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Comprehensive surface analysis of hydrophobically functionalized SFM tips

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Abstract

Tip-sample interactions have been of interest since the early development of the scanning force microscope. Investigations of interfacial interactions at the molecular level are of importance for fundamental studies of bi-molecular interactions and for possible applications in biomedical research and industrial settings. By engineering the surface chemical properties of the SFM probes, specific force interactions may be measured. However, as these modification schemes become more widely applied, detailed chemical analysis of the modified cantilever surfaces becomes crucial. In this paper, we describe two approaches to coat SFM cantilevers with hydrophobic coatings: a silanization protocol and radio frequency plasma enhanced chemical vapor deposition. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Interfacial interactions, from the macroscopic to the molecular and atomic scale, have a profound impact on a variety of processes in chemistry, physics, and biology. Advances in understanding the interaction mechanisms at the solid-liquid,

solid-gas or solid-solid interfaces are crucial for applied research and industrial applications. An important focus in material surface research is in the development of next generation biomaterials. Today's biomaterial, although they are called "bio-compatible", are not fully accepted by the host when implanted and are walled off from normal tissue by a fibrous capsule. It has been proposed that by incorporation of recognition motifs on biomaterial surfaces, improved healing and integration can be realized [1].

Modern surface analytical tools such as the scanning force microscope (SFM) enable real-space

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characterization of surface properties on the micro- and nanometer scale [2,3]. Typical SFM applications are investigations of surface material properties, such as wear, friction, elastic moduli, or adhesion. Only recently, the focus of much of the SPM research has shifted to probing specific interfacial properties. To measure such interactions, the SFM cantilever tip is “tailored” i.e. functionalized, to exhibit the desired material and chemical properties at its surface. At first, tip functionalization was performed by physisorption of molecules. These tips were found to be ill defined and material was easily removed during the scanning process. However, this effect of material transfer has been soon used to write and produce lithographic pattern on surfaces [4,5]. More stable functionalization of SFM lever is attained by surface grafting or self-assembly with strong surface interactions. At first, modification of SFM cantilevers has been achieved by silanization [6,7], and later by self-assembly of nucleotides [8] or alkanethiols [9] onto gold-coated levers.

Chemically modified SFM cantilevers were as well proposed to sense specific chemical functionalities. This later became known as chemical force microscope [7,9,10]. In numerous publications, chemically modified cantilevers were used to probe surface energies and surface pK [11–13]. In addition to the pure chemical functionalization, cantilever modification was carried out with biomacromolecules in order to sense biological interaction [14–16]. Even since, a growing number of research teams have applied the methods mentioned above.

However, the preparation of functionalized tips is quite often far from an exact science. A great deal of research is devoted to analyzing and interpreting force measurements and images obtained with functionalized tips, but little time is usually invested in careful tip preparation and analysis. Unfortunately, poorly defined physisorption techniques flourished until recently because the preparation procedures for functionalization were unsatisfactory. Also, many different techniques reported for tip modification are not suitable for certain experiments and methods. For example, due to the high reactivity of silanes with water, coatings produced with silanes often polymerize uncontrollably

and may peel from the surfaces. Similar problems are experienced with the popular method of self-assembly of alkane thiols on gold which may not result in a uniform monolayer. Contaminated gold and oxidized sulfur prevent tight chemisorption of the thiol on the gold resulting in monolayers with many defects and poor wear resistance.

Whenever SFM tips are functionalized there are several concerns that have to be addressed (I) Did the functionalization reaction take place at the surface? (II) Is it a homogenous modification? (III) Did the reaction alter the tip shape? (IV) How stable are the functionalities?

In this paper, we demonstrate and discuss the advantages and disadvantages of two strategies for tip functionalization. Silanization, as one of the earliest methods mentioned in literature, was tested for stability and morphology. As a second method, we used radio frequency enhanced chemical vapor deposition to modify the lever surface. Earlier the coating of STM tips with an insulating film produced by plasma deposition was described [17] and the method was applied to change adhesive properties of the SFM [18]. The quality of the SFM cantilever modification was carefully surveyed regarding chemical and topographical properties with ESCA and TOF-SIMS. Stability issues of the plasma deposited coatings were addressed by repeated force versus displacement curves.

