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Force Spectroscopic Investigations During the Local Oxidation of *n*-Octadecyltrichlorosilane Monolayers**

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Scanning force spectroscopy (SFS) is a powerful tool for investigating surface properties with high precision. Unlike most common spectroscopic techniques, information about local properties can also be obtained from surface areas with nanometer dimensions. This makes SFS a useful investigative tool for small lithographic structures. We apply the continuous recording of force curves to extract valuable information about the local oxidation of a monolayer of *n*-octadecyltrichlorosilane molecules self-assembled on silicon. The oxidation is carried out while simultaneously recording the force curves during the application of a bias voltage to the tip. The dynamics of the induced surface modifications and changes in the surface properties are followed by analyzing specific spots in the force curves.

1. Introduction

The electrochemical patterning of substrates for the creation of small nanostructures[1] is the subject of a large number of investigations, and has also been topic of interest recently because of its potential with respect to nanofabrication, and its compatibility with standard silicon-processing techniques.[2] To date, special attention has been paid mostly to investigation of the scanning force microscope (SFM)-mediated anodization of silicon oxide by the application of a tip bias voltage. As a result, studies on the growth and kinetics have been performed to examine the nature of the anodization mechanism in detail.[3] More recently, attention has been focused on substrates that are covered with an additional organic monolayer. These monolayers offer more versatile possibilities for generating chemically patterned substrates by the chemical functionalization of the grown silicon oxide area with additional silane molecules,[4] or the direct functionalization of the self-assembled monolayer by the electrochemical oxidation of the monolayer.[5] Moreover, self-assembled monolayers are even suspected of accelerating the growth of silicon oxide,[6] and of decreasing the obtainable line-width of oxide patterning to less than 20 nm.[5,7]

Monolayers of *n*-octadecyltrichlorosilane (OTS) self-assembled on silicon substrates[8] are the subject of this report, as they allow, depending on the patterning conditions, both mechanisms to occur (Fig. 1).[9] Under mild oxidation conditions, an electrochemical oxidation of the surface terminal, hydrophobic methyl groups is initiated by the local application of a sufficiently high negative tip bias voltage via a conducting SFM tip, which converts them into hydrophilic, chemically active surface –COOH groups (Fig. 1, schematic A).[5] These surface patterns have been used in nanofabrication, as they can be utilized as site-specific binding areas for additional molecular layers,[5,10,11] nanoparticles,[11] etc., thus demonstrating the interesting potential for the bottom–up assembly of functional nanostructures and nanodevices.

More rigid oxidation conditions result in the monolayer's breakdown, and initiate the local growth of silicon oxide[4] (Fig. 1, schematic B), and the parameter space for both mecha-

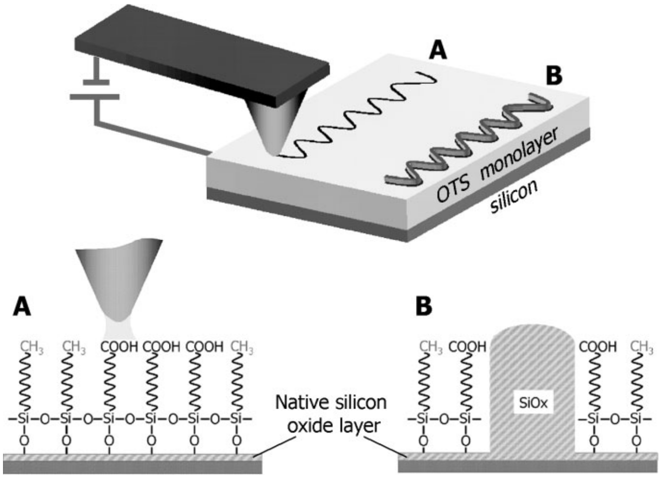

Figure 1. Schematic representation of the electrochemical oxidation of OTS-covered silicon substrates. A) At small negative bias voltages and short interaction times, a selective oxidation of the surface terminal –CH$_3$ end groups to –COOH functions takes place. B) Under more rigid oxidation conditions, the monolayer breaks down and a selective anodization of the silicon/silicon oxide substrate occurs. Within this process, silicon oxide is locally grown in the vicinity of the SFM tip.

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nisms was recently determined.[9] The mechanism of both processes on self-assembled monolayers is not entirely clear, and a more detailed analysis of the oxidation mechanism is required. Owing to the restricted size of the modified areas, only a limited number of analytical tools can be used to investigate the surface modification on a nanoscopic scale, presenting a further challenge since studies of the oxidation kinetics are desirable to obtain a fundamental understanding of the mechanisms.

