Surface stress of polyelectrolyte adsorption measured by micromechanical cantilever sensors*

Masaya Toda
Graduate School of Engineering Science, Osaka University,
1-3 Machikaneyamacho, Toyonaka 560-8531, Japan,
National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047, Japan, and
Max Planck Institute for Polymer Research, Ackermannweg 10, Mainz D-55128, Germany

Akiko Nakamura Itakura
National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047, Japan

Karsten Büscher, Karlheinz Graf, and Rüdiger Berger†
Max Planck Institute for Polymer Research, Ackermannweg 10, Mainz D-55128, Germany

(Received 15 October 2005; Accepted 22 December 2005; Published 19 January 2006)

We studied the mechanical stress during the adsorption process of polyallylamine hydrochloride (PAH) and polystyrenesulfonate (PSS) polyelectrolytes using highly sensitive micromechanical cantilever sensors (MCS). Single side adsorption was achieved by functionalizing individual MCS with a 2-mercaptoethylamine (2-MEA) self-assembled monolayers. Exposure of the MCS to PAH solution resulted in a constant surface stress change of 1.6 ± 0.2 N/m between the 2-MEA functionalized and silicon sensors. We attribute the surface stress change to the formation of a stable PAH polyelectrolyte layer on top of the silicon surface. We found that a second layer consisting of PSS did not result in a negligible surface stress change. [DOI: 10.1380/ejssnt.2006.96]

Keywords: Adsorption kinetics; Biological molecules; Biosensing and devices; Nano-films; Surface stress

I. INTRODUCTION

In biotechnology, sensors are required for screening of small amounts of analytes. Here micromechanical cantilever sensors (MCS) are investigated as low-cost and highly integrated measurement systems [1]. Recently, DNA hybridization [2], glucose detection [3, 4], protein adsorption [5, 6], and pH changes [7] have been studied using MCSs. It was shown, that MCS is sensitive to a chemical or a physical reaction on surfaces. In particular, the swelling of polymer brushes in solvents can be detected [8]. Furthermore, mass changes upon adsorption of molecules can be investigated by tracking the resonance frequency of MCS [9].

Polyelectrolytes are used for biodegradable films, as drug delivery capsules, for separation of membranes and for thin films of a cellular matrix [10, 11]. Adsorption of polyelectrolytes on substrates is well known as a simple way to functionalize appropriate surfaces [12–15] (Fig. 1). After chemical cleaning of a silicon substrate the surface has negative surface potential [16]. On such surfaces positively charged polyelectrolytes can be adsorbed leading to a thin film of only a few nanometer thickness [17] (Fig. 1a). Further on a negatively charged polyelectrolyte can be adsorbed on the latter surface [18]. By subsequently exposing the sample to solutions of the oppositely charged polyelectrolytes, multilayers can be built up (layer-by-layer method).

Alternatively to SiO$_2$ surfaces, amine functionalized alkanethiol molecules (2 MEA 2-mercaptoethylamine) can be used, which self assemble on Au as starting layer. Hereby, we obtain a positively charged self-assembled monolayer (SAM) surface (Fig. 1b). The adsorption of polyelectrolytes results in layers of well-defined nanometer thickness. At a certain adsorption density, the electrostatic self-repulsion of the polyelectrolytes prevents further adsorption [19]. Repulsive forces can build up mechanical stress in the thin polyelectrolyte film. Since the polyelectrolyte is adsorbed onto a thin MCS surface the stress is transduced into a bending of the MCS. The interaction of surfaces with polyelectrolyte layers has been studied by means of atomic force spectroscopy [20]. Here, we study the mechanical stress during the adsorption process of polyallylamine hydrochloride (PAH) and polystyrenesulfonate (PSS) polyelectrolytes using highly sensitive MCSs.

FIG. 1: (a) Adsorption of positively charged polyelectrolyte molecules on a SiO$_2$ surfaces and (b) of negatively charged polyelectrolytes on a self assembled monolayer of 2-mercaptoethylamine (2-MEA) functionalized gold surface.