2. Materials and methods

2.1. Chemical modification of SFMI levers

All chemicals and solvents were of ultrapure quality and obtained from commercial sources. Prior to chemical modification, all SFM levers (oxide sharpened silicon nitride, Digital Instruments, bar-shaped silicone levers, Nanosensors, Germany, and NT-MDT, Russia) were solvent cleaned by rinsing in acetone and methylene chloride. Plasma-coated levers were additionally etched (30 s, 80 W) in an argon plasma. For preliminary optimization of the tip modification methods, cut silicon pieces (10 × 10 mm, Silicon Quest International, Santa Clara, CA) were used as flat control

surfaces. This approach allows for detailed chemical and morphological investigation of the surfaces. After optimization of the protocols, cantilever tips and flat silicon were treated and modified in parallel.

*Radio frequency plasma enhanced chemical vapor deposition (RF-PECVD)*¹ experiments were carried out in a home-built reactor equipped with symmetric, external capacitively coupled electrodes, with an electrode separation distance of 10 cm. The plasma was induced with a radio frequency of 13.56 MHz and maintained via a matching network. A detailed description of the plasma reactor has been published earlier by Favia et al. [19], and Luginbühl et al. [20]. All samples were placed in between the electrodes. Following the deposition, the samples were “annealed” for 5 min in a monomer flow before they were brought back to atmospheric pressure under nitrogen. Applied reactor power, monomer pressure, gas flow, and deposition time were 80 W, 250 mTorr, 5 sccm and 90 s for methane (U.H.P., Matheson) and 5 W, 150 mTorr, 2 sccm and 4 min for hexafluoropylene (HEP, C₃F₆, PCR Gainesville, FL). The deposition of these two monomers was conducted in separate systems in order to avoid cross-contamination. After each experiment, the reactor was cleaned with solvent and etched with an oxygen plasma for 60 min. Plasma polymer samples were sealed in small sample trays and stored until further use.

Silanization of the surfaces was carried out with *n*-octadecyltrichlorosilane (OTS, Aldrich) because previous studies suggest that long chain functional groups produce the most tightly packed films [21]. Trichlorosilanes are very reactive and will rapidly polymerize in the presences of water. Therefore, it is extremely important to remove any traces of water from the solvents, glassware, and sample surfaces. To ensure this, all of the glassware was baked to 200°C in a vacuum oven overnight. The OTS and all solvents were freshly distilled and kept under argon.

The samples surface were cleaned in a UV/ozone cleaner for 15 min and dipped for 30 s in hot, freshly prepared Piranha solution (70% H₂SO₄, 30% H₂O₂). Subsequently, they were flushed copiously with ultrapure water ($R > 10^{18}\Omega$) and blown dry in nitrogen. Before reacting with a 5 mM solution of OTS in bi-cyclohexyl for 90 s, the samples surfaces were rinsed in bi-cyclohexyl [22]. Finally, after the silanization they were rinsed in toluene. The silanized samples were not used for 24 h after preparation.

2.2. Electron spectroscopy for chemical analysis (ESCA)

ESCA measurements were conducted on an S-Probe instrument (SSI, Mountain View, CA) equipped with an aluminum K _{α} 1,2 monochromatized X-ray source and a hemispherical energy analyzer. All spectra were recorded at a take-off angle of 55° from the sample normal unless otherwise noted allowing for investigation of the outermost 60 Å. Survey scans (159 eV pass energy) and high-resolution scans (25 eV pass energy) were acquired. Surface charging of the non-conducting films was minimized with an electron flood gun. SSI data analysis software was used to calculate elemental compositions from the peak areas in survey spectra. Spectral binding energies were referenced to the C–H hydrocarbon peak assigned to 285 eV [23], or in the case of the HFP plasma coating, to the CF₂ peaks, assigned to 292 eV [24].

