TRIBOLOGICAL PROPERTIES OF ADSORBED SURFACE LAYERS IN THE MONOLAYER RANGE

T. SCHNEIDER 1
Federal Institute for Materials Research and Testing (BAM), Unter den Eichen 44 - 46, D - 12203 Berlin, GERMANY;
e-mail: thomas.schneider@bam.de

T. GRADT
Federal Institute for Materials Research and Testing (BAM), Unter den Eichen 44 - 46, D - 12203 Berlin, GERMANY;
e-mail: thomas.gradt@bam.de

SUMMARY
Measurements were conducted on silicon substrates under ultra high vacuum (UHV) conditions using an atomic force microscope/friction force microscope (AFM/FFM) in the nano Newton range. The same Si-cantilever/Si-tip was used for all measurements. By measuring so called force/distance curves (f/d-curves) different adhesion forces could be distinguished for the clean, 7×7 reconstructed Si-surface and other Si-surfaces prepared differently. In addition, FFM measurements revealed a different behaviour as well. Although the clean Si-sample exhibited stick/slip friction the overall friction coefficient was comparatively low. The Si-sample with saturated dangling bonds (H-terminated) showed smooth FFM images but with higher coefficient of friction and higher adhesion. A thick adsorption layer containing hydrogen and carbon exhibited the lowest friction coefficient under low normal forces. With increasing loads the friction coefficient increased while no adhesion could be measured.

Keywords: UHV, AFM/FFM, adsorption, monolayers, microtribology

1 INTRODUCTION
The influence of thin adsorbate layers on the tribological behaviour of materials is well known. E. g. the amount of humidity often is crucial for friction and wear behaviour of ceramic materials on both the macroscopic and microscopic scale as it can alter topography as well chemistry of a surface [1, 2]. Because of the fundamental influence of adsorbates, surface layers could become even more important for micro-systems and high precision tribo-systems where not even the slightest wear can be tolerated. In order to completely understand the environmental influence on a tribo-system it is necessary to start with a clean surface. Then, adding the adsorbates of interest layer by layer according to surface science routines. This concept has been employed among others by Gardos et al [3] in performing tribological measurements on several different silicon and diamond samples in a SEM apparatus. Loads of up to 0.5 N were used with temperatures reaching 850 °C. However, their vacuum conditions achieved still could leave some ambiguities in interpreting the results. This can be overcome by using true ultra high vacuum systems (UHV) as has been done e.g. by the Group of Gellman measuring the influence of atoms or molecules respectively adsorbed on two copper specimens [4]. The single crystals used consisted of a flat Cu(111) surface and one with a radius of approximately 2.5 cm. Both where brought into contact under loads ranging from 10 – 80 mN.

The tribo-system used by the authors of this paper operates under significantly lower loads in the nano-Newton range by means of an AFM/FFM silicon tip acting against a silicon surface (Si(111)). The aim of this paper was to correlate the tribological findings with characteristics of the sample on a molecular level. As a clean Si(111) surface is easily prepared under UHV-conditions it should be a good candidate for testing the ability of an UHV-AFM/FFM to monitor the tribological behaviour. The samples were prepared by different sputtering and/or annealing procedures eventually followed by adsorption out of the gas phase. Starting with a clean 7×7 reconstructed surface with unsaturated dangling bonds (DB) these then were saturated by hydrogen adsorption in the monolayer range followed by a thick multilayer adsorption to create three different tribo-systems. As the Si-surface is easily cleaned just by sufficiently heating in UHV even after being exposed to large amounts of gas the same starting point is obtained conveniently.

2 EXPERIMENTAL
All experiments were conducted under UHV-conditions with a base pressure of 5 × 10⁻¹¹ mbar for AFM/FFM-measurements. A commercial OMICRON-system was used evacuated by an ion pump and a titanium sublimation pump, the AFM/FFM being also of OMICRON manufacture. The analysis of the samples were obtained by low energy electron diffraction (LEED) combined with Auger-electron spectroscopy (AES) using a four grid retarding field analyser (RFA). A quadrupole mass analyser (QMA) allowed for residual gas analysis and measurement of species eventually desorbing from the sample.

