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Abstract
A miniature differential surface stress sensor consisting of two adjacent micromachined cantilevers (a sensing/reference pair) is developed for detection of chemical and biological species. Presence of analyte species is detected by measuring the differential surface stress associated with adsorption/absorption of chemical species on sensing cantilever. A novel interferometric technique is utilized to measure the differential surface stress induced bending of sensing cantilever with respect to reference cantilever. Sensor performance is characterized through measurement of surface stress associated with formation of alkanethiol self-assembled monolayers (SAMs) on gold coated sensing cantilever. Chemisorptions and self-assembly of alkanethiol molecules onto the gold-coated cantilever surface leads to development of compressive surface stress. Magnitude of measured surface stress compares well with data reported in literature.

Disciplines
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Comments
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Surface stress sensors for detection of chemical and biological species

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ABSTRACT

A miniature differential surface stress sensor consisting of two adjacent micromachined cantilevers (a sensing/reference pair) is developed for detection of chemical and biological species. Presence of analyte species is detected by measuring the differential surface stress associated with adsorption/absorption of chemical species on sensing cantilever. A novel interferometric technique is utilized to measure the differential surface stress induced bending of sensing cantilever with respect to reference cantilever. Sensor performance is characterized through measurement of surface stress associated with formation of alkanethiol self-assembled monolayers (SAMs) on gold coated sensing cantilever. Chemisorptions and self-assembly of alkanethiol molecules onto the gold-coated cantilever surface leads to development of compressive surface stress. Magnitude of measured surface stress compares well with data reported in literature.

1. INTRODUCTION

Cantilever deflection based chemical sensors are on the rise ever since Thundat et.al. [1] reported the deflection of atomic force microscope cantilevers due to changes in relative humidity and thus opened a myriad of possibilities for the use of atomic force microscope cantilever deflection technique for chemical and biological sensing. They predicted possibilities of adsorbate detection of the order of picograms and immediately followed up with another study in which they detected mercury adsorption on cantilever from mercury vapor in air with picogram resolution [2]. In current state of art surface stress sensors, the surface stress change is inferred from the deflection of a single or multiple laser beams reflected from the sensing surface. A large optical path (~ 1 m) is required between sensitized surface and position sensitive detectors to achieve high sensitivity in surface stress measurement. As a result, it is difficult to implement the sensing scheme into a single micro-fabricated device.

A novel differential surface stress sensor is developed to overcome the limitations of the current state of art sensors. The surface stress sensor consists of two flexible surfaces, a sensing/reference pair, where only the sensing surface is activated for adsorption/absorption of analyte molecules. High resolution interferometry is utilized to directly detect surface stress difference between the two surfaces. Hence, the detected signal will represent only the molecular absorption that occurs on sensing surface and not on the other. Direct detection of differential surface stress eliminates the influence of environmental disturbances such as nonspecific adsorption, changes in pH, ionic strength, and especially the temperature (due to the bimaterial effect caused by a thin metal layer deposited on one side to aid functionalization and laser reflectivity). Measurement of surface stress associated with formation of alkanethiol self assembled monolayer (SAM) on the sensing surface is utilized to characterize the performance of differential surface stress sensor.

Berger et. al. [3] reported the generation of compressive stresses on an AFM cantilever during the formation of alkanethiol self-assembled monolayer on the cantilever's surface. They showed a surface stress on the order of 0.1-0.5 N/m and also reported that the magnitude of surface stress increased linearly with the carbon chain backbone of the monolayer. Since the first report by Berger et. al. [3], SAMs have been used as test system for almost all cantilever based sensing techniques [4-7]. This is because they are relatively easy to prepare, form well-ordered close packed films and offers limitless possibilities of variations in chain length, end group and ligand attachments[8]. One of the commonly studied SAMs are alkanethiol SAMs ($HS\text{-}(CH_2)_{n-1}CH_3$). Godin et. al.[4] have shown that the kinetics of formation of self-assembled monolayers on gold-coated cantilevers and the resulting structure are dependent on the structure of the gold grain itself and also the rate at which the SAM reaches the surface. They showed a surface stress value on the order of 0.5 to 15 N/m. The surface stress generated was also shown to be dependent for different surface density (coverage) of the monolayer on the substrate.