We report here on scanning force spectroscopic investigations of the monolayer oxidation process and the transition between the monolayer oxidation and the start of the silicon oxide growth. These investigations rely on repeated force spectroscopic measurements on a surface spot, while a tip bias voltage is applied to the SFM tip. This voltage induces the gradual oxidation of the substrate, and allows the almost instantaneous probing of the surface properties of the substrate, which is covered with a self-assembled monolayer of OTS.

This chemical oxidation is correlated with changes in the surface properties, which are locally converted from hydrophobic to hydrophilic. Such changes in the surface properties will certainly also occur if the monolayer is degraded upon the application of higher bias voltages or longer oxidation times. In this case, the breakdown of the monolayer takes place, and the anodization of the silicon/silicon oxide substrate is favored (Fig. 1, schematic B), whereby the hydrophobic surface properties are also diminished because of the hydrophilicity of the growing silicon oxide. The silicon oxide is formed at the interface between the native silicon oxide layer and the silicon wafer where the silicon oxide is formed. Here, an additional increase in the topography is observed, which indicates the growth of silicon oxide.[4,7b,9] This growth is supposed to be self-limited, as electrical charge is stored in the fresh silicon oxide which prevents, at some stage, the further diffusion of OH^- species to the interface. Moreover, such structures are generally surrounded by a small rim, which shows the typical characteristics of an oxidized monolayer in contact-mode friction imaging.[9] These changes in the surface properties are used in this investigation to monitor the gradual progress of the oxidation process by scanning force spectroscopy.[12]

2. Results and Discussion

The properties of surfaces can be directly extracted from specific features of the force–distance curves that monitor the local, specific interactions between the SFM tip and the sample. Figure 2a gives an overview of the common force-spectroscopic measurement approach. The different representations of force–distance curves used in the present studies are depicted in Figures 2b,c.

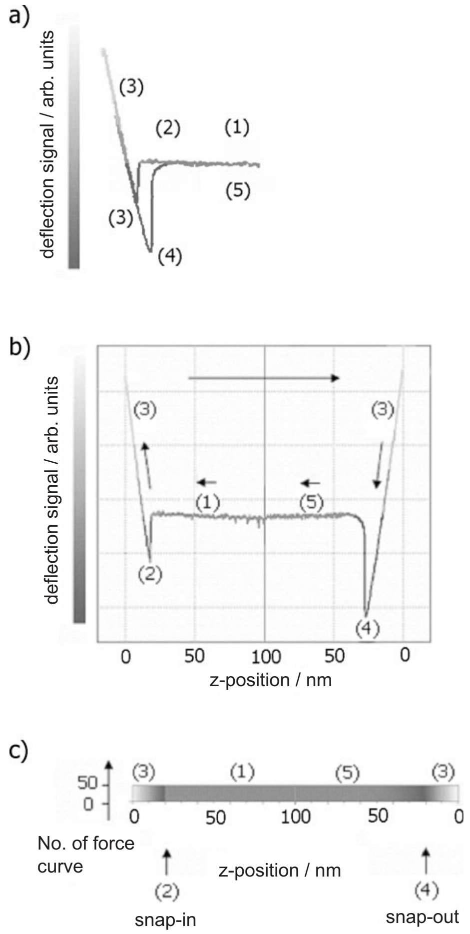

Figure 2. Force–distance curves: a) Representation of the different stages during the recording of a force–distance curve. 1) The tip is relatively far away from the surface, and only long-range interactions influence the cantilever bending. 2) The tip is close enough to the surface that a stable water meniscus can form between the tip and sample. This snap-in point is characterized by a sudden bending of the cantilever towards the surface. 3) The tip is further approached to the surface, and, on sufficiently hard substrates, a linear increase in the cantilever bending away from the surface is observed. This bending is gradually released when the tip is slowly retracted. 4) Upon further retraction, the tip actually loses contact with the substrate, while the cantilever still bends towards the surface because of the adhesive forces of the water meniscus. After a certain amount of stretching, realized by the movement of the tip away from the surface, the water meniscus becomes unstable and the cantilever bending suddenly vanishes at the snap-out point. 5) Subsequently, the cantilever bending is no longer influenced by interactions between the tip and sample, and remains on a constant deflection level. b) Example of a force–distance curve, in the representation scheme that is used in the following studies. c) Set of 50 force curves. The deflection signal is shown in a false-color representation. Each line of this image represents an individual force curve depicted according to the representation given in (b).

