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Influence of Molecular Arrangement in Self-Assembled Monolayers on Adhesion Forces Measured by Chemical Force Microscopy

Anne-Sophie Duwez,*[a, b] Ulrich Jonas,[a] and Hubert Klein[c]

Introduction

With the advancing developments in miniaturization, the properties of surfaces and interfaces become more relevant due to the increasing surface-to-bulk ratio in small structures. In this respect, the study of reactivity and chemical heterogeneity of high-performance materials requires the development of surface-chemical imaging tools for direct analysis of complex and multifunctional systems on the nanoscale. Chemical force microscopy (CFM) combines chemical discrimination with atomic force microscopy by chemical derivatization of the scanning probe tip;[1, 2] it enables interaction forces between chemical groups on the probe tip and molecules on the analyzed surface to be measured. Up to now, little attention has been paid to the effect of parameters other than plain surface chemistry on the measured adhesion forces.[3] However, the forces are not only influenced by the chemical nature of the surface, but also by physical properties (morphology, mechanical properties, orientation and arrangement of molecules, etc.), and by the surrounding medium,[4] which regulates the tip – sample interactions. In the case of complex surfaces, these numerous factors act simultaneously and complicate the correct interpretation of adhesion forces. Since many parameters can affect the interaction forces measured by CFM, it is not always possible to interpret adhesion contrast solely in terms of chemical specificity. The use of this technique can be drastically limited if the influence of the individual factors is not known in detail.

The frictional behavior of methyl-terminated self-assembled monolayers (SAMs) has been extensively studied, whereas no systematic studies on parameters influencing their adhesive properties have been reported to our knowledge. It was shown that the adhesion forces do not necessarily correlate well with the coefficient of friction.[5] The proposed explanation is that the adhesion force is influenced mainly by the nature of the tip – sample chemical interaction, whereas the frictional force may be strongly influenced by the mechanical properties. Adhesion force measurements on alkanethiols and alkyltrichlorosilanes in ambient air were reported, and the values obtained for both types of monolayers were very similar.[6, 7] It was concluded that the adhesion properties were similar, since the surface energy of all the studied films are of the same magnitude due to their common CH_3 termination. A slightly higher force was obtained for short chains than for longer chains and was attributed to a higher contact area between the tip and the layer due to higher compressibility. It could also be attributable to the higher surface energy of films made of shorter and/or disordered chains.[8] As suggested by Leggett et al., systematic CFM studies must address the difficulties posed by layers that differ mechanically.[5a] The study of physical parameters besides surface chemistry is clearly a central issue in clarifying the origins of contrast in adhesion force images.

Here we report on the use of chemical force microscopy in the force – distance mode to discriminate between CH_3-terminated SAMs obtained from thiol, trichlorosilane, and trimethoxysilane precursors. The fixation of the anchor group is different for each of these precursors, and this gives rise to slightly different arrangements and packings of the alkyl chains in the resulting films.[9] Our aim is to study the influence of this chain organization on adhesion forces. The adhesion forces were measured in water to eliminate the effects of capillary condensation, which occurs in air, strongly depends on humidity, and thus severely hinders quantitative and reproducible measurements. Moreover, it was shown earlier that this tip – environment combination gives the best contrast in pull-off forces between hydrophobic surfaces.[10]

In the following section, we briefly describe the structural organization of the different monolayers used in this study and then we undertake a systematic investigation of the adhesion forces measured between CH_3 modified tips and these films.

Results and Discussion

Characterization of Monolayers

The CH_3-terminated monolayers were prepared by self-assembly of octadecanethiol ($C_{18}SH$) on gold, octadecyltrichlorosilane ($C_{18}SiCl_3$) on silicon, and octadecyltrimethoxysilane ($C_{18}Si(OCH_3)_3$) on silicon (see Experimental Section). It is well-known that the packing differs for $C_{18}SH$, $C_{18}SiCl_3$, and $C_{18}Si(OCH_3)_3$ monolayers due to their different adsorption mechanisms.[9] This difference is illustrated by the different tilt angle of the chains in the film.[9] We estimated this tilt angle in our monolayers by comparing the thickness of the films, measured by ellipsometry (Table 1), and the theoretical chain length in an *all-trans* conformation. In films formed from $C_{18}SiCl_3$, the tilt angle is about 10°, whereas it is about 30° for $C_{18}SH$ chains and about 40° for $C_{18}Si(OCH_3)_3$. These values are in very good agreement with those reported in the literature.[9] The packing density is influenced by the fixation of

