

# Surface stress in the self-assembly of alkanethiols on gold probed by a force microscopy technique

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Received: 25 July 1997/Accepted: 1 October 1997

**Abstract.** The extreme sensitivity of scanning force microscopy allows its application to be extended well beyond the probing of surfaces. We discuss micromechanical force microscope cantilevers, with a thin Au receptor layer on one side, as sensors for gas-phase adsorption of alkanethiols, which self-organize into well-ordered, densely packed films. Quantitative data show that surface stress develops during the self-assembly process for alkanethiols of different chain lengths. In particular, we present an analysis of the kinetics of the replacement process of adsorbates by butanethiol molecules, details of the acquisition analysis, and a quantitative calibration technique.

Numerous local tip–sample interactions are used to obtain information on sample surface properties such as topography, conductivity, elasticity, friction, and magnetic responses. Recently, the scanning force microscope (SFM) tip has been used to probe the stretching and unfolding of individual molecules [1]. The alternative concept to using the tip of the cantilever as a local sensing element that is scanned over the surface is to use the entire cantilever surface area as a receptor. This technique constitutes a new avenue for further experiments to gather information on specific and nonspecific interactions and reactions on the nanoscale.

One concept is the use of “bimetallic” cantilevers to probe temperature changes. This concept was pioneered to follow heat evolution during the catalytic reaction of O<sub>2</sub> and H<sub>2</sub> to form water on a thin Pt layer evaporated on an SFM cantilever [2]. The bimetallic technique was also applied to probe local temperature differences along a biased resistor [3]. It also enabled photothermal spectroscopy to be conducted on a picogram quantity of material [4]. Signals from the cantilever response can be detected with the high sensitivity, speed, and bandwidth of conventional SFM technique. In addition to probing subtle temperature differences, a cantilever-type sensor can additionally be used as a transducer for femtoscale effects in science [5–13]. We applied the micromechanical sensor technique to probe the self-organization of alkanethiols – HS–(CH<sub>2</sub>)<sub>n–1</sub>–CH<sub>3</sub> for

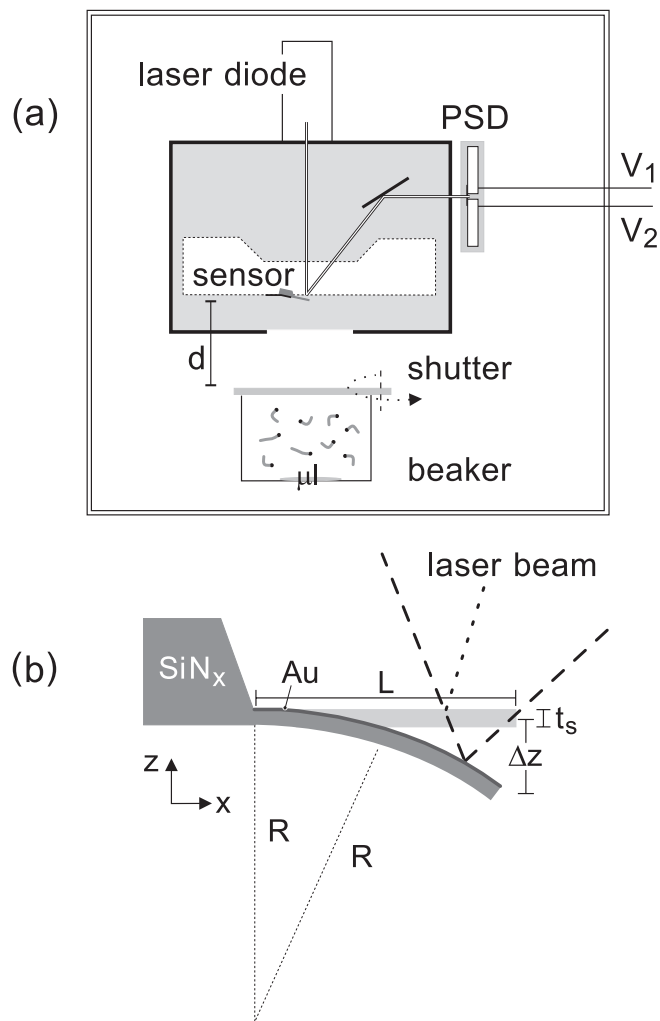
$n = 4, 6, 8, 12,$  and  $14$ , where  $n$  is the number of carbon atoms in the alkyl chain – on Au [14, 15]. Self-assembled monolayers (SAMs) are used in applications such as microcontact printing [16] and voltametric microsensors [17], and have recently been applied to molecular host–guest recognition [18].