2.3. Time-of-flight secondary ion mass spectrometry

TOF-SIMS spectra were acquired using a Model 7200 Physical Electronics PHI instrument (Eden Prairie, MN). The 8 keV Cs⁺ ion source was operated with a current of 1.5 pA, a pulse length of 10 μs and a repetition rate 3 kHz (0–2000 *m/z* spectra). The applied ion dose was kept in the static regime, below 2×10^{12} ions/cm². The secondary ions were extracted into a two-stage reflectron time-of-flight mass analyzer with a potential of 3 kV. A secondary ion-focusing lens between the analyzer entrance and drift region was held at 1 kV, promoting high angular acceptance and good transmission of ions. The band pass of the analyzer was 100 eV and an

¹RF-PECVD is also referred to as plasma polymerization and samples are noted as pp-samples.

independent adjustable grid voltage (deceleration) allowed energy focusing to be performed. The ions were post-accelerated to 10 kV and converted to charge pulses by a stacked pair of chevron-type multichannel plates (MCP). The signals were detected using a 256 stop time-to-digital converter (TDC) with 156 ps time resolution.

2.4. Scanning force microscopy

All scanning force microscope experiments were carried out with an Explorer stand-alone system (TopoMetrix Inc.) equipped with a standard 100 μm X–Y scanner and a 12 μm Z-piezo. All SFM measurements were performed at ambient temperature (20–25°C) in a sealed glove box in a dry nitrogen atmosphere of 1 atm (humidity < 5%). For topographical imaging of surfaces, tip–sample forces was minimized (≤ 5 nN), and scan rates were between 0.5 and 1 Hz. Raw images were flattened to correct for non-linear curvature of the piezo response.

Force versus displacement curves were performed in 50 mM sodium phosphate buffer pH 7. Approach and retract speeds were 0.1 $\mu\text{m}/\text{s}$. The normal spring constant of bar-shaped cantilevers was either calculated through the exact dimensions of the levers measured by SEM and the elastic modulus E (for silicon 169.3 GPa) or measured through the “thermal noise” method [25,26].

3. Results and discussion

All tip modification methods were first optimized on flat silicon pieces (10 \times 10 mm, 100 orientation). Only subsequently were SFM cantilevers functionalized. This approach allowed for detailed chemical and morphological investigation of the surfaces.

The coatings deposited with the plasma method were all found to be smooth, defect free, and featureless. The rms roughness varied between 3 and 10 Å for images 3 \times 3 μm (Table 1). These values were all in the same range as the silicon substrate or lower. The low roughness is indicative of surface directed polymerization and film growth with an absence of gas-phase polymerization. The morphological quality of the silane films was found to

Table 1
SFM roughness measurements on functionalized surfaces

Sample	Roughness rms (nm)
Silicon substrate	0.56
“Good” OTS film	0.57
“Bad” OTS film	22.93
pp-methane	0.39
pp-hexafluoropropylene	0.37

be strongly dependent on the modification protocol used. Fig. 1 depicts two OTS films of differing quality. The rms roughness measured on the film in Fig. 1a was 22.93 nm. It displayed features of incomplete and uncontrolled polymerization due to a high water content during polymerization. Here it should be noted that if uncontrolled polymerization reactions were observed, they nucleated preferably along scratches and large step features on the silicon. This fact is of special concern with respect of the SFM tip shape, as it displays pronounced edge features [27]. Another concern with silanization reactions is incomplete film formation. As observed with thioalkane self-assembly, silanization may result in incomplete film formation. The problem may occur if the reaction conditions (time, temperature, solvent) are not optimized for the silanes used. Uncontrolled inhomogeneous polymerization was always observed either when the OTS silane was not freshly distilled or when residual water was not removed from the surface, glassware and solvents. The problems described above were not observed when residual water was meticulously removed from the solvents and surfaces. Fig. 1b depicts a silicon surface coated with a single monolayer of OTS. The roughness on the OTS film was 0.57 nm, similar to bare silicon. The lines observed on the coated surface are stress fractures in the monolayer. We believe that they are formed during the curing process when the film slightly shrinks. Imaging of the modified silicon surfaces proved to be a good indicator of how well this silanization reaction went.