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Table 1. *Thickness (obtained by ellipsometry), advancing water contact angles θ_a, hysteresis of water contact angle $\theta_a - \theta_r$, and adhesion forces measured with CH_3-functionalized tips in water for octadecanethiol, octadecyltrichlorosilane, and octadecyltrimethoxysilane monolayers. Adhesion forces are average values obtained from a minimum of 3072 force curves.*

Monolayer	Thickness [nm]	θ_a (H_2O) [°]	$\theta_a - \theta_r$ [°]	Force [nN][c]		
				Tip 1	Tip 2	Tip 3
$C_{18}SH$	2.2 ± 0.1	111	0.5	22.9 ± 1.2	22.3 ± 1.1	23.8 ± 1.2
$C_{18}SiCl_3$	2.4 ± 0.1	110	1	18.2 ± 1.1	17.7 ± 1.2	19.1 ± 1.3
$C_{18}Si(OCH_3)_3$	1.9 ± 0.1	108	1	15.6 ± 1.3	15.3 ± 1.1	16.5 ± 1.2
$C_{18}Si(OCH_3)_3$[a]	–	76	5	8.3 ± 1.9	8.6 ± 2.2	8.9 ± 2.1
$C_{18}Si(OCH_3)_3$[b]	–	41	8	4.6 ± 2.1	4.1 ± 2.4	4.4 ± 2.5

[a] Incomplete monolayer after a reaction time of 10 min. [b] Incomplete monolayer after a reaction time of 1 min. [c] The relatively small variation of less than 10% between the results obtained from the three tips is attributed to careful selection of tips with very similar spring constants (see Experimental Section), and it is independent of the monolayer structure. The relative error for the adhesion forces measured with an identical tip increases significantly from about 5 – 7% for the complete layers to about 20 and 50% for the incomplete $C_{18}Si(OCH_3)_3$ layers after 10 min and 1 min adsorption time, respectively. This increase in the relative error is concurrent with a decrease in layer quality and a larger number of defects (coexistence of expanded and condensed phases).

the anchor groups and is correlated with this angle, since the alkane chains tilt to maximize their lateral van der Waals interactions (Figure 1). The interchain distance in $C_{18}SiCl_3$ monolayers is 4.4 Å.[9] There is thus very little free volume, which allows

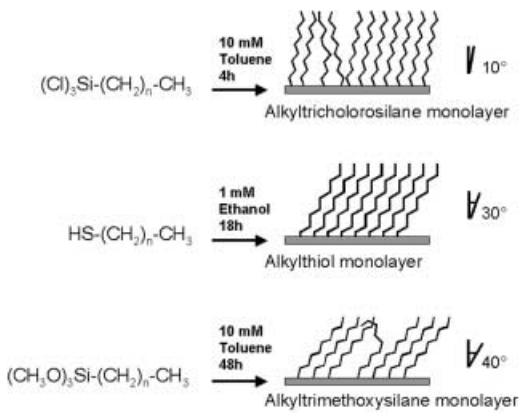


Figure 1. *Schematic representation of the molecular arrangement in monolayers obtained from the adsorption of alkyltrichlorosilanes, alkanethiols, and alkyltrimethoxysilanes.*

only a little chain tilt. The chain density in the $C_{18}SH$ film is lower, the interchain distance being 4.97 Å for hexagonal symmetry of the sulfur atoms on Au(111).[9] The higher average tilt angle of $C_{18}Si(OCH_3)_3$ than for $C_{18}SiCl_3$ is due to their different adsorption mechanisms, since the methoxy groups are much less reactive than the chloro substituents. The scenario usually proposed to explain the formation of the films is based on the rapid reaction of chlorosilanes with traces of water to form oligomers in solution. The reactivity is further enhanced by the autocatalytic effect of HCl released during hydrolysis. This mechanism is supported by AFM studies that evidenced the formation of numerous islands on the surface in the case of chlorosilanes.[11–13] In the case of methoxysilanes, hydrolysis and oligomerization in solution are strongly reduced in the absence of a hydrolysis catalyst. As a consequence the species reacting on the surface are shorter oligomers or monomers.[14] As the mobility of the monomers anchored to the surface is reduced and the methoxy groups are bulky, the packing of the chains is less dense, and thus the tilt angle is higher.