*This paper was presented at International Symposium on Surface Science and Nanotechnology (ISSS-4), Saitama, Japan, 14-17 November, 2005.
†Corresponding author: berger@mpip-mainz.mpg.de

ISSN 1348-0391 © 2006 The Surface Science Society of Japan (http://www.sssj.org/ejssnt) 96
FIG. 2: Schematic drawing of the optical read-out principle based on beam deflection: 8 light beams are focused on individual MCS. The read-out is multiplexed at time intervals of $< 100$ ms. In this picture MCS number 4 is read-out (solid red line). The reflected light from the MCS apex is focused on a position sensitive detector (PSD). The signal voltage of the PSD is proportional to the bending of the MCS. The top side of the four cantilevers on the right hand side is coated with a Cr and a Au layer to enable self assembly of alkanethiol molecules.

FIG. 3: (a) The averaged deflections of reference and Au-coated MCS in a 2-MEA solution. The individual deflection signals after 4 h vary by maximally 290 nm for the references. This corresponds to an error of about 13%. The Au-coated MCS vary by only 80 nm which corresponds to an error of about 2%. (b) The differential deflection of the averaged signals shown in (a). The differential bending is towards the Au coated side indicated schematically in the inset.

II. EXPERIMENTAL

The bending of MCS was measured by an optical beam deflection technique (SCENTRIS, VEECO Instruments, USA), which is schematically outlined in Fig. 2. Light from 8 individual superluminescence light emitting diodes (LED) is focused at the apex of 8 individual MCS. Switching on and off the light sources allows measuring the bending of each MCS sequentially. For our measurements, we used arrays of 8 MCS made from single crystalline silicon (thickness $h$ of 5 µm, effective length $l$ of 750 µm and width $w$ of 90 µm (Micromotive GmbH, Mainz, Germany)). Four MCS were subsequently coated by 2 nm Cr and 20 nm Au on the top side (Baltec MCS-010, Germany). The bending signals of identically prepared sensors should exhibit the same response. Therefore we averaged the bending signals of 4 MCS, i.e. the response of the Au-coated and the non-coated MCS, respectively. The averaging procedure reduces noise from the electronics and accounts for small differences of the mechanical properties of the MCS. To compensate chip drift and non-specific adsorption arising in the setup, the differential signal between Au and non-coated MCS was determined.

Before using the MCS chips they were cleaned and hydrophilized with a modified RCA method ($\text{H}_2\text{O}_2:\text{NH}_2\text{OH} : \text{H}_2\text{O}=1:1:5$, at 80°C for 10 min), a standard cleaning procedure for Si-substrates [21, 22]. The chip carrying the MCSs is mounted in a small liquid cell,
which allows exchanging the surrounding media using a syringe (typically 1 ml/s). The sample cell volume is 30 µL.

For single side adsorption of negatively charged polyelectrolytes on the MCS we functionalized the Au surface by 2-MEA (2-mercaptoprothylamine). A solution of 4 mM 2-MEA in ethanol (Fisher Scientific, U.K.) was injected into the sample cell by using the syringe. The MCS are kept for 15 h in the 2-MEA solution. Hereby, a SAM of 2-MEA is formed on the Au surfaces only. The amine end-groups of the SAM form a positively charged surface (Fig. 1b). After that the 2-MEA solution was removed by rinsing the MCS with ethanol in the liquid cell for 1 h at a flow of 0.5 ml/min through the liquid cell. Then 2 ml of 3 mM PAH solution was injected using a syringe. The bending signals of each MCS are investigated during the formation of the polyelectrolyte layers. Afterwards a second polyelectrolyte layer having the opposite charge can be deposited in the same way (3 mM PSS solution).