In order to have a good sensitivity for lateral forces a relatively soft I-type Si-cantilever had to be employed. Thus, the normal forces to be applied were limited
30 nN approximately. Exceeding this value would lead to a loss of linearity of the laser beam detection system. The spring constant of the cantilever used was 0.12 Nm⁻¹ in normal direction based on geometrical calculations given for each cantilever individually by the manufacturer (NANOSENSORS). The torsional spring constant was calculated to be ten times as high. The etched Si-cantilever had a Si-tip with a radius of approx. 20 nm. The sensitivity of the instrument measuring the normal force was established using the slope of the repulsive part of the so-called force/distance curve (F/D-curve) in conventional fashion. In a similar manner the corresponding value for detection of the lateral forces was given by evaluating the slope of the friction signal detected by the photo diode at the beginning of a line scan (fig. 1).

![Figure 1: Calibration of FFM sensitivity to lateral force (see text)](image)

The voltage measured by the instrument (L-R-signal of the four quadrant sensor) then can be recalibrated using the estimated cantilever spring constant (c_torsion = 1.2 Nm⁻¹) to obtain the lateral force in nN. Still, there is a high uncertainty about absolute values because of simplifications regarding the geometry of the cantilever as well as the critical influence in erring on cantilever thickness t (t³!). For a more detailed discussion the reader is referred to literature [5]. However, since for all measurements undertaken in this work the very same cantilever was used at least relative values could be obtained.

The lateral forces measured with the FFM were sampled over 300 × 300 pixel for each setpoint of the normal force (“frame-mode”). The measurements were conducted the following way: for each normal force set a line scan was performed in both directions (“friction loop”). Each image consisted of 300 lines, each line of 300 points. Images of both scan directions were evaluated by a histogram using the manufacturers standard software. Thus, for each direction a plateau of lateral forces was obtained, each histogram averaging 300 friction loops. Half of the difference between both values was taken as the friction force F_L. The statistical error given by the width of the histogram.

The sample consisted of a slab of a Si-wafer (111) surface with a size of 15 × 5 mm² mounted to an OMICRON sample holder with direct heating facility. The cleanliness was controlled by observation of the 7×7 LEED pattern and AES with the KLL carbon and LMM oxygen peak vanishing below the noise level. For initial cleaning argon-sputtering in a separate preparation chamber was employed, the sample was transferred without breaking the vacuum.

3 RESULTS

3.1 Si-tip on Si (111) (7×7)

The well-known 7×7 reconstruction of the clean Si-surface was easily obtained under UHV-conditions by heating the surface above 800 °C [6]. After sputtering and annealing the sample in the preparation chamber it was transferred into the analysis chamber, heated as mentioned above which led to the 7×7 structure as could be proved by LEED. By conducting F/D-measurements with the AFM an adhesion force of about 1 nN between tip and sample could be evaluated (fig. 2).

![Figure 2: F/D-curve for Si-tip on Si(111) - 7×7](image)

FFM-images showed the dependence of lateral forces on normal forces to be relatively low, giving rise to a friction coefficient of roughly f = 0.2 - 0.3 (Fig. 3).

![Figure 3: plot of lateral forces measured versus normal forces on Si(111) - 7×7 surface, error bar ± 0.5 nN plus 10 % of F_N due to stick/slip](image)
Due to the rather low values of the lateral force the crosstalk of topographical features was rather prominent despite a flat sample with a roughness of only 1.8 nm RMS as measured by AFM over 200 × 200 nm². Applying forces above 15 nN led to increasingly “spiky” images, so only loads below 20 nN were used.

