Investigation of micromechanical cantilever sensors with microfocus grazing incidence small-angle x-ray scattering

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Micromechanical cantilever arrays coated with polymer brushes are an alternative to traditional chemical sensors. A critical parameter for the sensor sensitivity is the coating quality, and small changes in the coating uniformity generate a different behavior of the sensors. Microfocus grazing incidence small-angle x-ray scattering proved to be a sensitive tool to characterize coating quality, enabling a structural and chemical coating analysis. © *2006 American Institute of Physics*.
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Micromechanical cantilever (MC) sensors can be used in a wide variety of sensor applications.[1] A micromechanical cantilever sensor consists of a micromechanical cantilever acting as a transducer element and a selective coating.[2,3] Especially MCs covered with polymer brushes are of great interest for fundamental research and practical applications.[4,5]

One way to functionalize MCs is to chemically link a polymer layer on the MC surface. Such covalently bound coatings exhibit long-term stability in liquid and gaseous environments. The use of a MC array as transducer offers the possibility to integrate functionalized and reference cantilevers into one sample, in order to compensate for thermal drift and unspecific absorption.[6] We have used OCTOSENSIS silicon microarrays (Micromotive, Germany, see Fig. 1) consisting of eight rectangular cantilevers, with a length of 750 μm, a width of 90 μm, and a thickness of 1 μm arranged at a pitch of 250 μm.

Polymer brushes are polymeric chains covalently bound to the surface. By exposing polymer brushes to liquids or gases, they change their mechanical properties, due to a swelling or collapse of the polymeric chain. If polymer brushes are synthesized only on one side of the cantilever, their change in mechanical properties in various environments leads to differences in surface stress at opposite sides of the micromechanical cantilever and in consequence to a bending. In order to restrict the synthesis of polymer brushes to selective cantilever surfaces, we deposit a blocking gold layer via thermal evaporation (deposition rate 0.1 nm s^{-1}) on the entire backside of the cantilever array and on half of its topside by masking the other half using a shadow mask. The blocking layer restricts the functionalization of the cantilevers with an α-bromosilane to nongold covered surfaces if it is defective polymer, brushes will also be synthesized in the defect sites.

Utilizing an atom transfer radical polymerization "grafting from" technique, poly(methyl methacrylate) (PMMA, M_n=63 kg mol^{-1}) brushes were grown on the silanated surfaces.[4] The optical microscopy image of the MC array functionalized with PMMA brushes is presented in Fig. 1.

The response patterns of cantilever deflection to different environments such as a solvent (ethyl acetate) or nonsolvent (isopropanol) for the PMMA coating were monitored with a Scentris™ instrument (Veeco, USA) measuring the deflection of a laser beam reflected from the cantilevers and are shown in Fig. 2. The MC array is mounted in a closed sample cell, which allows the *in situ* exchange of solvents. A negative deflection is assigned to an upward bending of the cantilever, i.e., towards the PMMA coated topside. Whereas the gold (1) and polymer (8) coated cantilevers exhibit the same direction of deflection (with different magnitudes depending on their coating), the gold coated cantilever 4, which was at the edge of the mask during the coating process, deflects in opposite direction. The bending is originated from the mechanical stress due to the swelling of the one sided attached brushes or in case of the gold coated cantilevers by adsorption phenomena of solvent molecules. Whether the difference to the cantilever on the edge is due to a defect in the applied coating or due to an internal defect in the cantilever itself is a question that cannot be answered from microscopy and bending experiments alone.

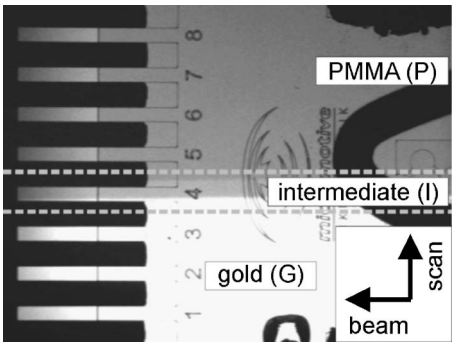

FIG. 1. Optical microscopy of a micromechanical cantilever array with eight cantilevers. The beam and scan directions for the microfocus grazing incidence small-angle x-ray scattering (μ-GISAXS) experiments are indicated by arrows. Three different regions of coatings are visible labeled with G (gold), I (intermediate), and P (PMMA polymer brushes).