III. RESULTS AND DISCUSSION

We investigated the bending of MCS during the self assembly process of 2-MEA on the one side Au-coated MCS (Fig. 3). The self assembly process of alkanethiols is known to generate compressive surface stress[23, 24] in a bending of MCS towards the Si-side. For the alkanethiols with alkyl chain lengths between \( n = 4 \) and 12, surface stress changes of 0.02-0.2 N/m were reported [25]. The averaged deflection signal of the 4 Au-coated MCSs and the 4 reference MCSs are plotted versus time (Fig. 3a). At \( t = 0 \) s the 2-MEA solution was injected. The Au-coated MCSs bend towards the Au side, representing a tensile surface stress change. This bending is significantly larger than the drift of the reference MCSs. The deflection signal was estimated to be 10 nm/min for both, the reference and the Au-coated MCSs after 2 h of 2-MEA injection. The differential signal of the Au-coated and the reference MCS signal saturates after approx. 150 min (Fig. 3b). We conclude that a stable SAM was formed on the Au surface. The differential deflection value is finally about \(-1800 \) nm for the 750 µm long MCS. Using Stonyfs formula a surface stress change of 5.8 ± 0.5 N/m was calculated [26] (the Young’s modulus of 170 GPa and the Poisson’s ratio of 0.23 for Si). Interestingly the surface stress change for 2-MEA SAMs has an opposite sign compared to alkanethiol SAMs. Furthermore, the surface stress change is much bigger than the surface stress of dodecanethiol SAMs. We attribute this difference to a contribution from differences in the end-groups (\(-\text{CH}_3\) to \(-\text{NH}_3^+\)).

After rinsing the liquid cell with ethanol for 30 minutes, rinsing with pure water for 1 h at a flow of 0.5 ml/min...
and waiting for a stable deflection signal in water for typically 15 minutes, 3 mM PAH solution was injected (Fig. 4a). We observed a positive deflection corresponding to a bending towards the Si-side. The Au-coated MCSs show a significant deflection response compared to the reference MCSs in PAH solution after 105 min. The drift of the reference MCS was 8.6 nm/min.

The differential deflection between the Au-coated and the reference MCS shows a constant magnitude of 485 nm after H₂O rinsing for 20 minutes. We attribute this bending of the MCS to the formation of a stable PAH polyelectrolyte layer on top of the silicon surfaces. The magnitude corresponds to a surface stress change of 1.6 ± 0.2 N/m. This experiment shows that the 2-MEA SAM can be used to functionalize MCSs. X-ray reflectivity measurements on larger reference samples indicated a thickness of 0.6 nm of the PAH layer on SiO₂. On the reference MCSs both sides allow adsorption of PAH. Since PAH adsorbs on both sides simultaneously no significant deflection is expected.

After injection of the PSS solution (indicated in Fig. 4a) we observed a nearly similar bending response for both, the reference and the 2-MEA functionalized MCS. The differential deflection shows an additional response of 34.7 ± 36.1 nm only, which is negligible. In this case, PSS adsorbs on the PAH layers as well as on the 2-MEA functionalized surfaces. Since we do not observe a significant bending of the MCSs we conclude that at the end of this step all MCS surfaces are covered by PSS. This indicates a similar quality of the PSS layer on 2-MEA as well as on PAH surfaces.

As a control we used 4 MCS coated with Cr and Au, but not exposed to a 2-MEA solution. Therefore we obtained no positively charged surfaces. The other remaining 4 MCSs were recorded as references again. When exposing such a MCS to PAH solution, we observed a similar signal for all MCS (Fig. 4b). The resulting differential signal shows a small positive deflection towards the silicon side of only 9.1 ± 18 nm. After consecutive exposure to a PSS solution (Fig. 4c), we obtained a signal of 7.9 ± 26 nm. Summarizing, both reference measurements reveal a negligible differential signal indicating an adsorption of PAH on Au and Silicon surfaces.

IV. CONCLUSIONS

Our measurements have shown that a single side adsorption of positively charged polyelectrolytes like polyaniline hydrochloride (PAH) on silicon was achieved by using 2-mercaptopethylamine self-assembled monolayers (2-MEA SAMs) on Au. The PAH adsorption is associated with a tensile surface stress change of 1.6 ± 0.2 N/m. A consecutive exposure to a solution of polystyrene-sulfonate (PSS) revealed no change of the bending, most likely owing to adsorption on all interfaces.

Acknowledgments

We gratefully acknowledge J. Gutmann, M. Wolkenhauer, S. Igarashi, J. Yanagisawa, Y. Akasaka, S. Moreno Flores, G. Gina Bumbu and U. Rietzler for fruitful discussions and technical support. The author (M. T.) is grateful to the 21st Century COE Program (G18) by JSPS and International Max Planck Institute Research School for financial support.