Considering a single linescan a stick/slip like behaviour with a period of approximately 4 nm (Fig. 4) could be observed which is clearly above the atomic length scale. The sample exhibited some waviness of the surface but this running parallel to the scanning direction was not mirrored by the stick/slip period. The difference between static and dynamic friction force was 10-15% of the applied normal force leading to an additional error when evaluating the images by the histogram method as described previously.

3.2 FFM measurements on H-terminated Si(111)

The dangling bonds of a clean Si-surface render it highly reactive. So, to check for an eventual influence on tribological properties the best way is to adsorb atomic hydrogen since molecular hydrogen does not affect the surface [7,8]. In order to obtain atomic hydrogen the so called hot filament method is mostly used where H₂ is dissociated via a tungsten-filament at 2500 K. In this way at least a mixture of atomic and molecular hydrogen is generated. Since the UHV-chamber used had no filament in direct line of sight to the sample, no absolute flux of atomic hydrogen to the sample could be calculated. Therefore, to check for the coverage Θ_H achieved the vanishing of the 7x7 LEED pattern was used. This occurs at Θ_H = 1 with a broadening of the spots at Θ_H = 1.5 [8] which was the coverage used in the experiments presented here. According to thermal desorption experiments [8] an exposure of 2 × 10⁶ Torr·sec is necessary to saturate the Si(111) surface with atomic hydrogen. After the measurements the surface could be conveniently restored to clean conditions by heating the sample. This was cross checked by means of LEED and the QMA which showed desorption of H₂ only, while no Si-O-species could be detected, stemming from eventually adsorbed H₂O.

The F/D-curves measured by AFM were of rather poor repeatability indicating values between 3 nN and 8 nN for the adhesion force. The latter being higher as for the clean Si-surface (fig 5). The dependency of lateral forces on normal forces also differed in the fact that even for a very low normal force lateral forces were much higher than on the 7x7 reconstructed Si(111)-surface (Fig. 6).

Despite the quite high adhesion it was impossible to perform complete 300x300 scans with negative normal forces applied externally according to (1) as the system then became unstable.

\[ F_{N(\Sigma)} = F_{Adh} + F_{N(ext.)} \] (1)

However some images could be taken without an additional loading (F_N = 0 nN) revealing values between 4.5 and 6.5 nN for the lateral force.

Applying a normal force of higher than 15 nN led to increasing wear showing itself by particles and giving rise to difficulties in keeping feedback. Therefore, experiments were terminated at this load and only results of images showing no signs of wear are included here.

![Figure 4: stick/slip behaviour on Si(111) - 7x7 surface, static/dynamic level of friction differ by 10-15% of normal force](image1)

![Figure 5: F/D-curve on H-terminated- Si(111), \( \Theta_H = 1.5 \)](image2)

![Figure 6: Lateral force plotted against \( F_N \), note high \( F_L \) for \( F_N = 0 \) nN! Error bars given by width of histogram](image3)
3.3 FFM-measurements on multilayer adsorption on Si(111)

Since at present only a single gas can be led into the UHV-chamber a simple way had to be used to alter the adsorption layer in order to obtain a third system beside the clean reconstructed 7×7 surface and the saturated Si-sample. Thus, a surface was prepared by simply using a much higher exposure. Again starting with the clean 7×7 structure the Si(111)-sample was subjected first to the saturation exposure of atomic hydrogen but deliberately using a higher pressure (limit of QMA, approx. 10⁻⁴ Torr). This admittedly crude procedure releases carbonaceous gases previously adsorbed at the walls of the vacuum chamber, leading to a complete vanishing of LEED-spots, only an increased background intensity was to be seen. This is indicating at least an amorphously adsorbed (mono)layer. But, as the Si-peak height of the AES diminished to 1 % of the initial value, an adsorbed multilayer can be safely assumed. As can be concluded from a content of roughly 5 % carbonaceous gases, released by the increased hydrogen pressure, adsorption is taking place resulting in a surface slightly covered with carbon as revealed by AES. In addition to the Si-peak at 90 eV (no chemical shift) the Auger spectra showed the carbon induced peak at 268 eV (Fig. 7). No oxygen could be detected. The relative height of the carbon peak was 6 % of that of silicon with no relative sensitivities taken into account. As hydrogen obviously gives no Auger-signal the high adsorption energy of hydrogen on silicon (3.1 eV/mol for a coverage of \( \Theta_H = 1 \), [8]) should result in a surface of the sample saturated with hydrogen for the first layer and additional layers consisting of a mixture of hydrogen and carbon species. As with the saturated Si-surface after the measurements were completed the original (7×7) structure could easily be obtained again by simply heating the sample.

