



Changes in surface stress at the liquid/solid interface measured with a microcantilever

R. Raiteri^{a,b}, H.-J. Butt^{a,*}, M. Grattarola^b

^a *Institute for Physical Chemistry, University of Mainz, Welderweg 11, 55128 Mainz, Germany*

^b *Department of Biophysical and Electronic Engineering, University of Genoa, via Opera Pia 11a, 16145 Genoa, Italy*

Received in revised form 4 November 1999

Abstract

The bending of microfabricated silicon nitride cantilevers was used to determine surface stress changes at solid–liquid interfaces. The radius of curvature of the bent cantilever is directly proportional to changes in the differential surface stress between its opposite sides. To demonstrate the possibilities and limitations of the technique, cantilevers coated on both sides with gold and densely packed monolayers of different thiols were put in a constant flow of aqueous electrolyte solution and the deflection was measured using an optical lever technique. Changes in the surface stress for the different thiol monolayers due to specific proton adsorption are presented. Possible applications and improvements of this technique are discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Atomic force microscopy; Surface stress; Cantilevers; Biosensors; Surface energy of solids

1. Introduction

For liquids, the surface tension γ is one of the most important parameters that characterize the surface. Several methods are available to measure it accurately and reliably. For solids, however, it is difficult to measure the equivalent quantity, the surface stress σ [1]. Most methods have some drawbacks, e.g. they are technically demanding, they can not be used to monitor changes of the surface stress, they are semi-empirical and depend on further assumptions, or they are not generally applicable.

Others and we have recently improved the bending-plate technique to measure changes in the surface stress of solids by using microcantilevers as stress sensors [2–8]. The principal of the experimental technique is straightforward. A microcantilever prepared with dif-

ferent opposite faces bends because of changes of surface stress. If, for instance, the surface stress on one side changes, say it increases, then that side tends to contract. Hence, changes of the surface stress cause the cantilever to bend (Fig. 1). For a uniform stress acting on an isotropic material, the radius of curvature, R , is given by Stoney's formula [9,10]

$$\frac{1}{R} = 6 \frac{1-\nu}{Et^2} (\Delta\sigma_1 - \Delta\sigma_2) \quad (1)$$

where E is the Young's modulus of the cantilever material; ν denotes the Poisson ratio; t is the thickness of the cantilever; and $\Delta\sigma_1$ and $\Delta\sigma_2$ are the surface stress changes of the top and bottom side, respectively. The applicability of Eq. (1) has been discussed thoroughly in [11,12].

Measuring the bending of a thin plate to determine surface stress changes was already proposed by several authors [13–16], e.g. to measure electrocapillary-like curves of gold and platinum [16–18], or to measure adsorbate-induced surface stress changes in vacuum

* Corresponding author. Fax: +49-6131-392970.

E-mail address: butt@wintermute.chemie.uni-mainz.de (H.-J. Butt).

[15,19,20]. In a variation of the bending plate method the deformation of a circular plate was measured [21–23].

All these measurements were facilitated by the fact that surface stress changes were relatively high, typically $0.1\text{--}1\text{ J/m}^2$, and these changes could be induced quickly, usually in few seconds. In contrast, measuring generally surface stresses, especially at solid–liquid interfaces, is more demanding: First, the sensitivity needs to be one order of magnitude higher because changes in surface stress caused by different concentrations of solutes are usually much smaller than 0.1 J/m^2 . Second, changes in surface stress have to be induced by changing the medium around the cantilever. Preferably this should be done in a flow-through experiment because, in that case, surface reactions could be continuously monitored. On the other hand changing the medium causes turbulence.

Using microfabricated cantilevers instead of thin, but still macroscopic plates (typically 0.1 mm thick and $1\text{--}10\text{ cm}$ long [13,17–20]), allowed us to monitor the