Homogenous, good-quality films were analyzed with ESCA for chemical composition. The elemental composition of the surface displayed dominant signals from carbon, oxygen, silicon, and fluorine

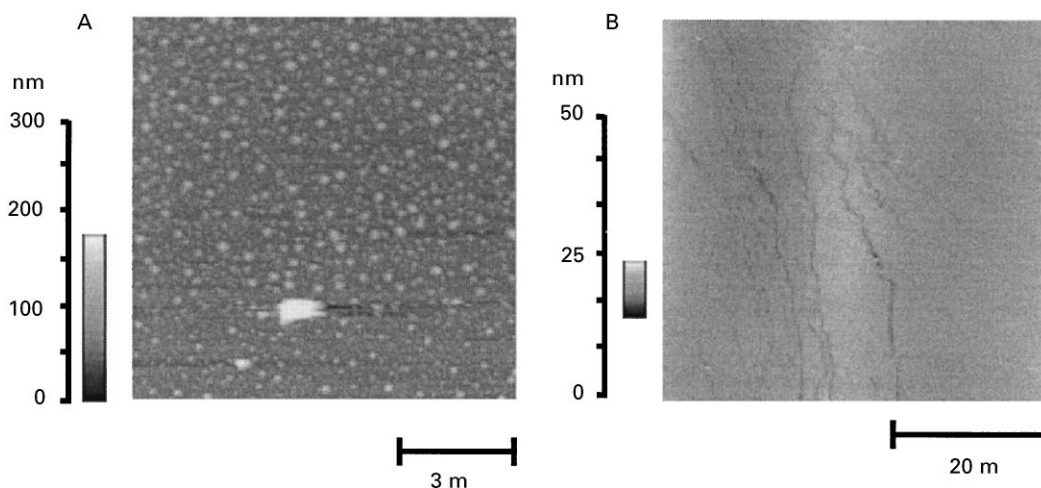


Fig. 1. Topographical scans of silanized surfaces. (A) Small polymer balls were formed on the surface whenever excess water was present during OTS film formation. (B) Films formed under optimal conditions did not show features on the surface. Cracking of the film was observed after curing Contact SFM images, scan rate 0.5 Hz, imaged in dry nitrogen.

Table 2
ESCA analysis of the surface compositions of tip modifications

Monomer	C 1s	O 1s	Si 1s	F 1s
OTS	59.25	22.41	18.33	
pp-methane	93.45%	5.41%	1.14%	
pp-HFP	30.06%	8.81%	13.08%	48.03%

(on pp-HFP samples) (Table 2). The silicon and most of the oxygen signal can be attributed to the underlying substrate. Attenuation of the silicon signal may be used to determine the film thickness. As expected, high-resolution analysis of the carbon C1s peak revealed a pure hydrocarbon composition for OTS and pp-methane samples (Fig. 2a,b). The symmetrical C1s peaks at 285.0 eV reflected mainly C–C and C–H bonds. Only a very small shoulder at higher binding energy indicated some C–O originating from unspecific adsorbed contamination and from the Si–O–C bond, respectively. The C1s signature of pp-HFP was more complex (Fig. 2c). The distinct envelope of the C1s photoemission peak allowed for identification of the species $\text{C}-\text{CF}_x/\text{C}=\text{CF}_x$, CF , CF_2 , and CF_3 . The ratio of carbon to fluorine changed from the monomer ratio of 1:2 to 5:8 for the pp-HFP