The F/D-curves showed no adhesion or jump to contact (JtC) for the Si-tip used on this sample but instead revealed an otherwise interesting form. When reaching the surface the cantilever bend at first as to be expected but by further expanding the piezo scanner repulsion increased resulting in two distinct slopes. Retracting again the signal closely followed this behaviour with only slight deviations due to piezo hysteresis (fig. 8).

The steeper slope corresponded to the stiffness of the cantilever as measured before for the clean and H-terminated samples respectively. After first touching the surface further expansion of the piezo scanner led to a lesser increase of normal force for a distance of approx. 20 nm. The resulting slope is about half the value of the cantilever stiffness.

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**Figure 7:** AES of the Si/H/C-surface, carbon peak shown (268 eV), approx. 6 % of Si-peak height

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**Figure 8:** F/D-curve on Si/H/C-surface, no JtC or adhesive force could be measured, steeper slope corresponding to cantilever stiffness

FFM-images were homogeneous with no stick/slip for the friction loops. Correspondingly, the histogram of each frame was centred narrowly around the respective plateau for each scanning direction. The error was estimated to be below 0.5 nN. The measured dependence of friction forces on normal forces as plotted in figure 9 clearly showed two distinctive slopes. Up to a normal force of 5 nN the increase in friction was only slow, corresponding to a friction coefficient of ca. \( f = 0.18 \). Increasing the force beyond 5 nN it increased to \( f = 0.75 \).

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**Figure 9:** Lateral forces plotted against \( F_N \), Si/H/C-sample, error bars given by width of histogram

4 DISCUSSION

Considering the F/D-curves it seems somewhat puzzling that the 7×7 surface with its dangling bonds has a lower adhesion force than the H-terminated one. However the chemistry of the AFM-tip has to be taken into account. It is sensible to assume that the as received AFM-tip is saturated by H or OH or some other contaminants. Therefore, when it touches the sample at least some of
the DBs are easily saturated. Starting with an already H-terminated sample could lead to the formation of dihydride (SiH2) and trihydride (SiH3) due to the higher hydrogen content in the contact zone. These Si-complexes have been detected by thermal desorption spectroscopy experiments and their concentration increases for higher exposures [8]. It is therefore likely that some tribologically stimulated chemical reactions between tip and sample could occur. However, an evaluation of the direct effect of such a chemistry on the F/D-curves is beyond the aim of this paper. No eventually desorbing amounts of reaction products could be detected by means of the QMA. This might be due to the very small contact area of which the desorbing products stem from. To test for effects of tribo-induced desorption a small area was scanned with the AFM/FFM for a prolonged time under high loads. After zooming out and using lower normal forces no friction trace could be detected in topography or friction image.