## 1 Experimental

Our measurement setup, outlined schematically in Fig. 1, is based on a NanoScope II SFM head (Digital Instruments, Santa Barbara CA, USA) which uses the laser beam deflection technique to detect sensor deflection  $\Delta z$  down to sub-Å levels. The normalized voltage difference  $\Delta V = (V_1 - V_2)(V_1 + V_2)^{-1}$  of two segments of a position-sensitive detector (PSD) is converted into a 12-bit value in an analog-to-digital converter and is displayed continuously on a monitor as well as being stored on a computer hard disk. All V-shaped SiN<sub>x</sub> sensors used here are of the same type and have thickness ( $t_s$ ) 0.6 μm, length ( $L_s$ ) 150 μm, and width ( $w_s$ ) 18 μm, giving a spring constant of  $\approx 0.5 \text{ Nm}^{-1}$  (Park Scientific Instruments, Mountain View CA, USA). The Au layer of the sensor was removed in aqua regia, and Ti ( $\approx 0.5 \text{ nm}$ ) and Au ( $\approx 20 \text{ nm}$ ) were freshly evaporated sequentially prior to each experiment by thermal evaporation. A sealed glass beaker with an opening of 2 cm, containing  $\approx 20 \mu\text{l}$  of alkanethiol liquid, was placed at a distance ( $d$ ) of 5 cm beneath the sensor housing. After thermal equilibrium between the liquid and the gas phase of alkanethiol was reached, the shutter was opened, thereby exposing the sensor to alkanethiol vapor. The sensor was shielded to minimize vibrations, turbulences, and thermal drifts.

## 2 Results and discussion

In Fig. 2 the PSD voltage indicating the response of the sensor is plotted as a function of time for experiments with alkanethiols of various chain lengths. We observed that the sensors deflect immediately after being exposed to alkanethiol



**Fig. 1.** **a** Measurement setup based on a NanoScope II head implemented in a measuring chamber with controlled humidity and temperature. The laser beam is reflected from the sensor apex and shines on the position-sensitive detector (PSD). The PSD consists of a four-quadrant diode and generates photocurrents (proportional to the incident laser power), which are converted into voltages  $V_1$  and  $V_2$ . The beaker contains  $\approx 20 \mu\text{l}$  of analyte liquid. A microscope glass slide with vacuum grease was used as a shutter to seal the glass beaker. Removing this shutter exposed the sensor to the vapor of the analyte. **b** The bending with radius of curvature  $R$  is schematically outlined to determine the surface stress from the detector voltage. The V-shaped  $\text{SiN}_x$  sensors have thickness  $t_s = 0.6 \mu\text{m}$ , length  $L_s = 180 \mu\text{m}$ , Young's modulus  $E = 150 \text{ GPa}$ , and Poisson's ratio  $\nu = 0.23$ . The sensor is coated on top with a thin (20 nm) Au receptor layer

vapors. The onset of exposure is indicated for each experiment by an arrow in Fig. 2. We observed a faster first response for lighter alkanethiols, corresponding to their higher vapor pressures. First, the sensor deflections undergo a local minimum (deflection towards the Au layer, and upwards in Fig. 1b), followed by an increase of  $\Delta V$  to a saturation value (deflection towards the  $\text{SiN}_x$  layer). Under our experimental conditions, the concentration of alkanethiols was assumed to change in the vicinity of the sensor [6]. Consequently, the time it takes to form a SAM was found not to be proportional to the vapor pressure of alkanethiols. The time scale between the onset of exposure and the saturated deflection is typical for the time it takes to form a SAM via the vapor phase [19], however, and was confirmed with a similar setup using el-

