A Mechanistic Model for Adsorption-induced Change in Resonance Response of Submicron Cantilevers

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ABSTRACT

Submicron cantilever structures have been demonstrated to be extremely versatile sensors and have potential applications in physics, chemistry and biology. The basic principle in submicron cantilever sensors is the measurement of the resonance frequency shift due to the added mass of the molecules bound to the cantilever surface.
This paper presents a theoretical model to predict the resonance frequency shift due to molecular adsorption on submicron cantilevers. The influence of the mechanical properties of the adsorbed molecules bound to the upper and lower surface on the resonance frequency has been studied. For various materials, the ratio between the thicknesses of the adsorbed layer and the cantilever where either stiffness or added mass is dominant will be determined. The critical ratio (which contribution of effect cancel each others) between the thickness of the adsorbed layer and the cantilever and ratio between stiffness and density of adsorbed layer and cantilever have been determined. The calculations show the added mass and stiffness how contribute to the resonant behavior. This model gives insight into the decoupling of both opposite effects and is expected to be useful for the optimal design of resonators with high sensitivity to molecular adsorption based on either stiffness or mass effects.

Keywords: Adsorption, Resonance frequency, Stiffness, Cantilever, Resonator

1. INTRODUCTION

Cantilever structures are the simplest micro-electro-mechanical systems (MEMS) that can be easily micromachined and mass produced. The ability to detect extremely small displacements makes the cantilever beam an ideal device for detection of extremely small forces and stresses.
Although many cantilever sensors take advantage of adsorption-induced bending as the transduction method, an approach based on resonance frequency shifts can potentially provide the ultimate sensitivity for detection of a single molecule. Furthermore, the resonance frequency is also strongly dependant on various environmental conditions.
The resonance frequency of a microcantilever varies greatly as a function of mass loading due to molecular adsorption [1]–[7]. The resonance frequency of a cantilever beam depends on its dimensions, stiffness and density. By changing the dimensions, the resonance frequency can be varied from hundreds of Hz to hundreds of MHz. In fact, with the right material and nanoscale dimensions, GHz frequencies can be achieved. For a given thickness, shorter cantilevers have higher resonance frequency than longer cantilevers. For a cantilever of given mass, higher resonance frequency implies a larger stiffness.
The quantification of the adsorbed mass is an issue still not resolved. First, when the molecules are not uniformly adsorbed, the resonance frequency critically depends on the distribution of the molecules on the resonator [8], [9]. Second, a discrepancy is, in many cases, found between the added mass calculated by the theory and the mass adsorbed on the cantilever. This discrepancy is generally justified by invoking the effect of the adsorption-induced changing stiffness and surface stress on the resonance frequency [10].
Most of previous theoretical analyses [11]-[13] on the problem of adsorption-induced surface stress changes in cantilever resonance followed the treatment given by Chen *et al.* [10] in which the differential surface stress induced by adsorption is simplified to external axial forces exerted on the cantilever. In this way, the problem of a self-balanced cantilever deformation due to mismatch stress without any external forces has been replaced by a problem of bending or vibration

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of the cantilever under an applied force. Although a taut string model [10] and a beam with axial force model [14] have been suggested based on this simplification, neither approach represents the correct physical model for a cantilever.
Dareing and Thundat [15] developed a model for molecular interaction based on potential energy in the first layer of atoms attached to one surface of a cantilever and elastic potential in the microcantilever itself in order to study the deflection of the cantilever. Huang *et al.* [16] extended this work for two layers of film attached, respectively, to the upper and lower surfaces of the beam.
Up to [17], the influence of the mechanical properties of the adsorbed molecules on the resonance has been neglected; Tamayo *et al.* [17] presented a theoretical model to study the effect of the stiffness of the molecules bound to a microcantilever on the resonance frequency.
This paper presents a modeling analysis that explains the resonance frequency shift of micro and nanocantilevers due to adsorption. The influences of material properties of adsorbed molecules have been demonstrated.

2. RESONANCE RESPONSE CHARACTERIZATION

A schematic illustration of the resonator modeled in the theoretical calculation is shown in Fig. 1. The resonator is made of a single cantilever with length *L*, width *w*, and thickness t_c, the Young's modulus and density of the cantilever material are E_c and ρ_c respectively. *z* is the coordinate in the load direction with the origin in the centroid of the cross section. The beam is oriented along *x* axis and the origin of the *x* axis is situated at the clamping. The adsorbates can be considered as a layer of film attached, to the upper surface of the beam of thickness t_a. The Young's modulus and density of adsorbates are E_a and ρ_a, respectively.