A major difference concerning the F/D-curves of the clean and H-terminated surface is the energy dissipated in the contact. Comparing the hysteresis of adhesion for both systems - that is: comparing the energy gained when the tip makes contact (JtC) and the energy needed to release it (adhesive energy) – it is evident that hysteresis on the H-terminated surface is much higher, approximately by a factor of 10. On that basis the difference in tribological behaviour of both surfaces is discussed. At first glance the friction measurements conducted by FFM on the Si(111)-7×7 surface showed a rather “conventional” behaviour. The data were fitting the (single asperity) Hertz model indicated by a $F_o^{2/3}$ dependency for the lateral force [10]. However, there is some contradiction here since this model is valid for a system without adhesion whereas F/D-curves showed an adhesive force of ca. 1 nN. Comparing this with the friction data of the H-terminated surface it is quite obvious that the latter has to be much more governed by adhesive forces (adhesive energy) for low normal loads. Such a behaviour is described according to the JKR-model [11]. Qualitatively, the adhesion as measured by the F/D curves supports these findings, but absolute values appear to be too high for Si(111)-7×7. On the other hand, adhesion forces seem somewhat too low for the H-terminated sample to explain the frictional data for low loads. However, F/D-curves are susceptible too rather high systematic errors due to applying the normal forces by bending the cantilever, leading to a lateral movement of the tip on the surface under varying loads. Therefore absolute values could be inaccurate and should be treated with care.

A further result of the saturation of DBs was the disappearance of stick/slip friction. A similar finding was reported by Gardos et al. for self mated Si-pairs in high vacuum conditions where hydrogen adsorption led to a “moderating” influence on the size of the friction noise [12]. Comparing the general trend of frictional data for both surfaces one can conclude that the Si-tip/Si(111)-7×7 surface tribo-system is best described as a single asperity contact with relatively low adhesion hysteresis resulting in a low coefficient of friction (COF). A much higher hysteresis as found for the H-terminated surface leads to a higher COF. This finding is consistent with studies by Yoshizawa et al. [13] using a surface force apparatus.

The frictional behaviour of the Si-surface with multilayer adsorption somewhat fell in between the 7×7 and the H-terminated samples. Starting with a low COF and showing no stick/slip for low loads up to 5 nN this surface combined the best properties. But increasing the load the COF increased drastically to $f = 0.75$ or by a factor of approx. 4. The absolute lateral force however was still lower than for the H-terminated surface. A similar increase of friction for a critical load for a Si$_3$N$_4$-tip on mica was reported by Hu et al. [14]. The increase of friction was ascertainment to the onset of wear above a critical normal force leading to holes corresponding to a depth of one atomic layer. Looking at the F/D-curve measured for this surface (fig. 8) one can clearly see that before the stiffness of the tribo-system is dominated by the cantilever the contact at first shows a much smaller compliance. While the critical normal force of ca.1 nN is lower than the value measured for the transition to higher friction this clearly is an indication of a softer layer on the sample. Taking the difference of both compliances this translates to a thickness of the layer of roughly 10 nm. The complete absence of an adsorption hysteresis however render it difficult to argue along the same line as above. Tentatively, the low friction regime for low loads could be ascribed to the tip sliding on a lubricating layer. Once getting over the critical load friction increases in a similar fashion as on the H-terminated sample, leading to a similar COF. As no adhesion was measurable however, the ruling mechanism of friction for this system needs further clarifying.

5 SUMMARY

First UHV-AFM/FFM experiments showed a clear dependence of adhesion force on the surface chemistry of substrates prepared differently. As could be expected the difference between the clean silicon surface with dangling bonds and the H-terminated surface was quite pronounced, the latter however showing a higher COF than the clean surface. This behaviour was ascribed to a higher adhesion hysteresis. Preparing a thick adsorption layer containing carbon and hydrogen led to a low COF for normal forces up to 5 nN. This system was becoming unstable above this critical load leading to an increased friction thereby getting closer to the values found for the H-terminated sample. This result however, could leave some ambiguities due to the simple method of preparation used. Therefore, a more advanced gas inlet system is under construction giving better facilities. Truly quantitative measurements of normal forces are still depending on the reliability of calibration of the cantilever force constant. This problem is further enhanced by the even more difficult calibration of the torsional force constant for LFM-cantilevers. However, semiquantitative results can be achieved. Despite remaining experimental difficulties it can be concluded...
that sample preparation according to surface science practice under UHV conditions can give deeper insight in fundamental tribological behaviour.

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7 REFERENCES