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2. PRINCIPLE OF DIFFERENTIAL SURFACE STRESS MEASUREMENT

2.1 Sensing principle

Principle of the differential surface stress measurement is schematically represented in Fig. 1 and Fig 2. The sensor consists of a pair of microlens arrays and two micromechanical cantilever, a sensing/reference pair, where only the sensing surface is activated for adsorption of chemical or biological molecules (Figure 2). Hence, the detected signal will represent only the molecular absorption that occurs on the sensing surface and not on the other. Sensing/reference cantilevers are symmetrically positioned about the lens axis on the focal plane of MLA2 and MLA1. The main role of microlens array 1 (MLA1) is to collimate the incident/refractive beams from off-axis; thus, the beams past through MLA1 are delivered precise positions on microlens array 2 (MLA2) as well as receive back to fiber couplers. As a result of this arrangement, a laser beam b_1 incident at point A always reaches point B while another incident beam b_2 at point C always arrives at point D regardless of their incident angle (Figure 2). Absorption of chemical or biological molecules sensing surface results in surface stress change and consequently bending of sensing cantilever. The bending of sensing cantilever produces a change in path length difference between two beams. After reflecting from the sensing and reference surfaces, the two beams b_1 and b_2 accumulate a path length difference, l.

$$l = y_s - y_r$$

where, y is displacement of the different points on the surface. Hence, the path length difference between the beams is equal to differential displacement between sensing and reference surface. Differential surface stress is determined using Stoney's formula (Stoney 1909) with obtained the path length difference allow calculating differential surface stress ($\Delta\sigma$).

$$\Delta\sigma = \left(\frac{E}{3(1-\nu)}\right)\left(\frac{L}{t}\right)^2 l$$

where, E, ν are elastic modulus and Poisson's ratio of the sensing cantilever. L and t are length and thickness of the sensing cantilever, respectively, and *l* is the path length difference.

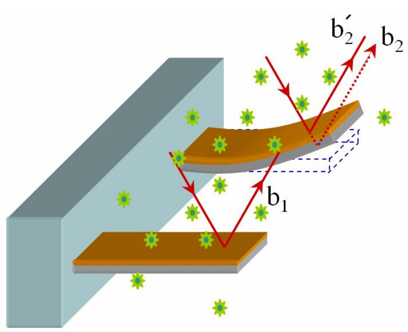

Figure 1. Conceptual view of acting alkanethiol molecules on the gold surface of sensing/reference cantilevers and their consequent reaction [4-7].

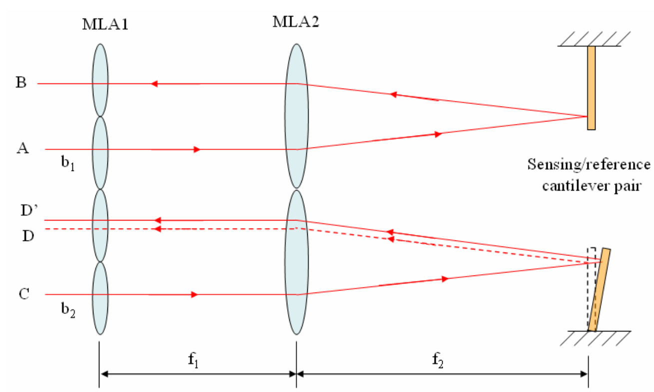

Figure 2. Principle of differential surface stress. The differential bending of sensing cantilever relative to reference cantilever causes path length difference.

Two reflected beams are interfered to determine the path length difference. Intensity of interference beam (I_{12}) is modeled as two component interferences (I_1 and I_2) and may be expressed as;

$$I_{12} = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\left(\frac{2(2\pi l)}{\lambda} + \phi_0\right),$$

where, ϕ_0 is the initial phase difference and λ is wavelength of monochromatic light. As a result, intensity of the interfered beams may be monitored to determine the differential surface stress change associated with absorption of chemical species on the sensing surface.

2.2 Differential surface stress sensor realization

An optical circuit shown in Figure 3 is utilized for assembling the surface stress sensor. In the system, pair of tipless Atomic Force Microscope (AFM) cantilevers with a top side coating of 5nm titanium/ 30nm gold are used as sensing/reference pair. The cantilevers used in the sensor realization had the following nominal dimensions: length of 450 µm; width of 80 µm and thickness of 1 µm (Nanoworld, Switzerland). A pair of microlens arrays with lens of 240 µm and 900 µm diameters; and pitches of 250 µm and 1mm, respectively were used to direct the beams towards the sensing/reference pair. Motorized and manual actuators were used to assist in aligning of MLAs with respect to the sensing/reference cantilever.