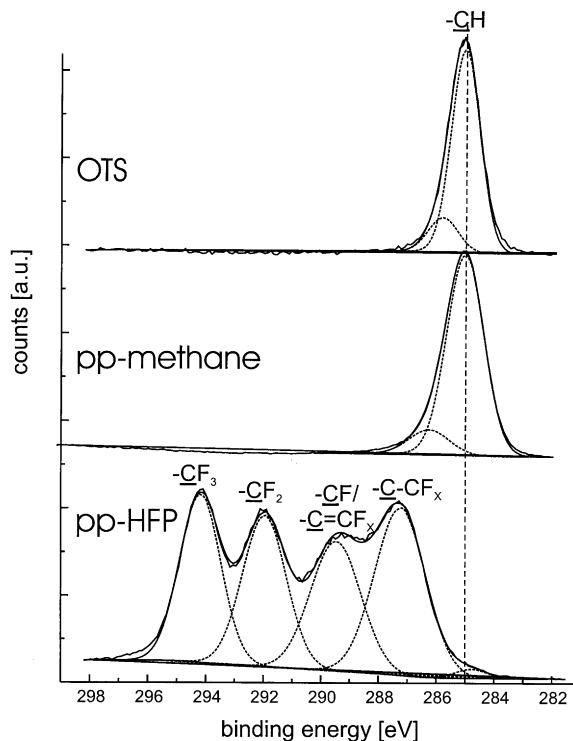


Fig. 2. High-resolution ESCA analysis of the C1s region. OTS and pp-methane consist of a pure hydrocarbon peak ($-\text{CH}$). In contrast, pp-HFP films reveals a complex envelope of $\text{C}-\text{CF}_x/\text{C}=\text{CF}_x$, CF , CF_2 and CF_3 .

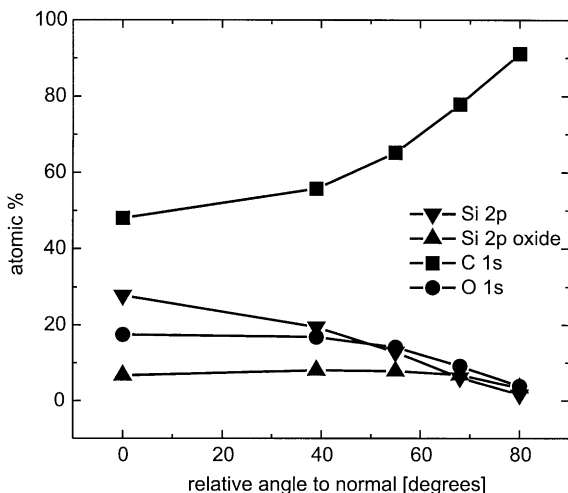


Fig. 3. Angle-dependent ESCA was used to determine the film thickness of the OTS monolayer. At 0° detection angle, the silicon and oxygen concentration was highest (greatest penetration depth) while at 80° take-off angles the silicon and oxygen decreased to close to zero, and the carbon signal reached 95%. The OTS film thickness was calculated to be around 2.4 nm.

indicating abstraction of fluorine during the deposition process. The crosslinking degree was calculated to be about 50% indicating a strong stabilization of the film. A detailed discussion of pp-HFP can be found elsewhere [28,29].

In order to test the film thickness of the coating produced, angle-dependent ESCA was performed. Fig. 3 shows the change in composition of an OTS film as a function of take-off angle. While the signature of the underlying substrate steadily decreased (silicon and oxygen), the contribution of the carbon film increased to 95%. Since the Si and O signals decay almost to zero with large take-off angles, the films must be reasonably uniform overlayers without large voids. This behavior is consistent with monolayer formation. We calculated an OTS film thickness of roughly 2.4 nm, which compares well to the theoretical thickness of 2.0 nm for an OTS monolayer. It could be argued that the silicon signal was measured because of discontinuous film formation or cracks on the surface, but the SFM data, contact angle measurements and the dependence of the ESCA signals with angle do not support this conclusion [27].

An analysis of the SFM tip shape was performed by ESEM (Philips Electroscan 2020, water vapor pressure 5 Torr) and by scanning a silicon tip-grating (TGTO1, NT-MDT Russia). Electron microscope investigations can be problematic in that the focused electron beam of the microscope induces charging of the tip and damages the organic thin layer. These effects make high-resolution micrographs difficult to obtain. As coating the lever with a conductive metal layer cannot be anticipated, the only way around this problem is by using a very low acceleration voltage and by making measurements in a water vapor atmosphere. This is only possible with environmental SEM. The investigations revealed a homogeneous coating without evidence of local uncontrolled polymerization as is often observed with silanization. The curvature of the tips was measured on a silicon tip-grating. The images obtained did not indicate an unexpected increase of tip radius after plasma deposition.