We assume those adsorbates are homogeneously distributed across the width of the beam.

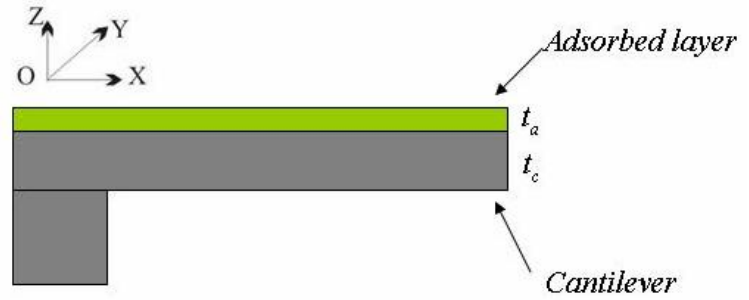

Fig. 1. Schematic depiction of a cantilever with molecules adsorbed on its surface.

In cantilevers or related areas the resonance frequency is based on the amount of kinetic energy and strain energy. For a multilayer cantilever beam in Fig. 1, the Rayleigh quotient is derived from the work-energy balance. The kinetic energy is

$$K.E = \frac{1}{2}\int_0^L \left(\rho_c t_c + \rho_a t_a\right) w \left(\frac{\partial u}{\partial t}\right)^2 dx, \tag{1}$$

and the strain energy is

$$S.E = \frac{1}{2}\int_0^L \left(EI\right)_{tot} \left(\frac{\partial^2 u}{\partial x^2}\right)^2 dx \tag{2}$$

Assuming $u(x,t) = Y(x)\sin\omega_n t$, and taking maximum values through the vibration cycle gives the Rayleigh quotient

$$\omega_{0n}^2 = \frac{\int_0^L (EI)_{tot} \left(\frac{\partial^2 Y}{\partial x^2} \right)^2 dx}{\int_0^L (\rho_c t_c + \rho_a t_a) w Y^2 dx} \tag{3}$$

where ω_{0n} is the unloaded Eigen frequency. The eigenmode shapes of the unloaded cantilever are given by [18]:

$$Y(x) = \sin(\beta_n x/L) - \sinh(\beta_n x/L) + \frac{\sin\beta_n + \sinh\beta_n}{\cos\beta_n + \cosh\beta_n}\left(\cosh(\beta_n x/L) - \cos(\beta_n x/L)\right), \tag{4}$$

the first eigenvalues β_n are given by:

$$\beta_n = 1.8751, 4.6941, 7.8548, ... \tag{5}$$

In order to determine the resonance frequency of the cantilever, contribution of bending stiffness and added mass of cantilever with its adsorbed layer has to be determined.
As many application involve a functional coating on the film, the means for calculating total bending stiffness for multilayer beams can be used as a substituted for the bending stiffness of this cantilever with its adsorbed layer as below,

$$(EI)_{tot} = \frac{E_c t_c^{\,3}}{12} \times \psi \tag{6}$$

and

$$\psi = \frac{1 + \left(\frac{E_a}{E_c}\right)^2 \left(\frac{t_a}{t_c}\right)^4 + 2\left(\frac{E_a}{E_c}\right)\left(\frac{t_a}{t_c}\right)\left\{2 + 2\left(\frac{t_a}{t_c}\right)^2 + 3\left(\frac{t_a}{t_c}\right)\right\}}{\left(1 + \left(\frac{E_a}{E_c}\right)\left(\frac{t_a}{t_c}\right)\right)} \tag{7}$$

similarly we can write functional density like:

$$\xi = 1 + \left(\frac{\rho_a}{\rho_c}\right)\left(\frac{t_a}{t_c}\right) \tag{8}$$

Equation (3) can be written in case of relative eigenfrequency as a function of t_a/t_c :

$$\frac{\omega_n^2}{\omega_0^2} = \frac{\psi}{\xi} \tag{8}$$

The relative frequency shift can now be characterized by the proportionality functions ψ, ξ. Thus, the resonance frequency shift is the result of two effects, the stiffness of the layer that produces a positive shift of resonance frequency (ψ), and the well known effect of the added mass that shifts the resonance frequency to a lower frequency (ξ). As the size of resonators is increasingly reduced, the thickness of adsorbed layer is getting comparable to the cantilever thickness, bringing about nonlinear effects and the coupling of the stiffness and mass effects.