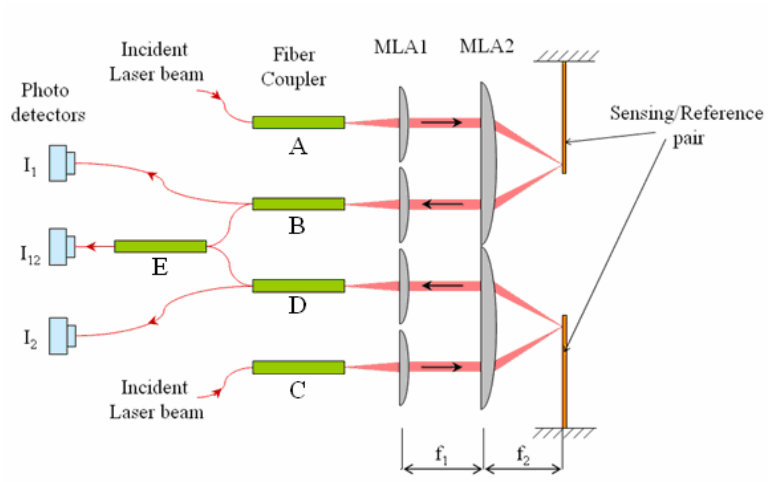

Figure 3. Optical circuit of differential surface stress sensor.

Two bi-directional couplers (B and D in Fig 3) were used to split the reflected beams and direct one component towards photodetectors to measure the intensity of reflected beams. Other components of two reflected beams were interfered using the third bi-directional coupler and intensity of interfered beam was monitored using a photodetector.

3. EXPERIMENT

Performance of the differential surface stress sensor was characterized through measurement of surface stress associated with alkanethiol SAM formation. Details of the tip characterization and surface stress measurement are explained in the following sections

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3.1 Microstructure and stiffness of cantilever

AFM tips are batch manufactured resulting in large variation of dimensions from the manufactured quoted nominal dimensions. In order to accurately measure the surface stress development, thickness of the cantilever was calculated based on material constants and the experimentally measured spring constant. Godin et al. [4, 9] have shown that the grain size of gold film affects the surface stress change during the formation of Alkanethiol SAMs. Gold film on the cantilever was imaged using intermittent (tapping) mode and grain size was determined to be 20 ± 10 nm (Figure 4). The mean square roughness of the gold surface was 2.07 ±0.23 nm for the 500 nm scan size. The resonance frequency and stiffness of the cantilever were found to be about 12.2 kHz and 0.3 N/m. Thickness of the cantilever assumed identical all around was determined based on the measured spring constant and material properties of cantilever as:

$$t = \left(\frac{4k_z L^3}{bE} \right)^{1/3}$$

Where, k_z and E are normal spring constant and Young's modulus of the cantilever, respectively; L and b are length and width of the cantilever. From the above calculation, the cantilever thickness was found to be 2.15µm.

a) b)

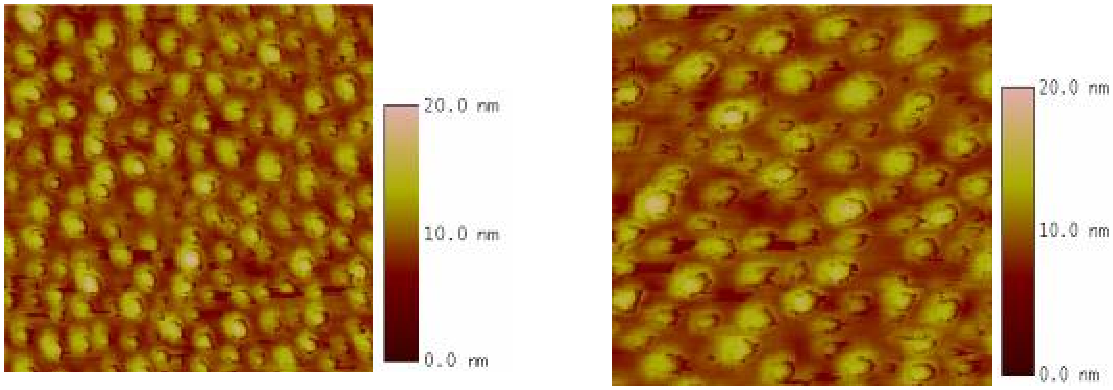

Figure 4. AFM images (500nm×500nm) and (300 X 300 nm) of grain structure of gold film on AFM cantilevers

3.2 Surface stress change during vapor deposition of alkanethiol

In order to ensure that alkanethiol are only absorbed on the sensing cantilever during the surface stress measurement, an alkanethiol SAM was deposited on the reference cantilevers before the experiments. The reference cantilever was prepared by incubating 2mM octadecanethiol [$HS(CH_2)_{17}CH_3$] /ethanol (200 proof) solution for 12 hours to protect formation of SAMs. It is then removed from the solution and rinsed in anhydrous ethanol for several time [4, 9]. Because exposing UV causes disulfides or dimers, all procedures were carried out in the dark under a standard fume hood.

