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Ultramicroscopy 97 (2003) 417–424
ultramicroscopy
www.elsevier.com/locate/ultramic

Enhancing chemi-mechanical transduction in microcantilever chemical sensing by surface modification

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Received 15 July 2002; received in revised form 23 October 2002

Abstract

The use of chemically selective thin-film coatings has been shown to enhance both the chemical selectivity and sensitivity of microcantilever (MC) chemical sensors. As an analyte absorbs into the coating, the coating can swell or contract causing an in-plane stress at the associated MC surface. However, much of the stress upon absorption of an analyte may be lost through slippage of the chemical coatings on the MC surface, or through relaxation of the coating in a manner that minimizes stress to the cantilever. Structural modification of MC chemical sensors can improve the stress transduction between the chemical coating and the MC. Surfaces of silicon MC were modified with focused ion beam milling. Sub-micron channels were milled across the width of the MC. Responses of the nanostructured, coated MCs to 2,3-dihydroxynaphthalene and a series of volatile organic compounds (VOCs) were compared to smooth, coated MCs. The analytical figures of merit for the nanostructured, coated MCs in the sensing of VOCs were found to be better than the unstructured MCs. A comparison is made with a previously reported method of creating disordered nanostructured MC surfaces.
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Keywords: Microcantilevers; Selective coatings; Surface modification; Chemical sensors

1. Introduction

The use of microcantilevers (MCs) as transducers in physical, chemical, and biological sensing systems has increased in recent years [1–15]. The increase in their use stems from certain inherent advantages over other transducers such as surface acoustic wave (SAW) and quartz crystal microbalance (QCM) devices. For example, MCs are well suited for miniaturization and can be used as elements in sensor arrays [16–18]. These arrays provide a higher degree of selectivity than can be achieved using a single MC due to the use of multiple chemical layers. Another unique feature of ultra-thin MCs is that they possess an extremely high surface-to-volume ratio. Thus, changes in the conditions on or near the surface resulting from the interaction with chemical species present in the environment of the MC can significantly modulate surface stress. This can result in bending and

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doi:10.1016/S0304-3991(03)00069-X

resonance frequency shifts of the MC if opposite sides are modulated by different degrees. When a uniform surface stress is applied to an isotropic material it either increases (compressive stress) or decreases (tensile stress) the surface area. If this stress is not compensated by an equal stress on the opposite side of the MC, it will cause a bending of the entire structure with a constant radius of curvature. The deflection of the tip of the MC, z_{max}, resulting from differential stress on its opposite sides, $\Delta\sigma$, is described by the Stoney equation (Eq. (1)) [19]

$$z_{max} = \frac{3l^2(1-\upsilon)}{Et^2}\Delta\sigma, \quad (1)$$

where υ and E are, respectively, Poisson's ratio and Young's modulus for the MC, and l and t are its length and thickness, respectively. When MCs are used as chemical sensors, this differential stress can be generally assured by using asymmetric MCs where one side of the MC interacts preferentially with the target analyte(s) through absorption into a thin chemical film on that surface. The untreated, opposite side is essentially passive with respect to the chemically treated side creating a situation that produces a differential stress.

Recent work from several research groups [1–10,16–18] confirms that sensors based on MCs have substantial potential for various analytical applications. In order to fully realize this potential, however, further optimization of MC designs and chemical coating selections may be required. A clean smooth solid surface generally exhibits a tensile (positive) surface stress due to the electronic arrangement of the atoms composing the surface. Significant changes in stress on a surface can occur when surface atoms are caused to rearrange due to adsorption by a chemical species [20]. The change in stress can be either compressive or tensile depending upon the nature of the adsorbed species. The surface stress and surface free energy are related by the Shuttleworth equation (Eq. (2))

$$\sigma = \gamma + \frac{d\gamma}{d\varepsilon_e}, \quad (2)$$

where σ is the surface stress, γ is the surface free energy per unit area of the strained surface, and ε_e is the elastic surface strain that is defined as dA/A where A is the surface area and dA is the elastic increase in surface area [20–22]. In principle, the second term can be comparable to the surface free energy and assume a positive or negative value [22]. However, a general trend is that if the initial surface Gibbs free energy is large, then modulation in surface stress and, hence, MC response can be large. For example, pure gold surfaces in contact with air have large surface free energies, typically exceeding $1\,N\,m^{-1}$. Not surprisingly, when MCs coated on one side with gold are exposed to alkylthiols in the gas phase very large total responses are observed as the thiol compounds covalently bond to the gold [23,24].