Topographic AFM images of the complete monolayers formed from the alkanethiols and alkylsilanes after sufficiently long adsorption times show no domains or defects, but only a flat surface of the condensed phase with the roughness of the underlying substrate (topographic images shown in Supporting Information). The incomplete monolayers are characterized by the coexistence of condensed phase islands and an expanded phase in the surrounding region,[11] as evidenced by the images in Figure 2. These images are very similar to those reported in the literature for such incomplete monolayers.[6, 11, 15–17] After incomplete monolayer formation, domains of a condensed phase appear, 1.0 – 1.5 nm higher than the surrounding expanded phase in the topographic image (Figure 2 A) and show a lower lateral friction force. The surrounding expanded phase forms a thinner layer (dark regions in Figure 2 A) with a larger friction force (bright areas in Figure 2 B and C). Such a frictional contrast between the condensed and expanded phase in incomplete monolayers of silanes has been studied in detail[6, 15–17] and can be explained by two mechanisms: first, the liquidlike regions interact more strongly with the contacting tip due to enhanced

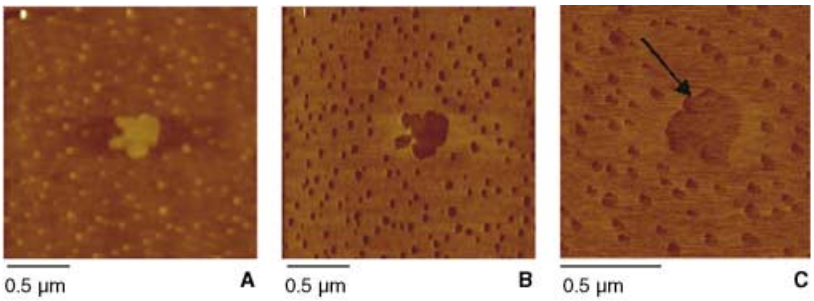


Figure 2. *Topographic image (A) and lateral force microscopy (LFM) images (B, C) of a partial $C_{18}Si(OCH_3)_3$ monolayer on Si formed after 1 min immersion time. The images were obtained with a CH_3-modified tip in a dry nitrogen atmosphere (A, B) and in water (C). A lower friction force is observed on the crystalline domains (dark areas). The large crystalline domain marked by an arrow corresponds to that observed in Figure 3. Max z height for the topographic image is 10 nm.*

contact area as compared to the crystalline regions, and thus give rise to a higher frictional response. Second, with decreasing packing density and order, the number of kinks, gauche defects, and chain distortions that provide many excitation modes for energy dissipation increases. This also contributes to an increased friction.

Adhesion Force Measurements

Adhesion forces were measured in water with gold-coated tips modified by octadecanethiol. The average values of adhesion forces obtained on the various monolayers are summarized in Table 1. The adhesive forces, at least one order of magnitude higher than the predicted van der Waals forces,[18, 19] are directly related to the work required to exclude water from the tip–sample interface.[20] It is clear from the data in Table 1 that besides the chemical nature of the surfaces, which are all CH_3-terminated, there are other parameters that govern the adhesion forces measured between methyl-terminated surfaces in water.

For incomplete monolayers obtained after short dipping times, the influence of chain packing is quite evident. A disordered liquidlike monolayer is less hydrophobic than its closely packed counterpart. Exposure of methylene groups to the surface increases the surface free energy and thus decreases the hydrophobicity of the surface, as shown by the small water-contact angle θ_a (Table 1). Penetration of water is expected to be more significant in a less densely packed film than in a closely packed, highly hydrophobic monolayer, as shown by the hysteresis of the water-contact angle $\theta_a - \theta_r$ (Table 1). As the hydrophobicity decreases a smaller pull-off force suffices to break the tip–sample adhesion.

Force–distance curves were measured on the liquid-expanded phase corresponding to the surrounding region and on the islands. A force of about 4 nN was obtained on the liquid-expanded phase, and a force of about 15 nN on the island structures. The adhesion map (Figure 3), recorded on the same area as Figure 2, shows that higher adhesion forces are obtained on the islands (condensed phase), and lower forces correspond to the expanded-phase region. The contrast is thus inverted relative to the friction image. It seems that the disorder does not increase the adhesion (through an increase in the contact area), as is the case for friction; instead, it decreases the adhesion forces. Apparently, there is thus no direct correlation between friction and adhesion in this system, in contrast to the conclusion proposed from experiments with different functional groups (COOH, OH, CH_3) on tips and samples.[1c]