The cantilever deflection, which represents a measure of the force sensed between the tip and the sample, is recorded depending on the z-displacement of the piezo of the SFM, which is moved towards the sample at a constant speed. The tip jumps into contact, and is afterwards retracted from the surface. Two specific situations are of special interest for determining the surface properties; namely the snap-in point, where the tip actually jumps into contact with the sample and forms a stable water meniscus during the approach phase of the measurement, and the so-called snap-out point, where this water meniscus breaks again because of the increasing tip–sample distance during the retraction phase. Both points allow the determination of the hydrophilicity of the surface, and provide, therefore, valuable information about the surface properties of the sample. We use a continuous force-curve recording approach to

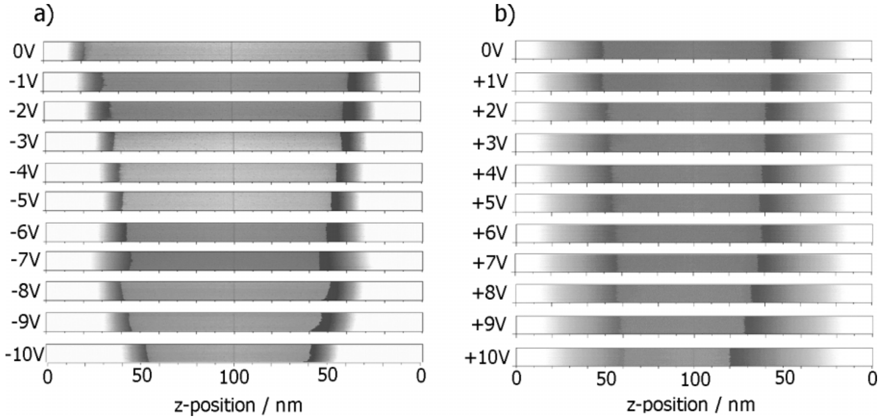

Figure 3. Force spectroscopy of OTS self-assembled monolayers in the presence of an applied tip bias voltage. a) Sets of 50 force curves recorded at different negative tip bias voltages. Surface modification was only observed for voltages more negative than –7 V. b) Sets of 50 force curves recorded at positive bias voltages. According to expectations, no surface modification, and therefore no change in the surface properties, was observed within each data set.

follow the change in surface properties, while a tip bias voltage is applied that mediates the electrochemical oxidation. The oxidation therefore takes place gradually, during the time period when the tip is in contact with the sample. Simultaneously, the force–distance curves are recorded, which allows the probing of surface properties at different times in the oxidation process.

Each recording cycle consists of 50 force–distance curves that are continuously recorded. For easy comparison of the curves, the deflection signal is converted into a false-color representation, an example of which is depicted in Figure 2c. Each line of this representation contains a force curve, which is plotted according to the scheme given in Figure 2b. The numbers are in accordance with the labels included in Figures 2a,b. Bright areas in the false-color representation indicate the repulsive force regime within the force–distance curves, whereas the dark regions on the left and the right represent the snap-in and snap-out events, respectively. Although this representation is unusual, it allows the convenient illustration of changes within the force curves with time (especially the snap-in and snap-out events, which are used as reference points in these studies). For an easy interpretation, it is sufficient to keep in mind that a shift in the snap-in position to the left (and a shift in the snap-out position to the right) is to be interpreted as a smaller adhesion sensed by the tip (and vice versa). In order to improve the *z*-resolution of these measurements, relatively stiff cantilevers, for tapping-mode operation, with a typical force constant of 0.6–1.75 $\mathrm{N\,m^{-1}}$, were used in order to minimize adhesion forces. In this way, it was possible to obtain a *z*-resolution of 0.2 nm within each force curve. This approach was used to investigate the changes in surface properties, which are induced on an OTS self-assembly layer during the electrochemical oxidation process. The influence of the applied voltage was determined.

Figure 3a depicts the results of a voltage-dependence study of the oxidation process. Within each dataset obtained for voltages less negative than –8 V, it can be seen that the position of the snap-in and snap-out events is very reproducible, as indicated by the sharp, straight boundaries of the snap-in and snap-out regimes within the whole set of force curves recorded for each voltage. It has been previously reported that the electrochemical oxidation of the monolayer only takes place if the applied voltage exceeds a certain threshold value. For Pt–Ir-coated SFM tips, which were used in this study, relatively high negative bias voltages of –7 to –8 V are necessary to initiate an oxidation reaction. Thus, no changes in the surface properties were expected for small negative bias voltages, and no change in the snap-in and snap-out positions were observed within one dataset. Additionally, we checked that no surface modification took place by subsequent imaging of the area using tapping-mode and contact-mode SFM imaging; no indication of changed surface properties was found. This was additionally confirmed by measurements that allow a comparison between force curves that were recorded before, during, and after the voltage was applied to the sample. Figure 4a depicts the result