In order to impart selectivity to MCs used in analytical sensing, chemically selective receptor phases need to be immobilized on one of the sides of the MC. Ideally, the interaction of the analyte with the receptor phase, while being selective, is reversible and exhibits reasonable kinetics for sensing applications. The use of MCs with reversible receptor phases for measurements in liquids (e.g., aqueous solutions) has not received a great deal of attention. In part, this is because organic receptor phases in water possess surface free energies that are substantially smaller than the gold–gas phase case mentioned above. Therefore, modulation of surface stress is smaller and often within an order of magnitude of the inherent noise of MCs mounted in aqueous environments [1]. This gives rise to low signal-to-noise levels and somewhat limited dynamic range.

Recently, we reported on the use of nanostructured MCs in aqueous environments to improve the transduction of molecular recognition events into cantilever responses [25]. The limitations of smooth surface MCs were overcome by creating a highly disordered nanostructured surface on one side of the MC and further modifying the surface with a self-assembled monolayer (SAM). The nanostructuring process increased the available surface for SAM phases and analyte binding and creates a quasi-3D structure that is colloidal in nature. Importantly, the short-range forces associated with intermolecular interactions in the tight interstitial spaces of colloidal systems can be very large [26]. The in-plane component of these forces can serve to efficiently convert the chemical energy

associated with analyte–receptor binding into mechanical energy manifested as MC static bending. The same disordered nanostructured MC was used to stabilize thin films of a vapor-deposited chemically selective phase. It was shown that limits of detection for both modes of operation, SAMs and thin films could be improved by orders of magnitude over MCs with smooth surfaces [25].

Herein, we report on another approach to improve sensitivity of MCs in liquid-phase measurements using patterned modification of the MC surface. The surfaces in our present work have larger features than the nanostructured surfaces reported previously and are created by controllably milling the silicon surface using a focused ion beam (FIB). Nanoscale channels are milled across the width of MCs and then filled with an organic receptor phase. As analytes absorb into the receptor phase the stress created in the phase can be more efficiently transferred to the surface creating a greater differential stress and thus more bending.

2. Experimental

The silicon MCs that were used in this study are commercially available, approximately 1.5 μm thick, beam shaped and coated with a layer of aluminum (MikroMasch, Tallinn, Estonia). Each chip carried two sizes of MCs, 400 nm long by 100 nm wide, and 200 nm long by 50 nm wide, the latter size was used for these studies. The aluminum layer was removed from the MCs by immersing them in aqua regia (75% HCl, 25% HNO_3) for 5 min. The MCs were then rinsed in deionized (DI) water for 10 min, and dried under a gentle stream of nitrogen. The MCs were cleaned in piranha solution (75% H_2SO_4, 25% H_2O_2) and then rinsed in DI water and dried under a gentle nitrogen stream. The surfaces of the MCs were then modified using an FIB (FIB 200, FEI Co., Hillsboro, OR, USA) by milling grooves across the entire width of the MCs to depths of 200 or 400 nm. An example of a milled lever is shown in Fig. 1. As seen in the figure the grooves are positioned approximately every 800 nm and are roughly 400 nm wide. The grooves covered the