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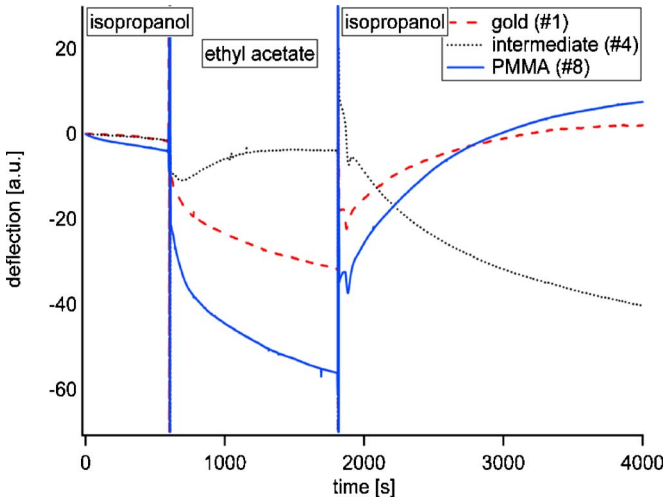

FIG. 2. Response patterns of three representative cantilevers on an external stimulus with isopropanol or ethyl acetate. The cantilever numbers correspond to those in Fig. 1. The times of liquid exchange are indicated by peaks caused by the flow (vertical lines).

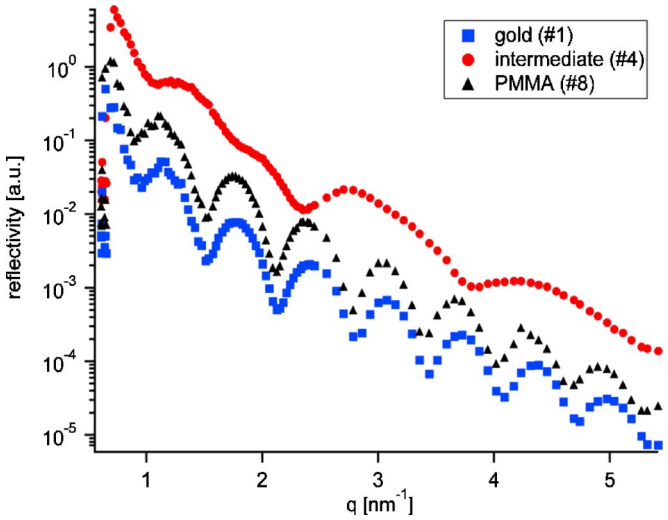

FIG. 3. X-ray reflectivity curves of three representative different coated cantilevers: gold (squares), intermediate (at the edge of the mask), and polymer brushes.

We therefore turn to microfocus grazing incidence small-angle x-ray scattering (μ-GISAXS) experiments[7] in order to investigate the differences in the cantilever coatings in detail. The experiments were carried out at the beamline BW4/HASYLAB using the microfocus option, with a sample-to-detector distance of 1.9 m, a wavelength $\lambda = 0.138$ nm, and a beam size of 32×17 μm^2 (horizontal $\times$ vertical). The MC was mounted on a two-dimensional goniometer equipped with an $x/y/z$-translation stage. The small dimensions of the beam allow to match the footprint of the x-ray beam completely onto a single cantilever.

One of the most prominent features of the GISAXS scattering pattern is the occurrence of a specular and a material dependent Yoneda peak. The Yoneda peak occurs when the exit angle of the scattered beam is close to the critical angle of total external reflection due to a maximum in the Fresnel transmission function of the reflected beam.[8] It is an interference effect due to the superposition of incoming and outgoing waves at the critical angle. Since the critical angle is a material property, each entity in a multicomponent system has its own Yoneda peak. This makes the Yoneda peak a material dependent property and allows in GISAXS measurements to yield chemical sensitivity.