Experiments were conducted in three different steps. In the first step, stability of the interferometer was monitored to ensure that measured signal is not affected by drift and ambient noise. In the second step, liquid octadecanethiol was introduced and the differential bending of sensing cantilever was monitored to determine the surface stress change associated with alkanethiol SAM formation. Before the alkanethiol deposition experiment, sensing and reference cantilevers were aligned to the microlens arrays and interferometer was allowed to settle for some time to minimize the variation of intensity of individual beams before introducing the liquid octadecanethiol solution. A droplet about 0.1 cc of alkanethiol solution was then introduced near the cantilevers. The vapors of alkanethiol solutions were confined near the cantilevers and interferometer was utilized to measure the deflection of sensing cantilever associated with deposition and formation of alkanethiol molecules SAM layer. Intensity of the interfered (I_{12}) as well as reflected beams from reference (I_1) and sensing cantilevers (I_2) were monitored throughout the experiment. Differential surface stress which is proportional to the cantilever deflection is then calculated by using Stoney's Formula with obtained spring constant and geometry of the cantilever.

In the final step, sensing and reference cantilevers were again exposed to alkanethiol vapors to ensure that surface stress measured in the second step is associated with only alkanethiol formation. As the sensing as well as the reference cantilevers are covered with alkanethiol SAM therefore reintroduction of alkanethiol vapors should not cause differential bending of the cantilevers.

4. RESULTS AND DISCUSSION

Experimental measurements of surface stress induced due to vapor phase deposition of alkanethiol during a typical run are plotted in Figures 6(a), (b) and (c). Intensity of reflected and interfered beams monitored before introduction of alkanethiol vapor are plotted in Figure 6(a). Measured intensities are nearly constant and do not drift with time. The results clearly show that interferometer is stable and does not drift with time. All the intensity measurement display some scatter and it is most pronounced in the interference signals. The scatter may be the result of thermal noise, environmental vibrations or Fresnel reflections at the junctions between fiber optic cables. We are currently working on improving acoustic noise and vibration isolation of the system. All the fiber optic junction will be filled with index matching gel to minimize Fresnel reflections. In the current state, the interference signal displays some noise but the signal to noise ratio is still quite large. Further work is in progress to improve the signal to noise ratio in the interference signal.