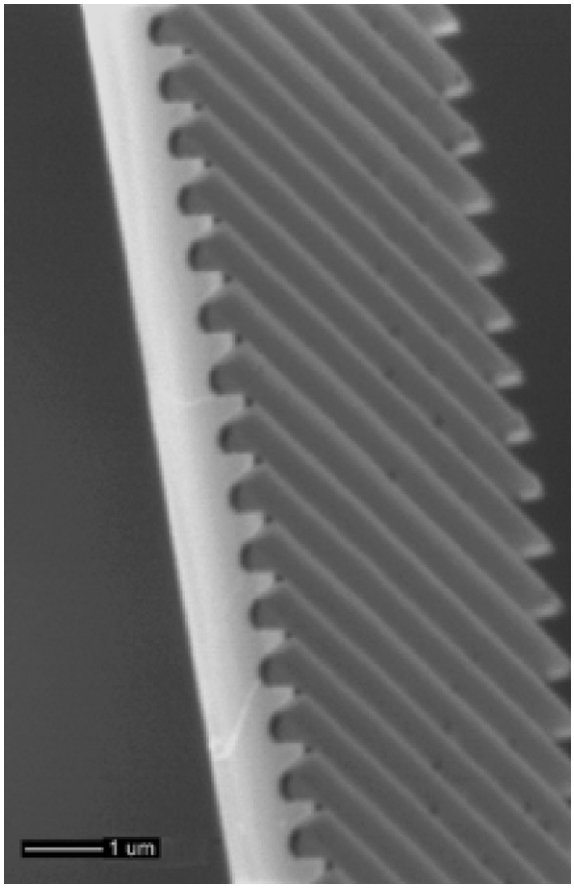

Fig. 1. Grooved MC with 400 nm deep grooves.

100 μm nearest the base of the 200 μm long MCs. The entire MC was not milled in order to leave an area to efficiently reflect a readout laser beam. Once the surface of the MC was modified it was placed into a physical vapor deposition (PVD) chamber (Cooke Vacuum Products, model CVE 301, South Norwalk, CT) to be coated with metallic and organic films. The modified surface of the MC was coated sequentially with a thin film (~5.0 nm) of chromium, a thin film of gold (~10 nm), and finally a film (100 nm) of (2,3-O-dimethyl-6-O-tertbutyl-dimethylsiyl)-β-cyclodextrin (MeSi-β-CD) synthesized in house [27]. The chemical structure and general appearance of this macrocycle, teacup-shaped, molecular receptor are depicted in Fig. 2. Film thicknesses were measured using a conventional QCM (Maxtek, model TM-100R, Sante Fe Springs, CA).

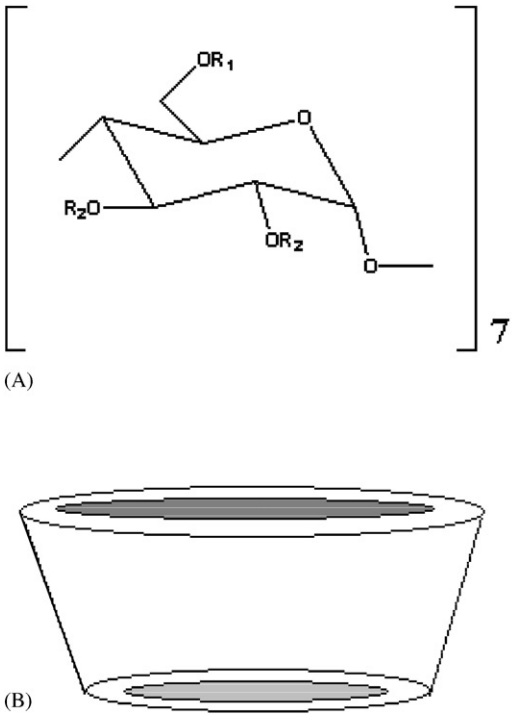

Fig. 2. Monomeric units (A) and general shape (B) of the functionalized cyclodextrins used as receptor phases. R_1 and R_2 are $(CH_3)_3Csi(CH_3)_3$ and CH_3, respectively.