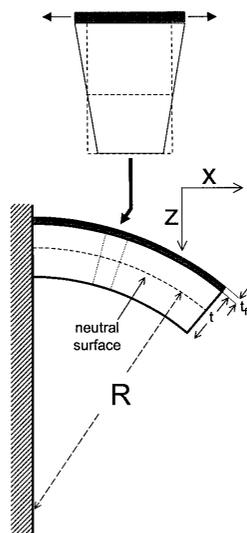


Fig. 1. Schematic side view of a silicon nitride cantilever of thickness t , with a thin receptor layer on one side of thickness t_r . Because $t_r \ll t$, one assumes that the mechanical properties of the cantilever are not affected by the added layer. Above: an increase/decrease of the surface stress on the coated side causes the area of that side to contract/expand around the neutral plane, i.e. the section of the cantilever which is not strained. For uniform surface stress and isotropic material, the resulting bending over the whole length is circular with a constant radius of curvature R . R is measured relative to the neutral plane. The neutral plane lays in the middle of the cantilever only if stresses of the same magnitude but opposite sign are applied to the two surfaces. However, for the large radii considered in this work (radius of curvature in the order of a cm), the error one makes in calculating the bending as if the neutral plane were in the middle is negligible.

small changes in surface stress due to variations in the pH of the surrounding solution. Microfabricated cantilevers, which are $100\text{--}400\text{ }\mu\text{m}$ long and $0.3\text{--}0.6\text{ }\mu\text{m}$ thick, are ideally suited because they fulfill two requirements: First, for a given change in surface stresses $\Delta\sigma_1$ and $\Delta\sigma_2$, of the two opposite surfaces 1 and 2, the deflection of the cantilever, z , is proportional to $z \propto (L/t)(\Delta\sigma_1 - \Delta\sigma_2)$ (see Eq. (3)) where L is the length of the cantilever. Hence, the sensitivity of the measurement increases with the ratio of cantilever length to thickness. To achieve a high sensitivity cantilevers should be long and thin. Second, the resonance frequency $\nu = 0.163 \cdot (t/L^2) \cdot \sqrt{E/\rho}$ should be as high as possible to prevent external vibrations from interfering with the measurement [24] and give fast response. ρ is the density of the cantilever material. High sensitivity and at the same time low noise can be achieved by using small cantilevers. Small cantilevers also have the advantage of being relatively insensitive to turbulence in a flow-through experiment.

In the last few years it became clear that micro-cantilevers can be used not only to study electrochemical processes [4,25], but that a number of different domains can be transduced into a mechanical motion of a cantilever with unprecedented resolution: changes in dissipated heat [26–29], mass [28,30,31], magnetic field [32], cellular and subcellular forces [33,34], polarized light [35] could be measured either as a static deformation or a change in the resonant frequency of the cantilever. In particular it has been shown that micro-cantilevers can be used to monitor adsorption processes both at the solid/air [7,36] and solid/liquid interface [5,8]. The feasibility of the technique was first demonstrated by measuring changes of the surface stress of silicon nitride upon varying the pH [5]. The affinity binding of proteins in aqueous electrolyte could be also monitored by observing changes in the surface stress [8]. A promising application of the technique is therefore to use microcantilevers as sensors for specific substances. One possible way of achieving this is to coat one side of the cantilever with a receptor while keeping the other side relatively inert. A first step in this direction is described in this paper. One side of the cantilever was coated with carboxylic groups. We could detect the proton adsorption to these carboxylic groups in aqueous electrolyte solution.

2. Materials and methods

Commercially available silicon nitride cantilevers (Nanoprobes, Digital Instruments, Santa Barbara, CA) were used. They are V-shaped to minimize lateral deflection. They are $L = 190\text{ }\mu\text{m}$ long, and each arm is $40\text{ }\mu\text{m}$ wide and $t = 0.6\text{ }\mu\text{m}$ thick. We approximated their elastic behavior with that of two parallel beams of

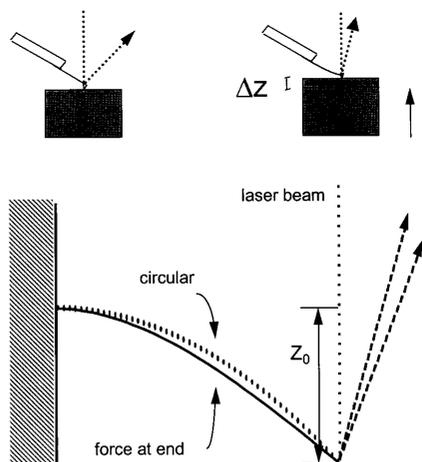


Fig. 2. (a) standard cantilever deflection calibration procedure to relate cantilever deflection to changes in the photodiode signal. Sample is displaced a known distance Δz and the corresponding change in reflected spot (dotted line) is recorded. (b) Comparison between different bending shapes of a thin beam clamped on one side (zero deflection and zero slope) for a given deflection z at its free end. Dotted line is circular, while continuous line is originated by a load applied at the free end.