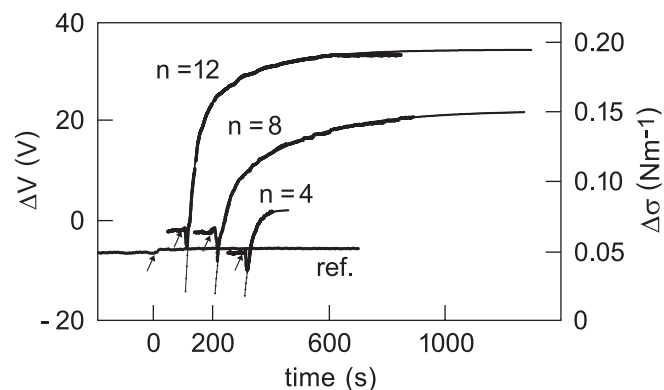
lipsometry by determining the thicknesses of the alkanethiol monolayers as a function of exposure time. The saturation value in the diagram corresponds to a monolayer of alkanethiols that is  $\approx 95\%$  complete. In contrast to the experiments done with alkanethiol vapors, all reference experiments performed with volatile alkane vapors showed no such response (reference experiment in Fig. 2).

Several mechanisms can contribute to the characteristic measured signal for exposure to alkanethiol vapor, such as thermal effects or mass loading. Because self-assembly of alkanethiols on Au is reported to be exothermic with an enthalpy of adsorption  $\Delta E \approx -150 \text{ kJ mol}^{-1}$  [20] and the sensor is coated with Au, bending due to the “bimetallic” effect has to be considered a contribution to the measured signal. We found that the transient bending for  $\approx 25 \text{ nJ}$  of reaction heat reveals the correct sign for deflection at saturated alkanethiol coverage (the sensor bends towards the  $\text{SiN}_x$  because its expansion coefficient is lower than that of Au), but is less than 1% of the recorded signals [2]. The local minimum at the beginning of the alkanethiol experiments cannot be explained by heat either, because of the incorrect sign in the measured signal. Nor can the gravimetric deflection due to the molecular loading, calculated to be  $\approx 1 \text{ mV}$ , account for the observed bending. Based on both the permanent nature of the deflection and its magnitude, we attribute the sensor response to changes in surface stress  $\Delta\sigma$  [21–23].

Surface stress bends the micromechanical cantilever into an approximate circle segment as outlined schematically in Fig. 1b. The deflection of the apex of the sensor,  $dz$ , is determined by

$$R^2 = x^2 + z^2 \Rightarrow dz = \frac{L}{\sqrt{R^2 - L^2}} dx, \quad (1)$$

where  $R$  is the radius of curvature. The deflection of the cantilever was then calibrated by a standard force–distance curve



**Fig. 2.** The PSD voltage  $\Delta V$  and changes in surface stress  $\Delta\sigma$  of the sensors plotted as a function of time for exposure to alkanethiols and a reference vapor. The onset of exposure is indicated by arrows. Reference experiments consisted of exposing the sensor to vapors of alkanes, which are molecules that do not chemisorb on Au. This reference shown (octane) is representative of all the other control exposures. In each reference experiment, no significant deflection was observed, except for a small signal attributed to the removal of the shutter. In strong contrast to this, sensors start bending immediately after being exposed to alkanethiol vapors. Before each exposure, the sensor baseline was recorded in air for  $\approx 1 \text{ min}$  which reflected the adsorbate level of the Au layer in our laboratory–air environment and the stability of the environment

when the cantilever is in contact with a rigid sample. These deflections are described by [9]:

$$dz = \frac{3\Delta V}{2L} \frac{dz'}{dV'} dx, \quad (2)$$

where  $dz'$  is the piezotube elongation change and  $dV'$  is the corresponding PSD voltage change.