The MC was mounted in a 100-μl flow cell in which it could be exposed to various solutions. The solutions were delivered to the flow cell via a 10 ml syringe connected to a two-way valve. This valve was connected in series to a second two-way valve that was connected to a 50 ml syringe. Typically the 50 ml syringe was filled with a 25 mM phosphate buffer at pH 7, and the 10 ml syringe filled with the same buffered solution containing a specific concentration of an analyte. The pH of the solutions was measured using an Orion SA 520 pH meter (Thermo Orion, Beverly, MA). The deflection of the MC was measured using an optical beam bending method shown in Fig. 3 [24]. In this method the deflection of the MC is measured by reflecting a 5 mW diode laser (Coherent Laser Corp., Auburrn, CA) operating at 635 nm off the MC and onto a position sensitive detector [25]. The output of the detector was recorded using an Agilent 34970A data acquisition/switch unit (Agilent Technologies, Inc. Loveland, CO) and a Pentium computer interfaced by a GPIB connection. The flow cell was imaged using a Watec CCD camera (Edmund Industrial Optics, Barrington, NJ) to assist with alignment of the laser beam on the MC tip.

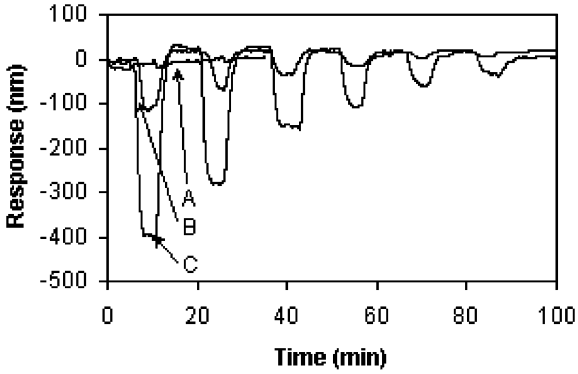

Fig. 3. Response curves for surface-modified MCs to 2,3-DHN: (A) ungrooved, (B) 200 nm deep grooves, and (C) 400 nm deep grooves.

The analytes and buffer components were obtained from Sigma (St. Louis, MO) or Aldrich (Milwaukee, WI) and used as received. All of the buffer solutions consisted of monobasic and dibasic sodium phosphate dissolved in DI water. The ratio of the two components was fixed to produce a buffer at pH 7. All of the analyte solutions were prepared in this buffer solution. The acids and bases used were obtained from Fisher Scientific (Pittsburgh, PA). The metals used during the coating process were obtained from Alfa Aesar (Ward Hill, MA) or the Kurt J. Lesker Company (Livermore, CA) at a purity of 99.9%. The MeSi-β-CD was synthesized using the method of Takeo et al. [28].

3. Results and discussion

When an MC is modified with an analyte permeable coating that is much thicker than a monolayer, a dominant mechanism of MC deflection is analyte-induced swelling of the coating. Such swelling processes may be quantified by evaluating the molecular forces acting within the coating and between the coating and the analyte

species. The absorption of analytes into a coating can alter dispersion, electrostatic, steric, osmotic, and solvation forces acting within the coating [26]. The absorption of analytes into the coating requires the creation of a vacancy in the bulk coating [29] and this can give rise to swelling that is characterized by an expansion coefficient [30]. The swelling may effectively produce a stress or a pressure change inside the coating, depending on whether it is described as a solid, or a gel, respectively. This pressure change multiplied by the thickness of the coating produces an apparent surface stress change ($\Delta\sigma_{\mathrm{app}}$) that can be used in Stoney's equation to estimate deflections of an MC coated with a thin, soft responsive film. In the case of thin-film coatings, nanostructured surfaces improve the transduction of this in-plane stress into cantilever bending by reducing the ability of the thin-film coating to slip along the MC surface as it swells. It is also important to note that swelling of soft films that are physically confined in the in-plane dimension on a cantilever surface may occur preferentially in the out-of-plane dimension and will not produce the desired MC bending.