To identify the different cantilever coatings, a μ-GISAXS scan across the MC array was performed. From the position dependent intensity of the specular peak, it is possible to determine the position of the cantilevers (marked with arrows in Fig. 3). Furthermore, the magnitude of the reflected signal allows to identify the coating material: Since in our setup the incidence angle α_i and exit angle α_f are fixed, the angular difference ($\Delta\alpha = \alpha_i - \alpha_c$) between the critical angle α_c of the coated cantilever and α_i determines the intensity of the specular reflected signal. Assuming a homogeneous coating, it is possible to distinguish between two cases: If the electron density ρ_{el} of the coating is higher than ρ_{el}(Si) of the cantilever, the critical angle α_c is determined by the electron density of the coating, this is the case for the gold coating. However, if $\rho_{el} < \rho_{el}$(Si), α_c is determined by ρ_{el}(Si). This is the case for PMMA coated surfaces. For cantilevers in region G, the intense specular signal implies a gold coating (small $\Delta\alpha$). The less intense specular signal in region P therefore implies a PMMA coating. Since specular reflectivity also depends on surface roughness, it is not possible to infer that cantilever 4 is only partially gold coated from the drop of the specular signal alone. However, the intensity of the Yoneda peak at the critical angle of gold is directly linked to the presence of gold and allows to determine a gold coverage in region G and PMMA cover in region P without model assumptions. Across cantilever 4 (region I) the intensity of the Yoneda decreases from ~30 counts to the readout noise of the charge-coupled device detector. This proves a lateral change from gold to polymer brushes within the coating of this cantilever.

Besides homogeneity, coating thickness is another key parameter. From a series of μ-GISAXS experiments at variable incident angle, it is possible to extract an x-ray reflectivity curve from the surface of a single cantilever (cf. Fig. 4). Due to geometrical constrains of the setup, we were not able to measure around the total reflection edge. Therefore we do not attempt to model the reflectivity curves. From the

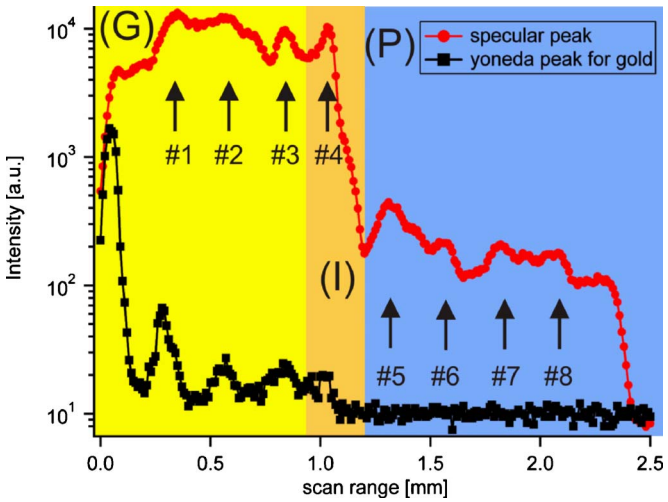

FIG. 4. Intensity of the specular peak and Yoneda peak of gold across the cantilever array. The arrows mark the positions of the eight cantilevers with their numbers on the array in Fig. 1.

width of the Kiessig fringes, we obtain a thickness of the gold layer on a reference cantilever (1) $d_{Au}=10.3\pm1$ nm and for the polymer brush layer (8) $d_{PMMA}=10.4\pm1$ nm. For the intermediate cantilever (4) the reflectivity curve is clearly different. This perturbed reflectivity is in agreement with our model of a laterally heterogeneous gold layer, based on our discussion of the static μ-GISAXS experiments.

In summary we have shown that μ-GISAXS is a suitable and powerful tool for investigating micromechanical cantilever sensors. The quality of the coatings of either the reference or polymer coated cantilevers is a critical parameter for the application as sensors. A careful structural characterization of the surface structures is therefore necessary, and microfocus GISAXS provides a valuable nondestructive tool to this end.

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