the same width of the arms [37–39]. We used a value for the Young's modulus of $E = 1.47 \times 10^{11}$ N/m² and for the Poisson's ratio of $\nu = 0.3$. The silicon nitride of the cantilevers, deposited by chemical vapor deposition (CVD) processes, is amorphous and, consequently, its mechanical properties are isotropic. The calculated spring constant is 0.09 N/m. One side is coated by the manufacturer with a 20–30 nm layer of gold in order to enhance optical reflectivity.

2.1. Cantilever preparation

We coated both sides of the cantilevers with thiol monolayers with different end-groups. Cantilevers were therefore treated in the following way: first, we removed the already deposited gold layer by rinsing in aqua regia (three parts HCl, one part HNO₃, one part H₂O) since we did not know its precise nature. Then we evaporated 3–5 nm of chromium and 30–40 nm of gold on one side only. The thin layer of Chromium is used in order to increase the adhesion of gold onto silicon nitride. Cantilevers were then immersed overnight in 1 mM octadecanethiol ethanolic solution. The octadecanethiol formed a stable, dense, and highly structured monolayer on the freshly coated gold [40,41]. After eliminating all excess of alkanethiols by rinsing with ethanol, an identical gold layer (3–5 nm of chromium and 30–40 nm of gold) was evaporated onto the opposite side of the cantilevers. The temperature during evaporation did not rise above 100°C. This is a

temperature thiol monolayers can stand. It is known that above that temperature they start to desorb [42]. Then we immersed the freshly coated cantilevers into 1 mM ethanolic solutions of thiols with different side groups. In particular we used 3-mercaptopropionic acid (HS(CH₂)₃COOH), 2-aminoethanethiol (HS(CH₂)₂NH₂) and 2-mercaptoethanol (HS(CH₂)₃OH, all from Fluka, puriss). The new thiol solution could not remove the previously bound octadecanethiol since the thiol–gold bond is relatively strong (binding energy 120 kJ/mol). Before use, each cantilever was thoroughly rinsed in ethanol and water. We assumed that the deposited thin gold/thiol layers did not change the elastic properties of the cantilevers.

2.2. Deflection detection and calibration

The radius of curvature of the cantilever was measured with the detection system of the head of a commercially available AFM (Nanoscope II, Digital Instruments, Santa Barbara, CA). Light from a laser diode was focused onto the end of the cantilever. The reflected laser spot hit a two-segment photodiode and the difference in intensity measured by the two segments, normalized by the sum of the intensities, was used as the deflection signal. Before each measurement, we calibrated the deflection signal by pushing the cantilever a known distance Δz against a hard surface and measuring the corresponding change in the photodiode signal (Fig. 2, top). This signal is a voltage proportional to the slope of the free end of the cantilever rather than its displacement. One has also to take into account the different resulting shapes of the cantilever due to a force applied at its free end, like during the calibration, and to a uniform stress (Fig. 2, bottom). We therefore followed the procedure already described in [4,5,43] which leads to the following approximated relationship between the radius of curvature R and the deflection z calibrated in meters:

$$\frac{1}{R} = \frac{3z}{L \sqrt{4L^2 + 9z^2}} \approx \frac{3z}{2L^2} \quad (2)$$

Eq. (1) together with Eq. (2) allowed us to calculate the differential surface stress from the calibrated deflection signal z .

$$\Delta\sigma_1 - \Delta\sigma_2 \approx \frac{Et^2}{4L^2(1-\nu)} z \quad (3)$$

The formula above is strictly valid only for rectangular cantilevers and contains other approximations that were discussed in details in [5,38,43,44]. It can be estimated that the results obtained using Eq. (3) deviate by at most 15% from the predicted behavior; this, together with the other approximations (e.g. effect of the deposited gold layer on the mechanical properties of the cantilevers, nominal values used for the dimen-

sions of the cantilever and the mechanical properties of the silicon nitride), can give rise to large errors in the estimation of the absolute changes in surface stress. This error however is rather systematic for all the performed experiments and does not influence the trend of the surface stress versus pH. This allowed us to make comparisons among the behavior of different thiol monolayers.