The responses of both surface-modified and unmodified MCs coated with a film of MeSi-β-CD to a series of analytes were measured to further study the effect of surface morphology on MC chemical response. Cyclodextrin macrocycle sugar cavitands were chosen as chemical coatings based on their molecular recognition capabilities. Interactions between the cyclodextrin and solutes are based upon size, geometry, and physiochemical properties of both the cyclodextrin and solutes and have shown high degrees of selectivity in chemical separations [31–35]. The response of two surface-modified MCs to 2,3-dihydroxynaphthalene (2,3-DHN) were compared with the response of an unmodified MC. The depths of the grooves were 200 nm for one MC and 400 nm for the second. The grooved region of each of these MCs was preferentially coated with 100 nm of MeSi-β-CD using a mask, as was an ungrooved MC. The response of these MCs to a series of dilutions of 2,3-DHN over the range 25–1000 ppm is shown in Fig. 3. As can be seen in the figure the 400 nm grooved MC gave the greatest response to each concentration of 2,3-DHN, followed by the 200 nm grooved MC. The unmodified MC showed no clear measurable response even for the higher concentrations of 2,3-DHN. The magnitude of the response of the 400 nm grooved MC was three times greater than that of the 200 nm grooved MC. The response of the 400 and 200 nm deep-grooved MCs were linear with linear regression (R^2) values of 0.97 and 0.96, respectively. The 2,3-DHN limit of detection for the 400 nm deep-grooved MC was 36 ppm. This demonstrates that the addition of grooves leads to improvement in MC sensitivity. In general, deeper grooves increased the sensitivity over shallower grooves. We believe that the confinement of the receptor phase in the grooves allows the stress generated within the phase by absorption of analyte to be transduced into surface stress of the MC more efficiently.

While confinement of the film in grooves may serve to reduce stress-induced slippage, there are other response factors involved. The addition of grooves to the MC will also reduce the spring constant, making the cantilever more responsive, but also more noisy. The resonance frequencies of the surface-modified MCs were measured and from this relative spring constants were determined from the equation

$$f \propto \sqrt{\frac{k}{m}}, \tag{3}$$

where f is the resonance frequency in Hz, k is the spring constant in $\mathrm{N\,m^{-1}}$, and m is the mass of the cantilever in kg. By measuring the resonance frequency and estimating the mass of each cantilever the spring constant can be estimated. The measured resonance frequencies were 61.4 kHz for the ungrooved MC, 52.0 kHz for the 200 nm deep-grooved MC, and 39.9 kHz for the 400 nm deep-grooved MC. The mass of the ungrooved MC was estimated from the volume of the MC and the density of silicon. For the grooved MCs the volume of the grooves was calculated and subtracted from the mass of the ungrooved MC. From this information the spring constants of the ungrooved, 200 nm deep-grooved and 400 nm deep-grooved MCs were found to be in the ratio of 2.7:1.8:1.0, respectively. Since E and k are proportional to each other [36], the expected changes in response (see Eq. (1)) due to underlying

structural changes should be a factor of 1.8 when comparing the smooth with the 200 nm grooved MCs and a factor of 1.5 when comparing the 400 with the 200 nm grooved MCs. The observed changes in responses to 2,3-DHN shown in Fig. 3 are considerably larger. This suggests that both changes in spring constant and confinement of the responding film within grooves for the milled MCs are contributing to the observed improvement in sensitivity. Finite element analysis of modified MCs could be used to investigate which of these factors is more important in the improvement of the MC sensitivity [37].

A surface modified MC with 400 nm deep grooves was exposed to a series of VOCs (trichloroethylene, chloroform, and methylene chloride) each at a concentration of 100 ppm. The responses of the modified MC to these analytes are shown in Fig. 4. The variations in response to these analytes demonstrate that the MeSi-β-CD film gives modest selectivity to the MCs. Fig. 5 also shows the reproducibility of the MC responses over multiple injections of an analyte. A calibration curve was obtained for the DNAPL trichloroethylene in the concentration range of 1–1000 ppm. Above a concentration of 50 ppm the responses leveled off indicating saturation. However, below 50 ppm the responses (Fig. 5) were linear and gave a linear regression (R^2) of 0.98. Although this particular MC system was not optimized (see below) it yielded a TCE limit of detection of 980 ppb.