By subtracting (1) from (2) in the limiting case of small beam deflections, one obtains the radius of curvature  $R$  as a function of PSD voltage:

$$\frac{1}{R} \approx \frac{3\Delta V}{2L^2} \frac{dz'}{dV'}. \quad (3)$$

Differences in the surface stress between the top and the bottom side of the sensor,  $\Delta\sigma$ , are described by Stoney's formula [24]:

$$\Delta\sigma = \frac{Et_s^2}{6R(1-\nu)}, \quad (4)$$

where  $E$  is Young's modulus and  $\nu$  is Poisson's ratio of the sensor material. The Equations (3) and (4) relate the measured PSD voltage to changes in surface stress in our setup plotted as the right-hand ordinate in Fig. 2. In our study, surprisingly, all the chemisorbed alkanethiols investigated caused a compressive surface stress during self-assembly. At first glance, this characteristic is counterintuitive: molecules in SAMs collectively tilt  $\approx 30^\circ$  from the surface normal and therefore reduce chain-to-chain separation to optimize their intermolecular van der Waals interaction energy. This should produce a monolayer-induced contracting lateral tension. If this effect were predominant, one would expect a tensile surface stress, i.e. a bending of the sensor towards the SAM film. An important quantitative result is the observation of increasing compressive surface stress,  $\Delta\sigma_{\text{sat}}$ , with increasing chain length (Table 1). From these data we conclude that compressive surface stress is directly proportional to alkyl chain length. The clearly resolved minima at the beginning of each chemisorption process can be explained as a replacement of residual adsorbates on the Au surface by chemisorbing alkanethiols. This has been proposed on the basis of X-ray photoelectron spectroscopy and second-harmonic generation studies of self-assembly of alkanethiols in solutions [25]. All surface stress curves except for the reference curve in Fig. 2 reveal the replacement process as a release of  $11 \times 10^{-3}$  to  $19 \times 10^{-3} \text{ Nm}^{-1}$  of residual surface stress [26] during the first  $\approx 10$  s of exposure to alkanethiols.

**Table 1.** The change in surface stress at saturation coverage,  $\Delta\sigma_{\text{sat}}$ , obtained from all stress measurements is listed as a function of alkyl chain length  $n$ . The estimated errors arise mainly from varying cantilever geometries. Based on these data we calculate the tension in the SAM to be  $\sigma_t = \sigma_{\text{sat}} t_f^{-1}$  of a film thickness  $t_f$