In a more simple way, to determine the equivalent stiffness of structures after adsorption, the bi-layer can be replaced with an equivalent single film by defining an effective modulus E_e and thickness t_e such that the bending and stretching stiffness are identical to that of the bi-layer:

$$E_e t_e = A_b, \ and \quad \frac{E_e t_e^{\,3}}{12} = D_b \tag{9}$$

Solving these two equations for the effective modulus and thickness, one obtains:

$$t_e = \sqrt{\frac{12 D_b}{A_b}}, \ and \quad E_e = \sqrt{\frac{A_b^{\,3}}{12 D_b}} \tag{10}$$

These effective properties can be then used to predict the response of the bi-layer. For a coating that is much thinner than the substrate, i.e. $t_a << t_c$, one obtains the following results:

$$t_e = t_c \frac{\sqrt{1+4\alpha}}{(1+\alpha)}, \ and \quad E_e = E_c \frac{(1+\alpha)^2}{\sqrt{1+4\alpha}}, \quad \text{with } \alpha = \frac{t_a E_a}{t_c E_c} \tag{11}$$

By way of illustration, consider a 10 nm thick gold coating ($E_a \approx 90 GPa$) on a 10 µm thick elastomer substrate ($E_c \approx 1 MPa$): this yields $E_e = 16.4 MPa, \ and \ t_e = 6.1 \mu m.$

3. RESULTS

We will analyze first the effect of a homogeneous adsorbates layer on the cantilever. Fig. 2 shows the relative frequency shift calculated from equation (8) for a wide range of ratios between thicknesses of the adsorbed layer and cantilever, and for various materials with a wide range of stiffness by assuming the ratio of densities 5. It has been demonstrated that for low stiffness values, first, the resonance frequency shifts to a lower frequency and then increasing the thickness produces a positive shift. For high stiffness values it is shown the resonance frequency shifts positively with a high slope and by increasing the thickness of adsorbed layers produces a positive shift.

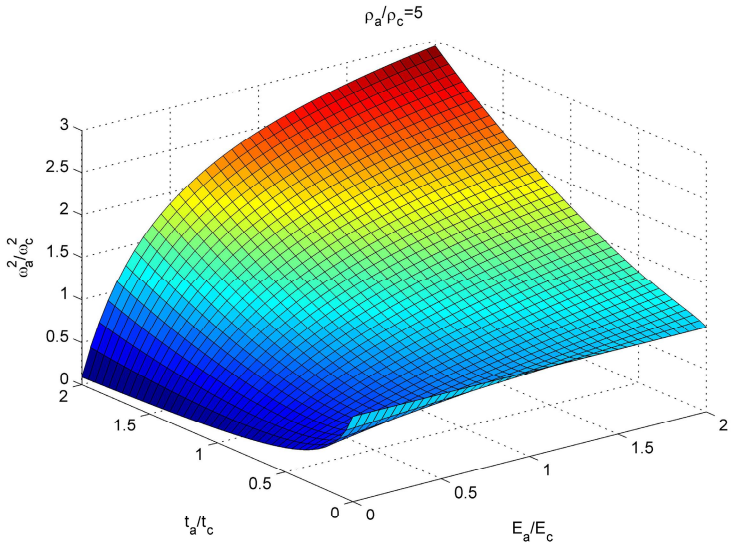

Fig. 2. Resonant frequency shift of cantilever vs. thickness and stiffness of adsorbates layer.

Fig. 3 shows the relative frequency shift by fixing the ratio of stiffness to 0.5 in order to see the contribution of the added mass. It has been shown for $\rho_a/\rho_c \le 0.5$ the resonance frequency increases approximately nonlinearly, and for $\rho_a/\rho_c \ge 0.5$, the resonance frequency increases linearly (added mass is dominated).