2.3. Experimental set-up

To continuously monitor stress changes induced by changes in the medium we used a fluid-flow set-up (Fig. 3). A commercial AFM head and a sealed fluid cell were used. The upper part of the cell was the standard commercial fluid cell, while the bottom plastic part and the flexible silicon sealing were home made. The need for a home made fluid cell raised for several reasons: one needs a reliable sealing since even small leakage over long periods can seriously damage the AFM head electronics and piezo scanner, moreover the cantilever needs to be far away from the bottom surface to avoid any interactions with it and to limit flow turbulence. Liquid flowed into the cell through an inlet via silicon and Teflon tubing from a reservoir flask. The liquid flow was driven by gravity and was kept constant during the whole measurement. Typical flow rates were 0.5–0.8 ml/min. Since the volume of the cell is ≈ 0.3 ml, the liquid in the cell was exchanged twice in ~ 1 min.

An experiment consisted in starting the flow with a neutral solution and letting the system stabilize for at least half an hour. We continuously monitored the pH value in the external reservoir and the deflection signal from the photodiode. Without stopping the flow, we then added into the external reservoir small quantities of a strong acid or base in order to vary the pH. After ≈ 30 s the new solution entered the cell and the cantilever started to deflect reaching a new steady state in a 2–3 min.

The flow induced a static bending of the cantilever, which is a function of the flow rate. Therefore, great care was taken to maintain a constant flow rate both by maintaining a constant pressure in the input Teflon tube and by preventing drop formation at the output.

Drift in cantilever deflection was reduced when cantilevers were allowed to equilibrate in the solution used for the measurement for few days before doing the actual experiment. However, there was usually a residual drift that could not be eliminated and limited the minimum speed at which changes in surface stress could be monitored.

3. Results and discussion

The results presented in this paper were obtained by coating both sides of a cantilever first with gold and then with different thiol monolayers. Hence, both sides display different thiol–liquid interfaces while the gold

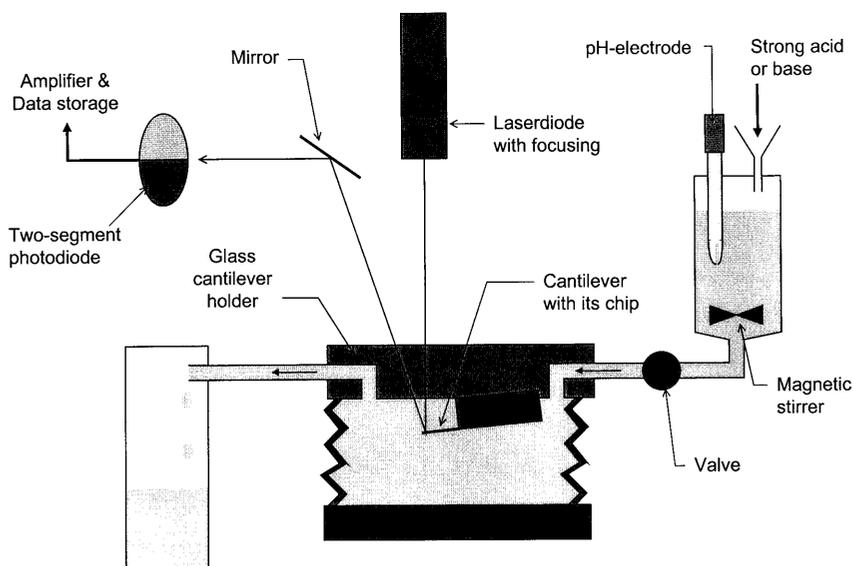


Fig. 3. Schematic of the experimental set-up. We used a commercial AFM head with its optical lever detection system. The cell was sealed with a homemade flexible silicon ring. Solutions flowed into the cell from an external reservoir and from the cell to a waste. Gravity drove the flow. By putting the external reservoir more than one meter higher than the cell and clamping the input tubing, we could keep a constant flow rate. pH was adjusted adding the corresponding acid or base of the salt used while continuously stirring. pH was also monitored with a glass electrode and an external pH-meter.