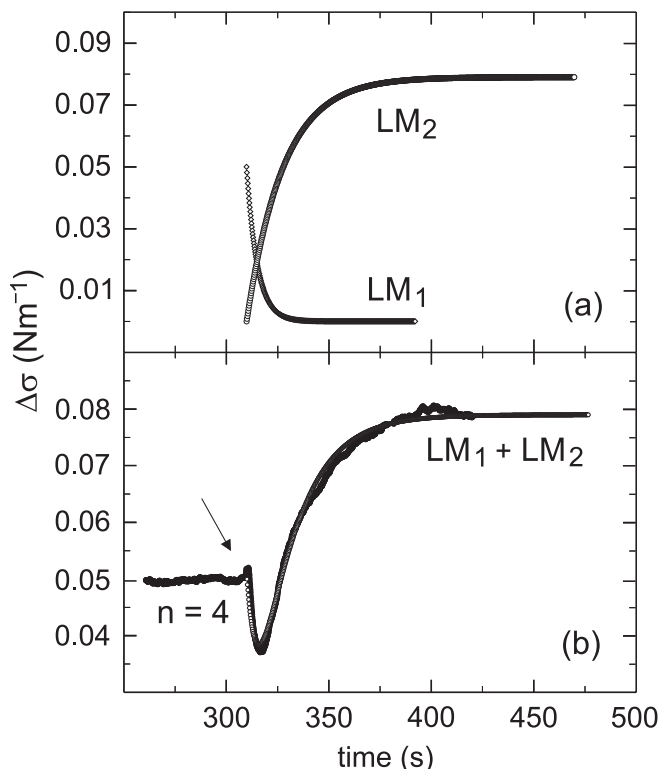
$n$	$\sigma_{\text{sat}} / \text{Nm}^{-1}$	$t_f / \text{nm}$	$\sigma_t / \text{GPa}$
4	$0.08 \pm 0.02$	0.4	$0.20 \pm 0.05$
6	$0.10 \pm 0.02$	0.6	$0.17 \pm 0.03$
8	$0.15 \pm 0.02$	0.9	$0.17 \pm 0.02$
12	$0.19 \pm 0.02$	1.5	$0.13 \pm 0.01$
14	$0.25 \pm 0.02$	1.8	$0.14 \pm 0.01$

To elucidate the kinetics of self-assembly, each measured stress curve was fitted by a simple adsorption isotherm (LM) [6, 19, 27]

$$\delta\sigma \propto 1 - \exp(-\kappa t), \quad (5)$$

where  $\kappa$  is the reaction rate and  $t$  is time [28]. LM describes our chemisorption data of alkanethiols and also the replacement of the adsorbates (Fig. 3a). The fitting procedure is demonstrated for the example of  $n = 4$  and is presented in Fig. 3a. The first part of the data, which is dominated by the release of surface stress, is described by  $\text{LM}_1$  ( $\kappa_a = 0.079 \text{ s}^{-1}$ ). The adsorption isotherm fits the second part of the data and additionally determines the zero point of the stressograms ( $\kappa_a = 0.19 \text{ s}^{-1}$ ). By adding both exponential dependencies  $\text{LM}_1 + \text{LM}_2$ , we can fit the entire surface stress change of the sensor (Fig. 3b). That the stress curves arising from alkanethiol chemisorption follow LM characteristics permits us to conclude that the surface stress change is proportional to the number of alkanethiol molecules adsorbed.

These findings can be interpreted in terms of electrostatic interactions between the monolayer components. The apparent dipole moment of the SAM is considered to contain a contribution from the  $\text{Au}^+ - \text{S}^-$  head group and from the  $\text{S}^- - \text{alkyl}^+$  chain. Even at low coverage, the sulfurs are bound to the Au and the  $-\text{CH}_3$  tail groups tend to emerge at the air-monolayer interface [15], providing a continuously increasing average apparent dipole moment during monolayer formation. This apparent dipole moment increases linearly



**Fig. 3.** **a** LM fits of the recorded data for  $n = 4$  for the desorption of adsorbates ( $\text{LM}_1$ ) from and butanethiol ( $\text{LM}_2$ ) on the Au layer. **b** The butanethiol stress curve is plotted together with the sum of  $\text{LM}_1$  and  $\text{LM}_2$ , which describes the entire measurement after exposure. The onset of the exposure is indicated by an arrow

with  $n$  [29], resulting in a linear increase in electrostatic repulsion. Such dipolar repulsive forces in adsorbate–adsorbant systems are generally expected to produce surface stresses in the range of  $10^{-3} \text{ Nm}^{-1}$  [30], which is consistent with the magnitude of our measurements.

The concept of sensing surface stress changes of a sub-monomolecular layer can be extended to the specific binding of a molecule to a receptor layer. We demonstrated this concept by using SAMs of  $\omega$ -functionalized alkanethiols as a host for molecular recognition. We experimentally studied the influence of gas-phase hexylamine (Fig. 4a I) on mercaptohexadecanoic acid (Fig. 4a II) SAMs (Fig. 4b). A significant decrease in  $\Delta\sigma$  was observed when hexylamine molecules docked onto the carboxylic endgroups (Fig. 4a III).

