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Short Communication

Effect of surface stress on microcantilever resonance frequency during water adsorption: influence of microcantilever dimensions

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ABSTRACT

This paper reports the effect of dimensions of microcantilever (MC) on its resonance frequency and bending upon adsorption of water molecules. Study is conducted on three MCs having the dimensions of $450 \times 40 \times 2.5\ \mu m^3$ (MC1), $225 \times 30 \times 3\ \mu m^3$ (MC2) and $125 \times 35 \times 4.5\ \mu m^3$ (MC3). The measured resonant frequency showed the expected negative shift in MC1, initially positive followed by a negative shift in MC2 and only positive shift in MC3 during adsorption. This behavior is attributed to changes in the stiffness of the MC associated with the surface stress. The surface stress generated on the MC has been derived from its bending measurements upon water adsorption. The change in the stiffness of MC evaluated from an independent estimate of expected frequency shift showed that the relative stiffness change of MC increases linearly with the surface stress scaled with cube of width to height ratio of MCs, confirming the dimensional dependence of adsorption induced stiffness change.

Microcantilevers (MCs) have been demonstrated to be extremely versatile sensors and have potential applications in physical, chemical, and biological sciences [1,2]. Measurement of adsorbed mass on these structures results in resonance frequency decrease, which offers one of the most sensitive mass sensing techniques, approaching single molecule detection [3]. Apriori, one would expect the frequency shift to be proportional to the square root of the added mass. However, apart from added mass, there are several factors, such as non-uniform mass loading [4], stiffness of the adsorbate [5], surface stress [6,7], and surface elasticity [8], which also influence the frequency shift. Therefore, one needs to take adequate care of the role played by these factors and need to be taken into account in mass determination.

Resonance frequency shifts in MCs are known to depend sensitively on both mass and stiffness variations induced by the adsorbed atoms/molecules [9]. Many theoretical models have been proposed to understand the influence of surface stress generated during adsorption on stiffness of MCs [10–13]. This effect is also dependent on MC dimensions and only few investigators have addressed this problem [5,14]. Tamayo et al [5] reported that the frequency response of a MC depends on the flexural rigidity change that results from stiffness of the adsorbate. Their model predicts that if thickness ratio of adsorbate to MC is less than 0.04 the resonance frequency decreases approximately linearly, indicating that mass effect dominates for small thickness of adsorbate. Lachut et al [14] developed a 3D model relating stiffness changes in MC with different dimensions and total strain independent surface stress generated. According to this model, a net in plane stress is generated in the immediate vicinity of the supporting clamp during adsorption that affects the stiffness. This effect will be dominant when length by width ratio of the MC reduces. However, no experimental work is reported on the effect of MC dimensions on its stiffness changes during adsorption.

In this paper, we study the resonance frequency shift upon adsorption of water molecules in three different MCs with reducing dimensions. We present experimental evidence to show that the effect of dimensions of MC leads to three distinct behaviors clearly depicting the competition between mass loading and stiffness changes. We have numerically estimated the expected frequency shift due to the added mass on MC surface and compared it with our experimental results. Difference between the observed and calculated is attributed to the stiffness change of the MC due to adsorption. The estimated spring constant change is corroborated with measurements of the surface stress generated during adsorption, through bending measurements.

Commercially available rectangular shaped, tip-less Silicon n-type (M/s Appnano, USA) MCs are used in the present study. Resonance frequency of MCs is measured using laser photo diode arrangement of an Atomic Force Microscope (AFM) head

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Table 1
Physical dimensions and properties of three microcantilevers studied in the present work.

Name	Model no. (M/s Appnano, USA)	Dimensions			Physical properties	
		Length (L) (μm) ($\pm$ 1 μm)	Width (W) (μm) ($\pm$ 1 μm)	Thickness (T) (μm) ($\pm$ 0.5 μm)	Natural frequency (f_1) (Hz)	Spring constant[a] (k) (Nm^{-1})
MC1	SICON-TL	450	40	2.5	12101.0 ($\pm$0.9)	0.121 ($\pm$0.006)
MC2	FORT-TL	225	30	3	66854.2 ($\pm$0.4)	2.5($\pm$0.1)
MC3	ACT-TL	125	35	4.5	332196 ($\pm$3)	28.6($\pm$1)

[a] Spring constant was estimated from measured resonance frequency and quality factor using the Sader's method [15].

(M/s NT-MDT Ntegra Prima, Russia). Three MCs with different aspect ratios are studied; their dimensions and measured resonance frequencies in air are shown in Table 1.[1] For each MC, the spring constant 'k' is estimated using the measured resonance frequency and quality factor values, using the Sader's method [15] and are also shown in Table 1. For adsorption of water molecules, experiments are performed by placing the AFM head along with the MC, inside an airtight chamber purged with nitrogen (N_2) gas which reduces the Relative Humidity (RH) to 6% over a period of 2 h. For increasing the RH, N_2 is bubbled through DI water. RH in the chamber is measured using a standard RH meter with an accuracy of $\pm$ 3.5% RH. All the MCs studied are Piranha cleaned, that removes the organic contamination on MC surface and grows a native oxide of about 5 nm [16], and then are loaded into the experimental chamber immediately. After Piranha cleaning the contact angle on the cantilever chip is found to reduce from 103° to ~10°. It may be noted, for each dimension of MC a minimum of three MCs (from the same batch) are experimented and on a given MC, experiment is repeated several times. The trends presented here for a given MC are typical and representative.