The chemical composition on modified SFM cantilevers could be further analyzed by time-of-flight secondary ion mass spectrometry. With imaging ToF-SIMS, spatial variation of the chemical composition could be measured. The ToF-SIMS technique is an excellent method to apply to surface functionalization as only chemical species in the outermost 20 Å are detected. Analysis of the HFP plasma polymer films displayed spectra that were dominated by a variety of lower mass fragments [30]. A ToF-SIMS image acquired with fluorine containing fragments is displayed in Fig. 4. While hardly any silicon signal was detected on a pp-HFP coated cantilever, the fluorine signal was high. This result suggests that the coating on the lever had few defects and the film thickness was more than 20 Å. The fact that the tip area can be distinguished from the cantilever surface is not due to a chemistry difference, but to the different geometric alignments of the ion source, surface, and detector.

At this point it should also be noted that these thin film deposition methods did not generate stress and bending of the levers as often observed for metal coatings. Cantilevers modified with such organic thin coatings do not induce thermal “bi-metallic strip-effects” as observed with gold-coated levers.



Fig. 4. ToF-SIMS image of a pp-HFP-coated lever. The contrast on the lever was obtained by the detection of C–F ions. No signal from silicon could be detected indicating that the lever was homogenous coated.

The stability and functionality of the tip coatings were tested with the SFM by force versus displacement curves (F/D). An important factor for tip functionalization is the performance with regard to mechanical wear. Therefore, we carried out a series of experiments in sodium phosphate buffer. Fig. 5 depicts the adhesion force measured between two similar surfaces. Unstable functional modifications displayed a large variation in adhesive interaction as a function of number of force curves. This was especially pronounced for low-quality silane films. We measured on such films a steady decay in interaction forces, plateauing around 50% of the original adhesive force (Fig. 5a). The observed wear has been described in literature and is not unusual for low-quality silane films where the silanol groups of the silane films are not covalently bound to the surface [31]. Incomplete covalent immobilization of the silanol groups in low-quality films could explain effects described by other groups where a partial detachment of the silane is suspected to introduce artifacts in recognition force measurements [32]. The slow decrease in adhesive interac-

tion excluded the possibility of a broken tip, which would result in an immediate change. No aging effect was observed for good-quality silane films. The difference between the mean values of the first 10 F/D curves and the value obtained for + 100 F/D curves was within the error range of the measurements. Plasma polymer-coated SFM tips performed similarly to the good silane films. The measured adhesion forces were stable around 38 nN for the pp-HFP and 44 nN for pp-methane. The large difference in adhesion between the OTS and plasma coatings can be easily explained by the fact that different type of tips were used (high aspect ratio versus pyramidal tips). It is well known that the interaction force strongly depends on the contact area [33,34]. Therefore, minute differences in tip radius may have a large influence on the interaction force.

The behaviour of coatings were also tested at different pH values [35]. As expected, experiments carried out as a function of pH did not result in changes in the adhesive force, which is in agreement with other publications [36].

4. Conclusions

In this paper, we describe a comprehensive analytical approach to functionalization of scanning force microscope cantilevers. We focused on hydrophobic coatings produced by silanization (OTS) and chemical vapor deposition (pp-methane, pp-HFP). Diced silicon chips were used as control surfaces to facilitate analysis. The chemical structure was examined by ESCA and ToF-SIMS. ESCA analysis revealed the pure hydrocarbon and fluorocarbon character of the coatings produced. Angle-dependent ESCA provided information about the film thickness. Imaging ToF-SIMS analysis was used to assess the homogeneity of the chemical derivatization of the cantilever tips. Topographical SFM scans were employed to test the quality and coverage of the polymerization reactions. The stability of the coatings was investigated with force versus displacement curves. It could be shown that the adhesive interaction did not change with increased number of force curves. Coatings of high quality were consistently produc-