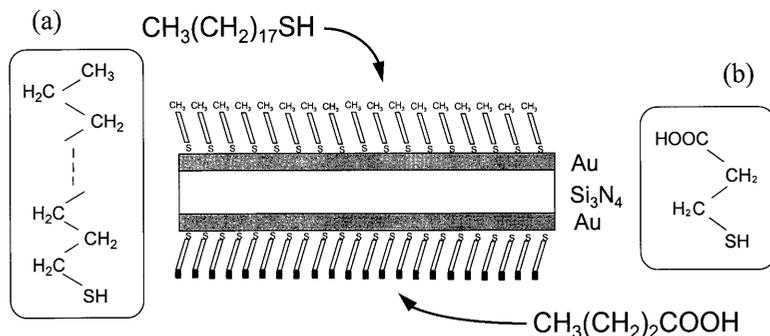


Fig. 4. Schematic of a cantilever used in the experiments (side view). The upper part was coated with a thin (30 nm) film of gold and a monolayer of octadecanethiols, $\text{CH}_3(\text{CH}_2)_{17}\text{SH}$ whose structure is depicted in inset (a). The lower side was also coated with gold and a monolayer of 3-mercaptopropionic acid, $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ whose structure is depicted in inset (b). Thiols covalently bind to gold forming self-assembled densely packed monolayers. Carboxyl groups, facing the solution at the bottom side, can lose a proton charging themselves and increasing the surface energy. On the other side, hydrocarbons are relatively inert to pH variations.

coating and the gold–thiol interface is the same for both sides. Since we monitor the difference in the surface stress between the two opposite sides, we attribute the observed effects to the thiol–liquid interface (i.e. ‘thiol surface’).

Surface stress changes measured with a cantilever coated on one side with octadecanethiols and on the other side with 3-mercaptopropionic acid (sketched in Fig. 4) are shown in Fig. 5. When referring to the carboxylic side the surface stress showed a minimum around pH 4–5. Increasing the pH above pH 5 or decreasing it below pH 4 the cantilever bent toward the mercaptopropionic acid side, that is its surface stress (tensile stress) increased.

For the interpretation, the proton dissociation of the carboxyl group



is probably important. For propionic acid, the dissociation has a pK of 4.87 [45]. Binding of a proton to a carboxylate group lowers the free enthalpy of that group by $\Delta G = kT \cdot \log(K)$, where K is the binding constant ($K = 10^{-\text{p}K}$). This could explain the increase in surface stress with increasing pH, as shown in Fig. 5: protons dissociate and leave high-energy carboxylate groups behind. The fact that the increase in surface stress looks ‘smeared’ (i.e. without an abrupt change) and shifted to higher pH values than it would be indicated by this dissociation mechanism can be explained in terms of local mutual interactions among the densely packed carboxyl groups on the surface. This mechanism, however, can not explain the small but significant increase of surface stress when reducing the pH below pH 4. We have yet no interpretation for this observation.

In experiments with 2-aminoethanethiol and 2-mercaptoethanol instead of the mercaptopropionic acid, only the increase of surface stress with increasing pH

was observed. The side groups of these molecules can dissociate according to



with pK values of ≈ 10 and > 10 , respectively. Results of these experiments are presented in Fig. 6. With both substances small changes in surface stress were observed compared with surface stress changes observed with mercaptopropionic acid. This is reasonable since the degree of dissociation should be relatively small. However, we did not detect any steep increase in surface stress in the case of 2-aminoethanethiol even for pH

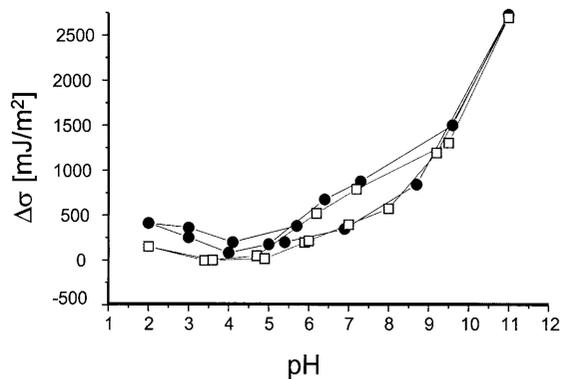


Fig. 5. Relative surface stress values for a cantilever coated as described in Fig. 4, vs. pH, in a 0.1 M KNO_3 solution. pH was varied while continuously flowing by adding 0.1 M KOH or 0.1 M HNO_3 . Dots and squares represent results from two different experiments with two different coated cantilevers. We always let the system stabilize at least for 5 min after a pH change before considering the reported deflection/surface stress value. Positive values correspond to deflections toward the 3-mercaptopropionic acid monolayer (tensile stress). Higher stress values correspond to higher surface energy.

