mass sensitivity and system integration. In addition, their small size ensures an intrinsically high spatial resolution. The principle of operation is based on the detection of the negative shift of resonance frequency when a small quantity of mass is deposited on top of the mechanical structure.

The most classical resonators are singly clamped beams, namely cantilevers. When some targeted mass is deposited or adsorbed on them, the resulting frequency shift can be dissociated between (i) a decreasing contribution related to the proper effect of mass loading, and (ii) another increasing one related to stiffness [3] or surface stress changes [4]. In order to decorrelate these two effects, some authors have actually measured simultaneously bending and resonance frequency changes [5].
Additionally, an important question to address in this type of experiments is to know up to what extent the observed frequency shift is exclusively due to the targeted mass accretion. Towards the objective of designing a compact and portable mass sensing platform operable in ambient conditions, a reliable sensing procedure has to be defined to evaluate the measurement uncertainties. Under ambient conditions, the resonator-based sensor faces two main issues: (i) high air damping resulting in low Q-factors and therefore less precise measurements, and (ii) parasitic loads of water thin film arising from ambient humidity and of extra adsorbed particles, which both cause additional fake frequency shifts. In order to analyze this source of error, an innovative design allowing the direct determination of the mass measurement error is presented. Two closely located and almost identical (in terms of material and dimensions) nanocantilevers are simultaneously operated: one serves as sensor and the other as reference. In this way, rapid and reliable measurements in air are made possible.

2. Design, fabrication and operation of double cantilever devices

The novel nanomechanical device is a polysilicon double cantilever (DBC). The DBC consists of two cantilevers with a common anchor (i.e. same readout electrode) orthogonally orientated one to each other (figure 1). DBC are operated in their fundamental in-plane flexural mode and their oscillations are capacitively detected through a specific CMOS circuit [6]. The electrical output signal of a DBC is the addition of the individual response of each cantilever. Individually, each one exhibits spring-softening effect [7] what means that their resonance frequency $f_{\text{RES}}$ can be tuned down when increasing the DC driving voltage $V_{\text{IN,DC}}$ ($f_{\text{RES}}$ depends linearly upon $V_{\text{IN,DC}}$). Both cantilevers are designated according to the nomenclature depicted in figure 1: so-called vertical (VC) and horizontal (HC) cantilevers. Typically, these cantilevers are 14 µm long, 350 nm wide, 450 nm thick and have a gap comprised between 400 nm and 1 µm with respect to the driving electrode.

DBC are defined by electron-beam lithography (eBL) on pre-fabricated CMOS substrates (figure 2). In our post-processing approach [7], CMOS circuits are first fabricated according to a standard technology. Then, dedicated open areas (called integration areas) formed by polysilicon on field oxide are selectively patterned by eBL using a PMMA resist, deposition of a 32 nm thick Al layer and lift-off. Al patterns serve as an etch mask for subsequent pattern transfer to polysilicon by reactive ion etching. Then, a standard photoresist is deposited and patterned in order to protect the CMOS circuits during the wet etching of buffered fluorhydric acid that releases the structures. In this way, monolithically integrated nanocantilevers with lateral resolutions down to 200 nm are routinely fabricated.

3. Experimental procedure

The principle of operation of DBC is to use one of the two cantilevers, on which a punctual mass accretion is deposited, to determine with high precision the amount of deposited mass by measuring its
resonance frequency shift. The other cantilever may also exhibit a shift, whether positive or negative, but much smaller. We want to evaluate if this deviation provides an estimation of the measurement uncertainty.

In terms of device design, a series of specifications have to be fulfilled. First, both cantilevers must be spatially separated enough in order to ensure that only one cantilever undergoes an addition of mass during material dispensing. However, they must be sufficiently closely located so that it can be considered that they face the same environmental perturbations (humidity, temperature changes, particles in suspension in air, etc).