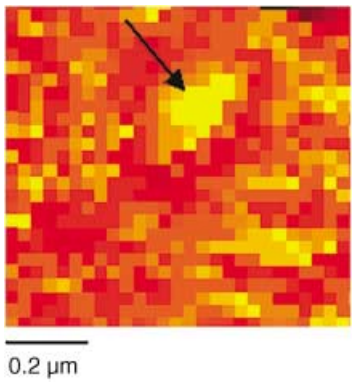


Figure 3. *Adhesion image of a partial $C_{18}Si(OCH_3)_3$ monolayer formed after 1 min immersion time, obtained in the force volume mode with a CH_3-modified tip in water. Dark areas correspond to a low adhesion force and bright areas to a high adhesion force (max. 15 nN). The arrow indicates the crystalline domain corresponding to that observed in Figure 2. This image was recorded at a resolution of 32 × 32 pixels; measurements were thus taken at about 30 nm intervals. This is likely to be close to the lateral resolution limited by the z gradient of adhesion forces.*

In the case of complete monolayers, the observed differences in adhesion forces might be related to the fact that there is a substantially different arrangement of the alkyl chains in the monolayers. Microscopic details such as the presence of defects and order along the hydrocarbon chains can play an important role in the interaction forces measured between the tip and the surface. The difference in adhesion forces between $C_{18}Si(OCH_3)_3$ and $C_{18}SiCl_3$ seems to be correlated to the tilt angle and thus to the packing density of the alkyl chains in the layers. Furthermore, a different tilt angle involves a different orientation of the terminal methyl group, and it has been shown that the wettability of the surface is strongly correlated to the orientation of this terminal group.[21]

Self-assembled monolayers of alkylsilanes lack the long-range order found in alkanethiol SAMs. Higher friction of silanes relative to the corresponding thiol films has been reported in the literature and attributed to the additional disorder of silane films.[6, 15] Penetration of solvent is thus expected to be more significant in alkylsilane SAMs. This could explain the fact that $C_{18}SiCl_3$ SAMs exhibit lower adhesion forces than $C_{18}SH$ SAMs. The long-range order of alkanethiols probably increases the solvent-exclusion effect and thus the hydrophobic interactions between the tip and the surface.

Another important parameter that might contribute to the adhesion forces is interdigitation.[22, 23] Poor packing or a greater fluidity at the chain end can increase interdigitation of alkyl chains between tip and sample and thus increase the adhesion forces. This is not the case here, since the $C_{18}Si(OCH_3)_3$ films, which are the least closely packed films, show the lowest adhesion forces. Moreover, interdigitation of the chains is very unlikely, as the measurements were performed in a very poor solvent for the chains. Although it has been shown that monolayer compressibility influences the adhesion forces measured in air,[6] it seems that in water the monolayer compressibility is not a parameter that contributes considerably to the forces, as lower forces are obtained on less densely packed layers and on liquidlike regions, as well as for monolayers obtained from shorter C_8 alkanethiol chains (11.5 nN).

It seems thus that interdigitation and compressibility are two parameters that are masked by the strong hydrophobic forces when measuring adhesion between very nonpolar surfaces in water. The solvent-exclusion effect is thus probably the dominant parameter.

In some cases, monolayers prepared from $C_{18}SiCl_3$ show much lower adhesion forces (12.7 ± 1.6 nN) than average complete monolayers, even lower than those of their $C_{18}Si(OCH_3)_3$ counterparts. This behavior is very likely caused by a higher degree of

gauche defects and a lower compactness, as supported also by a greater hysteresis of the contact angle (5°). Since the trichlorosilanes are highly reactive and sensitive to traces of water, the reaction conditions must be carefully controlled to obtain highly ordered monolayers of reproducible quality. The precursor concentration, the solvent and its water content, relative humidity, temperature, substrate cleanliness, and surface hydration strongly influence the quality of the final SAM. This result supports our conclusion that the packing of the layer and its order strongly influence the adhesion forces measured in water. Thus, chemical force microscopy in adhesion-force mode is a very sensitive method for detecting minor variations in monolayer quality that are not necessarily registered by advancing contact angle measurements or ellipsometry.

The Johnson – Kendall – Roberts (JKR) theory of adhesion mechanics[24] has been shown to describe data measured on SAMs with functionalized tips adequately.[1b, 1c, 4, 20] The JKR model predicts that the pull-off force F_{ad} required to separate a sphere from a planar surface is given by Equation (1):

$$F_{ad} = -(3/2)\pi RW \quad (1)$$

where R is the radius of curvature of the tip, and W is the work of adhesion to pull the tip off the sample. This relation has been used in the literature to estimate the tip radius from the measured adhesion force.[4, 20] Tabulated values of surface free energies are usually used to approximate the work of adhesion. It can thus be hazardous to estimate the tip radius by this method, since different apparent radii would be obtained for experimental values of F_{ad} measured on thiol, cholorosilane, or methoxysilane monolayers.