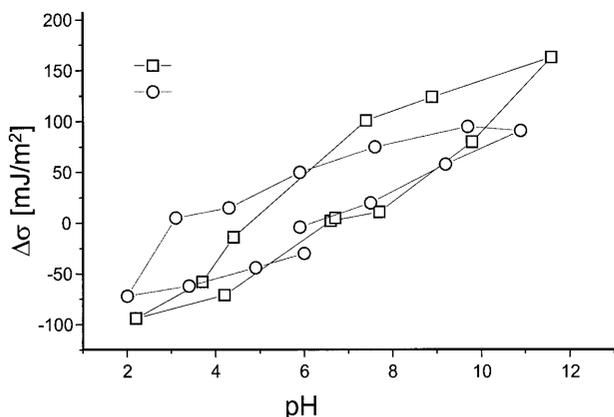


Fig. 6. Relative surface stress versus pH for cysteamine (squares) and 2-mercapto-ethanol (circles) in 0.1 M KNO_3 , pH was adjusted by adding 0.1 M KOH and 0.1 M HNO_3 . Cantilevers were prepared as in the experiments with 3-mercaptopropionic acid, coating first one side with octadecanethiols and then the other side with the thiol under study (see Fig. 4).

11–12, where proton dissociation should already take place. A possible explanation is the interaction between the amino or hydroxyl groups. The thiols typically occupy an area of 20–25 \AA^2 , which corresponds to a distance between the functional groups of 4–5 \AA . At such small distances the groups influence each other and the effective pK is smeared out.

For a test both sides of the cantilever were coated with the same thiol monolayer. No deflection was observed varying the pH of the electrolyte solution. We therefore assumed that the measured deflections were to ascribe to changes in surface stress only.

The method proposed measures changes in surface stress, $\Delta\sigma$. Sometimes is useful to speak in terms of surface free energy, γ . They are related through the Suttleworth equation [22,46–48]

$$\sigma = \gamma + \frac{d\gamma}{d\varepsilon_e} \quad (4)$$

where the elastic surface strain, ε_e , is defined as $d\varepsilon_e = dA/A$, where A is the surface area and dA is the infinitesimal elastic increase in surfaces area. For liquids the second term of Eq. (4) is zero and therefore surface stress and surface free energy correspond. For solids the second term takes into account the fact that when the surface is elastically strained the interatomic distance is changed from the value which would minimize γ , and it therefore requires a different energy to form a unit area of the strained surface than of the unstrained one. The second term in Eq. (4) can be of same order as γ and therefore the sign of $\Delta\sigma$ can be either positive or negative, which corresponds a tensile or compressive stress. This means that, in general, it is not trivial to compare changes in surface stress with

changes in surface energy and even foresee the behavior of the cantilever upon adsorption [15,16,49,50].

4. Conclusion

Commercially available cantilevers are made of silicon nitride, silicon, and polymers with dimensions ranging from 50 to 400 μm , and resonant frequencies ranging, in air, from 10 to 300 kHz.

The use of microfabricated cantilevers allowed several improvements compared to the previous bending-plate techniques using macroscopic plates: measurements can now be done in a relatively simple and reliable (commercial) set-up, the method is generally applicable to thin deposited films, it is now possible to monitor ‘in situ’ processes changing the surface stress, the achievable sensitivity is much higher due to the low noise sensitivity, and the time response allows following adsorption/desorption process kinetics.

The principle of the method implies the preparation of different opposite surfaces. One of the limiting factors regarding sensitivity in liquid environments is long term drift in cantilever deflection induced by slow electrochemical processes at the cantilever/solution interface and therefore reliable and flexible techniques to coat both the active and the inert surface are desirable.

Cantilever functionalization can be achieved in several ways like evaporating, sputtering, or spraying a thin layer of material on each side. Thiols, available with different end groups, are well suited to form highly ordered monolayers with different properties (for a review see: [40,41]). They bind covalently onto gold and show a high stability under AFM scanning [51–53] and to potentials applied to the gold substrate in electrochemical cells [54–57].