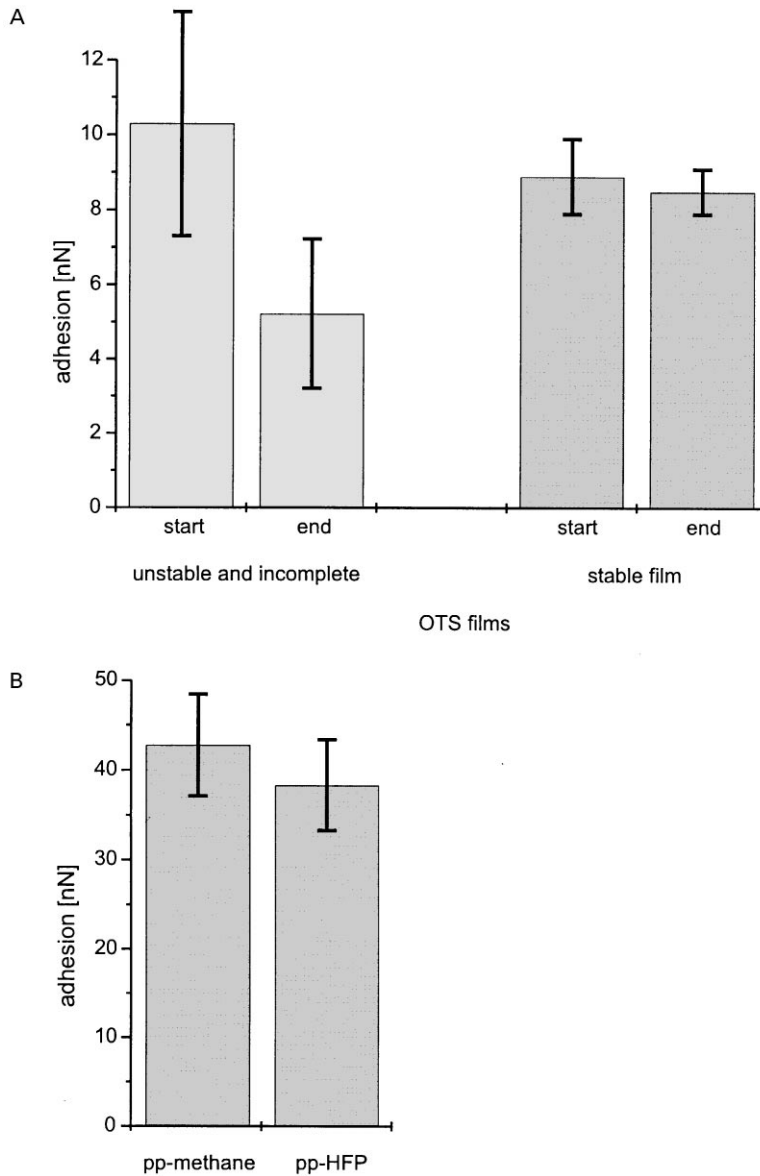


Fig. 5. Interaction force measurements with functionalized SFM cantilevers. (A) Comparison of adhesion as a function of the number of force curves shows that unstable OTS films exhibit a dramatic decay in adhesion with increased number of force curves while the adhesion did not change significantly for good-quality OTS films. (B) No aging effect was evident for plasma polymer films which stayed within the standard error of the measurements.

ed by radio frequency plasma enhanced chemical vapor deposition. The strength of this method is that the surface modification takes place in a solvent free environment at room temperature. The plasma deposition technique offers a functionaliz-

ation procedure that can be scaled up for manufacturing entire cantilever wafers. An important finding was that both modification techniques did not lead to stress-induced bending of the levers.

We consider this comprehensive analytical approach as an essential part of SFM tip functionalization. Only a well characterized tip chemistry allows for proper interpretation of interaction force measurements.

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