Conclusion

In summary, by using alkylthiol molecules chemisorbed on gold-coated AFM tips, we were able to distinguish between methyl-terminated monolayers obtained from alkylthiols, alkylmethoxysilanes, and alkylchlorosilanes on planar substrates, by means of differences in the adhesion forces measured by the probe. We have successfully shown that CFM, which is a versatile and tunable technique for studying intermolecular interactions and for chemically specific imaging of surfaces in air or in liquids, can be used to study aspects of the self-assembly process and to probe the quality of the resulting monolayers. This prospect of distinguishing molecular arrangements in organic layers introduces an additional parameter for chemical discrimination by CFM, which must be taken into account for a reliable interpretation of experimental data.

Experimental Section

Functionalized AFM probes were prepared by self-assembly of octadecanethiol on gold-coated tips, following the procedure described previously.[10] Gold films were obtained by evaporating 100 nm of gold at a rate of 2 Å s^{-1} onto mica sheets maintained at 460 °C. The typical grain size was 1 μm with Au(111) terraces larger than 100 nm.[25] Silicon substrates (100) and gold-coated mica were cleaned by treatment with UV/ozone before monolayer adsorption. Gold films were immersed in a 1 mM solution of octadecanethiol (Aldrich, 98%) in absolute ethanol for 18 h. Upon removal from the solution, the samples were sonicated in an ethanol bath for 10 min and then rinsed with *n*-hexane and ethanol and dried in a gentle flow of argon. Alkyltrichlorosilane monolayers were prepared on silicon from 10 mM solutions of octadecyltrichlorosilane (ABCR, 95%) in anhydrous toluene in a glovebox under nitrogen atmosphere. Complete monolayers were obtained after 4 h. Alkyltrimethoxysilane layers on silicon were prepared from a solution of octadecyltrimethoxysilane (ABCR, 95%) in anhydrous toluene (10 mM) in ambient air. An incubation time of 48 h was needed to obtain complete monolayers. Upon removal from the solution, the silane layers were sonicated in a chloroform bath for 10 min.

AFM experiments were conducted with a PicoSPM equipped with a fluid cell and an environmental chamber (Molecular Imaging) and controlled by Nanoscope III electronics (Digital Instruments, Santa Barbara, CA). All experiments were performed with functionalized probes. We used standard silicon nitride cantilevers (Microlever, TM Microscopes, Sunnyvale, CA) with a pyramidal tip. As shown previously, the cantilever spring constant may vary by up to 50% depending on the particular batch of the manufacturer; hence, cantilevers were chosen from adjoining chips of the same wafer.[10a] To evidence differences in adhesion forces in a comparative manner using the same tip, the knowledge of an absolute exact value of the spring constant is not mandatory. However, the individual spring constants were measured for the three selected cantilevers after gold coating to ensure that they were similar, using the method described in ref. [26]. The measured values (0.046 ± 0.007, 0.045 ± 0.007, and 0.049 ± 0.009 N m^{-1}) were identical within the error range of measurement. The tip radius was about 85 nm, as determined from SEM images. To eliminate parameters that could affect the pull-off forces (uncertainty in the spring constant, tip shape, radius of curvature, granularity of the evaporated gold film), all samples were analyzed with the same tip, and three series of experiments with three independent tips were performed. Comparing results obtained from different tips could be not reliable, since not every tip has exactly the same characteristics. The adhesive interaction between tip and sample was determined from force versus cantilever displacement curves by using the "force volume" mode. In this mode an array of hundreds or thousands of force curves is recorded over the entire probed area. We recorded arrays of 32×32 pixels; each measurement thus corresponds to 1024 curves. The results presented in Table 1 are average values obtained for a minimum of three locations on the sample for each monolayer, that is, for a minimum of 3072 force curves. The force volume data were treated by using a routine developed under Igor Pro (Wavemetrics, Portland, OR) to extract from every curve the adhesion force and build up an adhesion map. Only the force – distance curves for which there was no long-range attractive forces (long-range jump to contact) on approach were considered. These long-range forces are associated with the formation of submicroscopic air bubbles that bridge the tip and sample.[19] The appearance of such bubbles and their influence on the adhesion forces will be the subject of a subsequent report.

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Keywords: adhesion forces · chemical force microscopy · molecular packing · monolayers · self-assembly

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