The possibilities offered by this technique directly involve AFM operation. Changes in the static cantilever deflection are a fundamental matter to take into account in the interpretation of force–distance curves in AFM operation. Moreover, surface stress measurements can help in the characterization of the cantilever material (e.g. estimation of the surface charge both of metal coated or silicon nitride cantilevers).

A number of different applications based on the direct measurements of surface stress of micro-cantilevers can be foreseen:

- chemical sensors to monitor the concentration of substances in a solution or gas around the cantilever
- sensors to measure specific binding of ligands to cantilevers which are coated on one side with a receptor
- sensors to monitor chemical surface reactions occurring on one side of the cantilever.

Acknowledgements

R.R. acknowledges the support of a TMR fellowship (contract no. FMBICT972487).

References

- [1] A.W. Adamson, *Physical Chemistry of Surfaces*, Wiley, New York, 1990.
- [2] T. Thundat, P.I. Oden, R.J. Warmack, *Microscale Thermophys. Eng.* 1 (1997) 185.
- [3] G.Y. Chen, T. Thundat, E.A. Wachter, R.J. Warmack, *J. Appl. Phys.* 77 (1995) 1.
- [4] R. Raiteri, H.J. Butt, *J. Phys. Chem.* 100 (1995) 15728.
- [5] H.-J. Butt, *J. Colloid Interface Sci.* 180 (1996) 251.
- [6] S.J. O'Shea, M.E. Welland, T.A. Brunt, A.R. Ramadan, T. Rayment, *J. Vac. Sci. Technol. B* 14 (1996) 1383.
- [7] R. Berger, E. Delamarche, H.P. Lang, C. Gerber, J.K. Gimzewski, E. Meyer, H.-J. Güntherodt, *Science* 276 (1997) 2021.
- [8] R. Raiteri, G. Nelles, H.-J. Butt, W. Knoll, P. Skládal, *Sensors and Actuators B* 61 (1999) 213.
- [9] G.G. Stoney, *Proc. R. Soc. Lond. A* 82 (1909) 172.
- [10] R.W. Hoffman, *Physics of Thin Films*, Academic Press, New York, 1966, p. 211.
- [11] P. Müller, R. Kern, *Surf. Sci.* 301 (1994) 386.
- [12] F.J. Preissig, *J. Appl. Phys.* 66 (1989) 4262.
- [13] R.E. Martinez, W.M. Augustyniak, J.A. Golovchenko, *Phys. Rev. Lett.* 64 (1990) 1035.
- [14] J.W. Cahn, R.E. Hanneman, *Surf. Sci.* 1 (1964) 387.
- [15] H. Ibach, *J. Vac. Sci. Technol. A* 12 (1994) 2240.
- [16] H. Ibach, C.E. Bach, M. Giesen, A. Grossmann, *Surf. Sci.* 375 (1997) 107.
- [17] R.A. Fredlein, A. Damjanovic, J.O'M. Bockris, *Surf. Sci.* 25 (1971) 261.
- [18] R.A. Fredlein, J.O'M. Bockris, *Surf. Sci.* 46 (1974) 641.
- [19] D. Sander, H. Ibach, *Phys. Rev. B* 43 (1991) 4263.
- [20] D. Sander, U. Linke, H. Ibach, *Surf. Sci.* 272 (1992) 318.
- [21] T.J. Lewis, J.P. Llewellyn, M.J. Van der Sluijs, *IEE Proc. A* 140 (1993) 385.
- [22] G. Láng, K.E. Heusler, *J. Electroanal. Chem.* 377 (1994) 1.
- [23] W. Haiss, J.K. Sass, *J. Electroanal. Chem.* 386 (1995) 267.
- [24] D. Rugar, P.K. Hasma, *Phys. Today* 43 (1990) 23.
- [25] T.A. Brunt, T. Rayment, S.J. O'Shea, M.E. Welland, *Langmuir* 12 (1996) 5942.