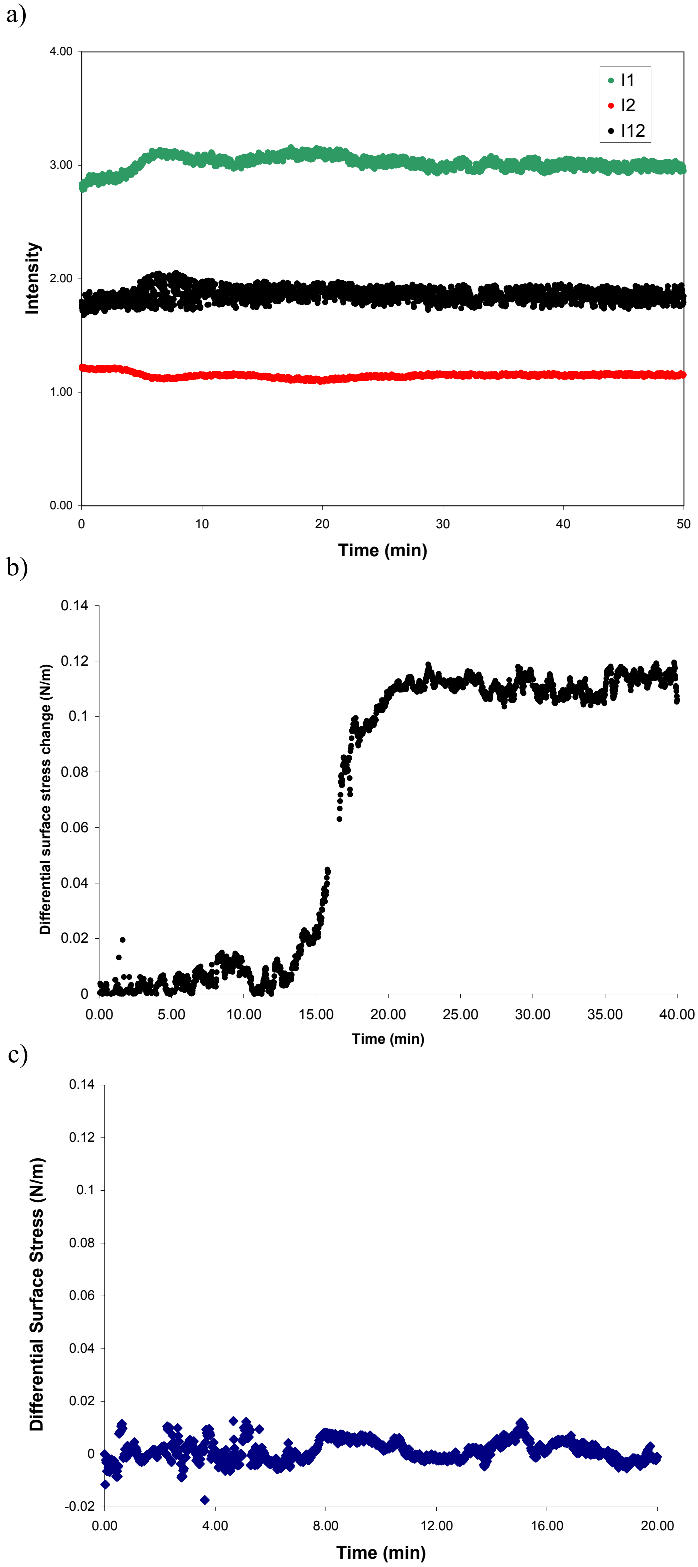

Figure 6: Differential surface stress measurement: (a) Intensity of reflected and interfered beams before deposition, (b) Differential surface stress during deposition; (c) Differential surface stress due to alkanethiol exposure after deposition.

After the initial monitoring of interferometer stability, alkanethiol vapor were introduced near the cantilever and differential bending of the cantilevers was monitored to measure the surface stress change associated with alkanethiol SAM formation on gold coated reference cantilever. Measured surface stress is plotted as a function of time in Figure 6(b). Surface stress buildup starts after 15 minutes of introducing the solution. Surface stress rapidly builds up and reaches a stable value about 0.12 N/m. Godin et al. [4, 9] have measured surface stress during alkanethiol SAM formation with lager grain sizes of gold and achieved surface stress of 0.51 ± 0.02N/m and 15.9 ±0.6N/m at grain sizes of 90 ± 50nm and 600 ±400nm respectively. The grain size of current gold film is about 20 nm. Previous experimental results and the current results indicate that surface stress associated with SAM formation is a function of film grain size.

Magnitude of surface stress change and kinetics of SAM formation are also influenced by the distance between cantilever and the location where alkanethiol droplets are introduced. [4, 9] During the experiment, octadecanthiol droplet was introduced at a distance of about 5 mm from the cantilevers. The kinetics of SAM formation observed in the current experiments compare well with other reported measurements for alkanethiols vapor introduced at similar distances [4, 9].

After the SAM formation on the sensing cantilever, sensor was again exposed to alkanethiol vapors. Surface stress change measured during the alkanethiol observed during second exposure of alkanethiol is plotted in Fig 6(c). As shown in the Fig 6 (c), monitored surface stress change was within the system's normal noise range, ±0.01 N/m. A minimal surface stress change during re-introduction of the alkanethiol vapors indicates that both sensing and reference cantilever are covered with alkanethiol SAM.

Furthermore, it indicates surface stress change observed during the first introduction is unambiguously associated with SAM formation on sensing cantilever.

5. CONCLUSIONS

A miniature sensor based on two microcantilevers – a sensing and reference pair – is developed for differential surface stress measurement and is explored for detection of chemical and biological species. High resolution interferometry is utilized to measure the differential surface stress developed due to absorption of chemical species on the sensing cantilever. Sensitivity of sensor measurement is not dependent on distance between the sensing surface and detector; as a result, surface stress sensor is amenable for miniaturization and array of sensors would be easily fabricated on a single MEMS device. Surface stress associated with alkanethiol formation on gold surface is measured to characterize the response of the sensor.

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