The unloaded resonance frequency, 'f_1', of an oscillating MC is given by $f_1 = \frac{1}{2\pi}\sqrt{\frac{k}{m^*}}$ where 'k' is the spring constant and 'm^*' is the effective mass of the MC. When adsorbates are deposited uniformly on the cantilever surface, the resonance frequency will shift to 'f_2', given by,

$$f_2 = f_1\sqrt{\frac{k+\Delta k}{k}}\sqrt{\frac{m^*}{m^*+\Delta m}} \quad (1)$$

where, 'Δm' and 'Δk' are the changes in mass and spring constant, respectively due to adsorption. It is evident from Eq. (1) that if $\Delta k = 0$, added Δm will always results in negative frequency shift ($f_2 < f_1$).

Fig. 1(a) shows the relative resonance frequency shift of three microcantilevers of different aspect ratios, referred to as MC1, MC2 and MC3 (see Table 1) as a function of increasing RH i.e., during physisorption of water molecules. Dramatically different behaviors are seen from this figure for the three MCs: For the cantilever MC1, the frequency decreases with added mass, as would be expected, but whereas for MC2 and MC3, the frequency hardens initially with the added mass. At higher mass loading, in the case of MC2, the frequency decreases. These trends clearly indicate that the observed frequency change is a combination of both the mass loading and stiffness change during the adsorption of water [9].

In order to discriminate the contribution of each of these two effects, we have numerically computed the frequency shift due to added mass on MC surface. Assay and Kim [17] through infrared experiments have studied the relation between the adsorbed water layer thickness and RH for SiO_2 surface. Using this data (Fig. 2 of Ref. [17]), we have evaluated the added mass Δm on three MCs studied in the present work with increasing RH, and these are shown in Fig. 1(b). The expected frequency shift, due to added mass alone, for each MC is calculated by substituting $\Delta k = 0$ in Eq. (1), wherein the effective mass $m^* = 0.24\rho V$, and 'ρ' and 'V' are density of silicon and volume of the MC respectively. The difference between the observed frequency shift (Fig. 1(a)) and calculated as above, is converted into to the variation in spring constant (Δk) for all the MCs. This was done by fitting the experimental frequency as "f_2" and added mass "Δm" values from Fig. 1(b), in Eq. (1) for each MC.

Fig. 1(c) shows the relative frequency shift with respect to relative mass ($\Delta m/m$) of MCs during adsorption. This figure also shows the estimated frequency shift for MC1. In the case of MC1, measured and estimated frequency shift coincides initially, indicating the adsorption induced stiffness changes is negligible i.e. the assumption of $\Delta K = 0$ is valid. However, the deviation at higher added mass may be due to the formation of continuous water film on MC surface at high humidity regime [18]. In MC2 and MC3, the positive frequency shift during initial stages is clearly due to the adsorption induced stiffness change i.e. the assumption of $\Delta K = 0$ is not valid here. Also, the change in the direction of ($\Delta f/f$) in MC2 and MC3 (shown by arrow marks) indicates the change from "stiffness dominated effect" to "mass dominated effect".

Fig. 2(a) shows the computed relative change in spring constant ($\Delta k/k$) for three MCs with added mass per unit area (surface density). From this figure it is clear that ($\Delta k/k$) is maximum in MC3 and as expected is negligible for MC1. The observed ($\Delta k/k$) arises due to the surface stress generated during adsorption. To estimate the surface stress, MC bending measurements are carried out. It is performed using the same set up after the resonance frequency measurements. The deflection sensitivity of the present AFM head is measured by contacting the MC with a calibrated piezoelectric element in motion and is found to be 20 pA/nm [19]. From the deflection data (Δz), differential surface stress ($\Delta\sigma$) is estimated using the modified Stoney's equation given by [20],

$$\Delta\sigma = \frac{ET^2}{4(1-\upsilon)L^2}\Delta z \quad (2)$$

where, 'E' is Young's modulus, 'υ' is Poisson's ratio and 'L' and 'T' are length and thickness of the MC used. The differential surface stress ($\Delta\sigma$) generated during adsorption with surface density in all the MCs is shown in Fig. 2(b).

It may be noted that the MCs used in the present work are uncoated, and it is expected that the surface stress generated during adsorption will be equal on both sides, resulting in zero differential stress leading to no bending. However, in a recent work [21], we have shown that difference in surface morphology on opposite sides of an uncoated MC induces bending, upon exposure to water molecules (see Fig. 2(c)). The presence of more number of localized surface features (stress concentrators) on back side, which renders the induced stress non uniform, is the reason for the bending of uncoated MC.

In Fig. 3(a), we plot ($\Delta k/k$), as obtained from Fig. 2(a) with $\Delta\sigma$, as obtained above. A linear correlation between the change in

[1] Length and width of MCs are measured using an optical microscope and has a variation of $\pm$1 μm. Whereas thickness of MCs is taken from manufacturer's datasheet and has a variation of $\pm$0.5 μm from its nominal value.