This auto-reference principle has been experimentally tested by locally depositing mass accretions by focused ion beam (FIB) only at the free extremity of the vertical cantilever (i.e. where the mass sensitivity is maximum [8]). An experimental procedure based on three steps has been defined.

(i) first, the frequency response of a DBC is electrically measured in ambient conditions. Its resonance spectrum exhibits two different peaks related to each cantilever. Several spectra have to be recorded at different driving voltages so that the spring-softening curve $f_{\text{RES}}(V_{\text{IN DC}})$ is characterized for both cantilevers.

(ii) then, the chip is placed into the vacuum chamber of a FIB (ZEISS 1560XB, GEMINI column) and a certain amount of material (a Ga/Pt/C alloy with a density of approximately 12.5 g/cm$^3$) is locally deposited at the tip of the vertical cantilever only (see figure 3). A typical rectangular-shape deposit is around 600 nm long, 300 nm wide and 120 nm thick, what approximately represents 250 fg.

(iii) the third step consists in taking the sample off the FIB chamber and measuring it again in ambient conditions with the same electrical set-up.

![Figure 3. SEM images of the vertical cantilever (VC) tip where a mass accretion has been deposited by FIB. (a) Tilted image. (b) Image in top view](image)

4. Experimental results

Following this procedure, six experiments have been carried out on several DBC of which the theoretical mass sensitivity $S_p$ is in the order of $1.2 \times 10^{-18}$ g Hz$^{-1}$. On each DBC, small mass accretions have been deposited only on the vertical cantilever. The sizes of the resulting deposits have been subsequently estimated by imaging them with SEM and AFM. The frequency shifts are calculated from the changes of natural resonance frequencies (extrapolating the measured spring-softening curves at $V_{\text{IN DC}}=0$). In figure 4, an example of resonance spectra recorded before and after FIB depositions is proposed. The graph of figure 4 illustrates the resonance frequency shift of the VC while the one of the HC remains nearly stationary. One can note that the peak of the HC is much weaker than the VC one: this is actually due to the fact that its gap is much larger than the VC one owing to a defect in the lithography step. In further experiments, the functionality of DBC will be improved by setting an equal gap for both the VC and the HC what should result in two similar peaks in terms of magnitude.
Theoretically, if the mass loading effect effectively dominates (see Introduction), then the stiffness must not be not modified during the mass deposition, especially if the mass is deposited at the free end [3]. In fact, the slope of the spring-softening curves depends on the cantilever stiffness: since we observed the slope was not affected by the deposition, the aforementioned assumption is confirmed.

Several FIB deposition experiments have been performed, using different DBC devices (figure 5). For all the measured DBC, the experimental deposited mass $\Delta m_{TH}$ was calculated as a function of the initial and final resonance frequency through eq.1 (the average shift was 150 kHz):

$$\Delta m_{TH} = \frac{k_{EFF,P}}{4\pi^2} \left( \frac{1}{f_f^2} - \frac{1}{f_i^2} \right)$$

where $k_{EFF,P}$ is the effective spring constant for a punctual mass deposition at the free end. Then, these values were compared to the values of mass (the ‘observed’ masses) calculated from the geometrical dimensions determined through SEM and AFM images.

We can observe in figure 5 that mass measurements deduced from SEM inspection and from shifts of resonance frequency of the VC follow a similar trend. This means that masses in the range of 250-400 fg have been successfully measured with an average uncertainty of 10 % except for the smaller mass. The experimental and ‘observed’ values of the mass are in very good concordance if ones takes into account that the mass evaluation from SEM images is also subject to error (i) because of the irregular shape of the FIB-induced deposition and (ii) because the composition of the deposited material is not exactly known. It can also be observed from these experiments that the change of resonance frequency of the reference cantilever (HC) does not account for the difference between the two methods for measuring mass accretions. In consequence, we can conclude that differential mass measurements would likely be more useful when performing on-line and ‘in-situ’ measurements.

References
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