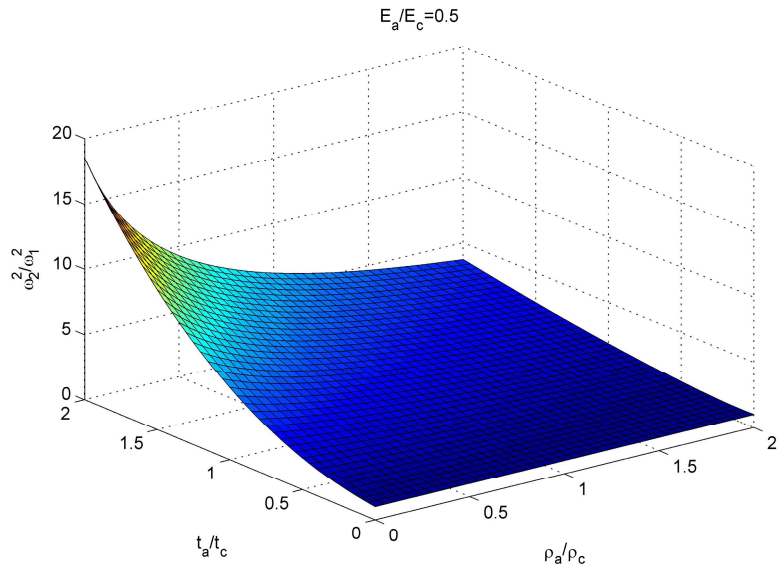

Fig. 3. Resonant frequency shift of cantilever vs. thickness and density of adsorbate layers.

As an example and case study we will compare the model with experimental work reported in literature [17]. The cantilevers are made of either silicon or the polymer SU-8, and two adsorbates, myosin protein and an alkanethiol are attached to the cantilever surface. The cantilever materials are silicon ($\rho_c = 2330\,Kg/m^3, E_c = 169GPa$) and the photoresist SU-8 ($\rho_c = 1190\,Kg/m^3, E_c = 4.0GPa$) [19]. As paradigmatic organic and biological layers on the cantilever, we use the self-assembled monolayer (SAM) ($\rho_a = 675\,Kg/m^3, E_a = 12.9\,GPa$), and the monolayer formed by the myosin subfragment 1 ($\rho_a = 183\,Kg/m^3, E_a = 0.7\,GPa$). The mechanical properties of these films were obtained from monolayers with a thickness of few nanometers via force-based techniques [20], [21].

As the results are shown in Fig. 4, for the highly packed SAM on the silicon cantilever, the contribution of the stiffness becomes more important and the resulting curve shows mass effect dominates for small thicknesses ($t_a/t_c \le 0.05$). In an intermediate regime between $0.05 \le t_a/t_c \le 0.08$, the contribution of monolayer stiffness and added mass practically cancel each other and the resonance frequency is practically insensitive to adsorption. For values of $t_a/t_c \ge 0.1$ the resonance frequency and its slope increase with t_a/t_c, implying that stiffness effect dominates over the added mass. For the protein adsorbed on the silicon cantilever for $t_a/t_c \le 0.5$, produces a decrease of the resonance frequency that is approximately linear with the amount of adsorption (Fig. 4, Si/ Protein) which is in agreement with experiments when the possible amount of adsorption taken in to account. Fig. 5 demonstrates the different behavior of the silicon cantilever due to adsorption of SAM and Protein myosin subfragment 1. It shows that after $t_a/t_c \ge 0.08$ the resonance frequency rapidly increases in case of SAM, while for protein it continues to decrease till 10 times thicker than SAM.

When the cantilevers are fabricated in SU-8, the stiffness of the adsorbed film dominates the resonance response due to the low Young's modulus of SU-8 (Fig. 4, SU-8/SAM, and SU-8/Protein). Thus the adsorption of both films produces large positive frequency shifts.

Fig. 6 shows the difference between resonance frequency shift calculated by Tamayo [17] which was fitted with experimental results and ones with present model for SAM on silicon.