- [26] J.R. Barnes, R.J. Stephenson, M.E. Welland, C. Gerber, J.K. Gimzewski, *Nature* 372 (1994) 79.
- [27] J.K. Gimzewski, Ch. Gerber, E. Meyer, R.R. Schlitter, *Chem. Phys. Lett.* 217 (1994) 589.
- [28] R. Berger, H.P. Lang, C. Gerber, J.K. Gimzewski, E. Meyer, H.J. Güntherodt, L. Scandella, *Chem. Phys. Lett.* 294 (1998) 363.
- [29] Y. Nakagawa, R. Schäfer, H.-J. Güntherodt, *Appl. Phys. Lett.* 73 (1998) 2296.
- [30] T. Thundat, R.J. Warmack, G.Y. Chen, D.P. Allison, *Appl. Phys. Lett.* 64 (1994) 2894.
- [31] T. Thundat, G.Y. Chen, R.J. Warmack, D.P. Allison, E.A. Wachter, *Anal. Chem.* 67 (1995) 519.
- [32] R.P. Cowburn, A.M. Moulin, M.E. Welland, *Appl. Phys. Lett.* 71 (1997) 2202.
- [33] M.D. Antonik, N.P. D'Costa, J.H. Hoh, *IEEE Eng. Med. Biol. March/April* 16 (1997) 66.
- [34] M.E. Fauver, D.L. Dunaway, D.H. Linienfeld, H.G. Craighead, G.H. Pollack, *IEEE Trans. Biomed. Eng.* 45 (1998) 891.
- [35] P. Krecmer, A.M. Moulin, R.J. Stephenson, T. Rayment, M.E. Welland, S.R. Elliott, *Science* 277 (1997) 1799.
- [36] H.P. Lang, R. Berger, F. Battiston, J.-P. Ramseyer, E. Meyer, C. Andreoli, J. Brugger, P. Vettiger, M. Despont, T. Mezzacasa, L. Scandella, H.-J. Güntherodt, C. Gerber, J.K. Gimzewski, *Appl. Phys. A* 66 (1998) s61.
- [37] T.R. Albrecht, S. Akamine, T.E. Carver, C.F. Quate, *J. Vac. Sci. Technol. A* 8 (1990) 3386.
- [38] J.E. Sader, L. White, *J. Appl. Phys.* 74 (1993) 1.
- [39] J.E. Sader, *Rev. Sci. Instrum.* 66 (1995) 4583.
- [40] A. Ulman, *Ultrathin Organic Films*, Academic Press, San Diego, 1991.
- [41] L.H. Dubois, R.G. Nuzzo, *Annu. Rev. Phys. Chem.* 43 (1992) 437.
- [42] H. Schönherr, H. Ringsdorf, M. Jaschke, H.-J. Butt, E. Bamberg, H. Allinson, S.D. Evans, *Langmuir* 12 (1996) 3898.
- [43] T. Miyatani, M. Fujihira, *J. Appl. Phys.* 81 (1997) 7099.
- [44] H.-J. Butt, P. Siedle, K. Seifert, K. Fendler, T. Seeger, E. Bamberg, A.L. Weisenhorn, K. Goldie, A. Engel, *J. Microsc.* 169 (1992) 75.
- [45] P.W. Atkins, *Physical Chemistry*, Oxford University Press, Oxford, 1992.
- [46] R. Suttleworth, *Proc. Phys. Soc. Lond. A* 63 (1950) 444.
- [47] P.R. Couchman, W.A. Jesser, D. Kuhlmann-Wilsdorf, J.P. Hirth, *Surf. Sci.* 33 (1972) 429.
- [48] P.R. Couchman, D.H. Everett, W.A. Jesser, *J. Colloid Interface Sci.* 52 (1975) 410.
- [49] R. Guidelli, *J. Electroanal. Chem.* 453 (1998) 69.
- [50] H. Ibach, *Surf. Sci. Rep.* 29 (1997) 193.
- [51] U. Dürig, O. Züger, B. Michel, L. Häussling, H. Ringsdorf, *Phys. Rev. B* 48 (1993) 1711.
- [52] R.C. Thomas, J.E. Houston, T.A. Michalske, R.M. Crooks, *Science* 259 (1883) 1993.
- [53] G.Y. Liu, M.B. Salmeron, *Langmuir* 10 (1994) 367.
- [54] J.A.M. Sondag-Huethorst, L.G.J. Fokkink, *Langmuir* 8 (1992) 2560.
- [55] T.T.T. Li, M.J. Weaver, *J. Am. Chem. Soc.* 106 (1984) 6107.
- [56] M.D. Porter, T.B. Bright, D.L. Allara, C.E.D. Chidsey, *J. Am. Chem. Soc.* 109 (1987) 3559.
- [57] C. Miller, M. Grätzel, *J. Phys. Chem.* 95 (1991) 5225.