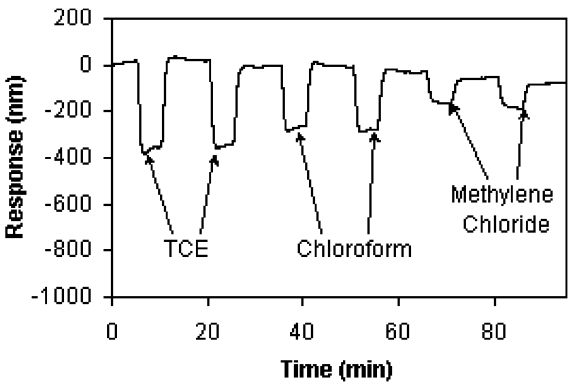

Fig. 4. Response curve of a 400 nm deep-grooved MC to a series of VOCs.

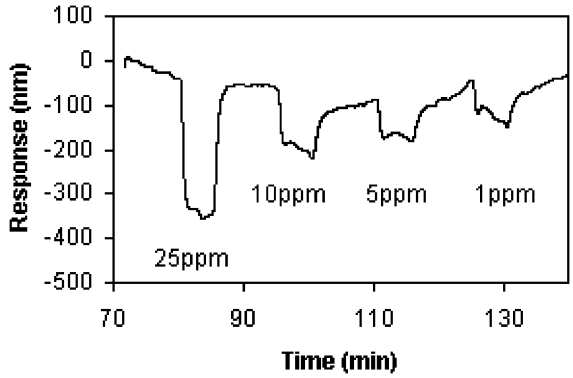

Fig. 5. Responses of a 400 nm deep-grooved MC coated with 100 nm MeSi-β-CD to trichloroethylene solutions of different concentrations.

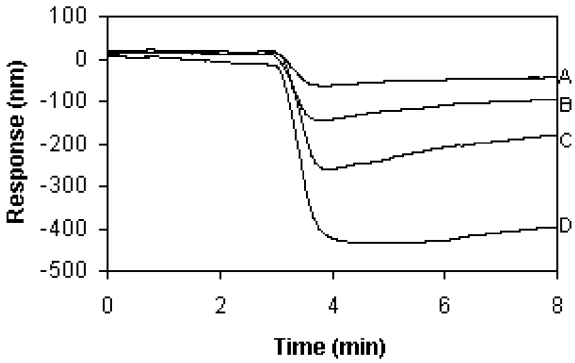

Fig. 6. Response of 400 nm deep-grooved MC to trichloroethylene after thinning of the MC surface: (A) unthinned, (B) thinned by 200 nm, (C) thinned by 400 nm, and (D) thinned by 600 nm.

The effect of MC thickness was studied on a 400 nm deep-grooved MC. Three MCs were thinned by 200, 400, and 600 nm, respectively, using the FIB. The surface of these MCs was grooved with 400 nm deep grooves and then coated with MeSi-β-CD. The responses of each of these MCs to 100 ppm trichloroethylene were measured and are shown in Fig. 6. As the MCs become thinner, the responses increase without an apparent decrease in the S/N ratio. Thus, a several-fold improvement in limits of detection over what we have found in this work above should be possible with thinning.

4. Conclusions

Surface modification of MCs has shown the potential to increase sensitivity of these devices as chemical sensors. This increase in sensitivity is produced by improvement of the transduction of stress created in a chemical receptor phase, by analyte adsorption or absorption, to surface stress on the MC. With an asymmetric MC this leads to a larger differential stress, which results in larger deflections of the MC tip. It should be noted that previous MC work with disordered nanostructured surfaces with smaller features yielded superior limits of detection (125 ppb for 2,3-DHN) using a similar coating [25]. This may indicate that the scale of the features on the grooved MCs (100s of nanometers) used in this work needs further optimization. Future optimization of MC chemical sensors will involve increasing the thickness of the coatings, and investigating further the effects of groove size and density and thinner cantilevers.

Acknowledgements

This research was supported by the US Department of Energy, Environmental Management Program under Grant DOE DE-FG07-98ER62718 and by DOE Basic Energy Sciences under Grant DE-FG02-96ER14609. Oak Ridge National Laboratory is operated for the US Department of Energy by UT-Battelle under Contract DE-AC05-96OR22464.

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