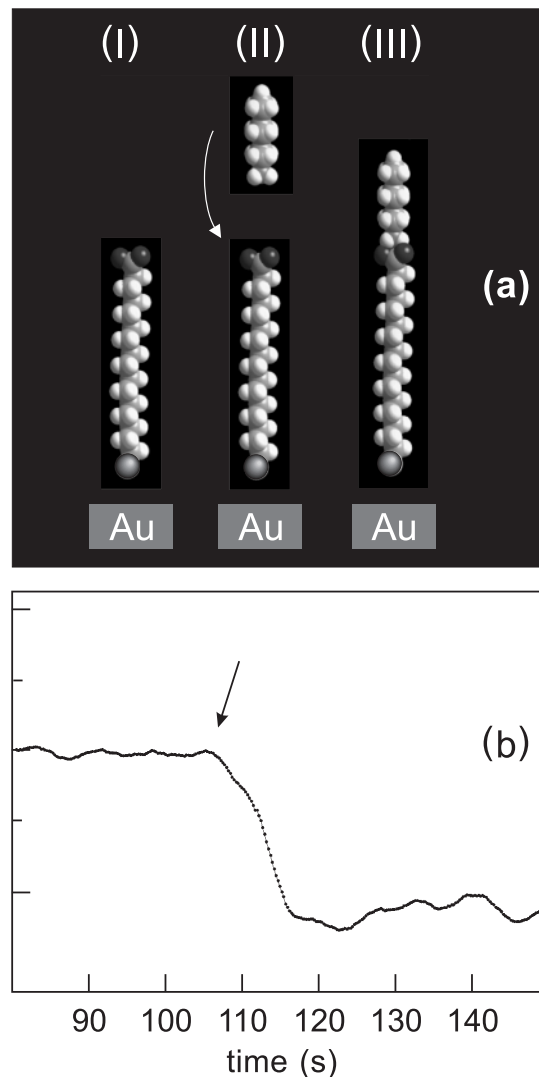
### 3 Concluding remarks

Surface stresses of deposited metallic films on macroscopic plates have been studied since the beginning of the 20th century [24]. The *micromechanical* approach outlined here that uses SFM techniques can be extended to a variety of chemical and biological systems [9] with unsurpassed sensitivity and with tiny samples. Commercially available, standardized sensors achieve a surface stress resolution for SAMs of  $10^{-7} \text{ Nm}^{-1}$ , which corresponds to a change of zeptomolar ( $10^{-21} \text{ mol l}$ ) quantities. Further reduction of sensor thickness into the nanometer realm [31] promises the detection limits of even smaller surface stress variations. We foresee no fundamental barrier that could preclude the application of the described technique to the detection of individual molecular events. In addition to their high sensitivity, such devices are attracting increasing interest in science and technology for *in situ* process control because they feature small size and compatibility with Si microelectronic fabrication, in particular CMOS [32].

*Acknowledgements.* We thank H. Biebuyck, P. Guéret, and H. Rohrer for helpful discussions as well as for their support. We thank P. Vettiger and the Zurich Micromechanics group for their contributions to optimize sensor performance. This work was partially supported by the Swiss National Science Foundation, NFP 36, and the Swiss Priority Program MINAST 7.04.

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**Fig. 4a,b.** Model experiment of a mercaptohexadecanoic-acid (I) SAM-coated sensor as a functionalized surface. Mercaptohexadecanoic acid acts as a specific receptor to bind hexylamine as an acceptor molecule. The resulting salt bridge formation is detected via a change in surface stress. The surface stress change is a reference to the surface stress of the mercaptohexadecanoic monolayer. The arrow indicates the onset of the exposure of the sensor to hexylamine vapors

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