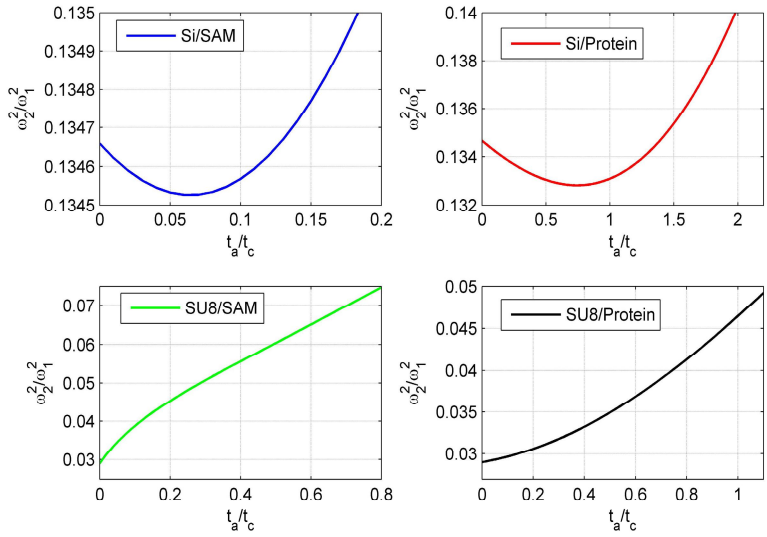

Fig. 4. Relative eigenfrequency shift vs. ratio between the thickness of the uniformly adsorbed layer and the cantilever.

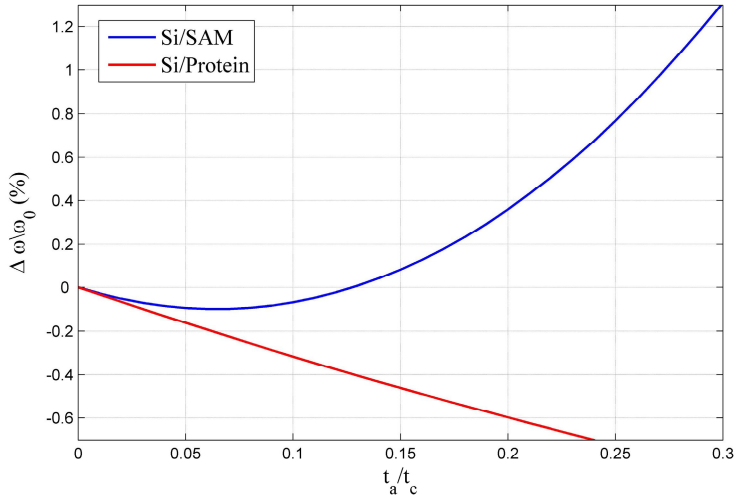

Fig. 5. Difference between Relative eigenfrequency shift for SAM and Protein adsorbed on silicon cantilever

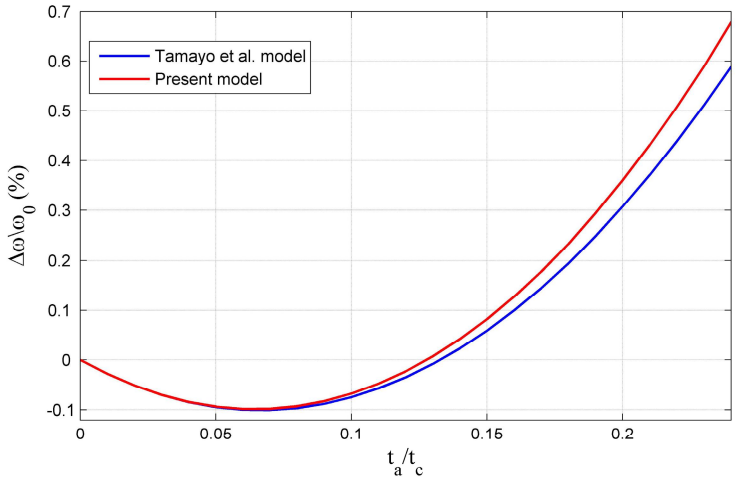

Fig. 6. Comparison between Present model and results of Tamayo [17] for SAM adsorbed on silicon

4. CONCLUSION

The present study clearly shows the important influence of the Young's modulus of the adsorbates in the response of biological and chemical sensors based on micro and nanomechanical resonators. The calculations show how the opposite contributions of the added mass and stiffness can cancel each other, producing small response. The result point at polymer materials, such as SU-8, as good candidates for future resonating sensors with enhanced sensitivity based on molecule stiffness.

From the results shown in this work, we conclude that the design of highly sensitive cantilevers to be used for Molecular detection must take into account the inhomogeneous nature of the adsorbed layers and also the important effect of the mechanical properties of the adsorbates in the dynamic response.

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