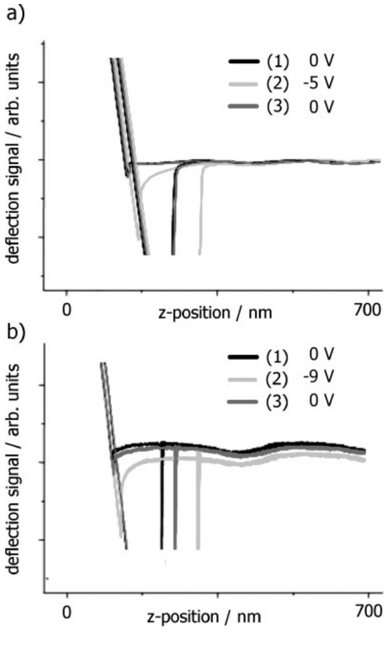

Figure 4. Force–distance curves recorded with a soft contact-mode cantilever coated with Pt–Ir. a) Curve 1 represents the first force-curve on the sample area, which was recorded without an applied bias voltage to the tip. Curve 2 shows the result of applying a –5 V bias voltage to the tip, which was not sufficient to induce a modification to the surface area. Increased adhesion was observed for this curve compared to curve 1. Curve 3 was recorded again in the same surface spot with no applied voltage. The shape, and also the position, of this curve is very similar to curve 1; it was only slightly shifted to the right for ease of comparison. b) Set of force–distance curves recorded before (1) and after (3) a sufficiently high oxidation voltage (–9 V) was applied to the SFM tip (2). Curves 1 and 2 are significantly different; whereas curve 3 shows a higher adhesion than curve 1, indicating that the surface properties have been rendered hydrophilic.

of such a measurement, performed with a soft contact-mode Pt–Ir-coated SFM tip (typical force constant: 0.03–0.08 N m^{-1}). Owing to strong adhesion forces, the deflection signal was cut off in the bottom part of the force curve because of the limited detection area of the position-sensitive photodiode. Force curve 1 was recorded before the voltage was switched on, whereas force curve 2 was recorded with an applied voltage of –5 V, which is well below the threshold voltage necessary to initiate the monolayer oxidation[5] and/or the growth of silicon oxide respectively.[7b] The shift in the snap-in region for force curve 2 is apparently induced by the strong bending of the cantilever due to the electric field, which is caused by the voltage, also indicated by the characteristic deflection prior to the snap-in.[13] After switching off the bias voltage, the force–distance curves returned to their original shape (compare Fig. 4a, force curves 1 and 3). The overall surface properties were not changed, as differences in the curve shapes were completely reversible after the switch-off of the external bias voltage.

Moreover, an influence of the applied voltage on the width of the force–distance curve (Fig. 4a, (2)), and therefore on the adhesion properties, was observed. The force curve that was recorded with an applied voltage (2) was significantly broader than those recorded without applied bias voltage (1). This effect was also nicely observed in the datasets that were recorded with applied voltages between 0 and –7 V (see Fig. 3a). Apparently, the adhesion of the tip–sample system increases with increasing negative voltages (as indicated by the shift in the snap-in region to the right, and the shift in the snap-out to the left), which corresponds to an increase in the adhesion sensed by the tip. The dependence of the adhesion forces on the applied bias voltage might be caused by strong electrostatic interactions. The electrostatic origin of the increased cantilever bending (Fig. 4a, curve 2) would suggest a shift in the sensed force, and therefore a deflection signal that is scaled, to a first approximation, with the square of the voltage.[13] However, the shift of the snap-in does not scale with V^2 but appears to be weaker. Moreover, no significant bending of the cantilever prior to the snap-in was observed, as relatively stiff tips were used. Another effect that could account for the increased adhesion properties might be electrowetting.[14] This effect occurs on dielectric surfaces, and is caused by a change in the surface properties due to the external electric potential, which is applied between a liquid and a solid. Thereby a redistribution of charges is induced, which is responsible for a modification to the surface energy at the interface. Specifically, the presence of a net electric charge at the interface lowers the surface tension because the repulsion between similar charges decreases the work necessary to expand the surface area. As a result, the contact angles, and therefore the wettability properties, are observed to be a function of the applied voltage between the liquid and the electrode.

This effect was also observed for positive applied bias voltages, which are also known not to result in any surface modification, as illustrated by the set of measurements shown in Figure 3b. The typical increase in the adhesion was observed here for the whole range of applicable voltages. More interesting for the electrochemical oxidation process of the OTS self-assembly layer is the voltage regime where significant changes of the surface chemistry can be observed during the application of higher negative voltages, where characteristic, detectable changes in the surface properties can be observed as the hydrophobic –CH_3 groups are converted into hydrophilic –COOH groups or silicon oxide. For voltages more negative than –7 V, a significant change in the force–distance plots was found in the snap-in and snap-out regions with increasing oxidation time. Sets of 50 measurements did not show reproducibility in the z-position where the snap-in and the snap-out events occurred, as was observed in the other force-curve sets, but showed significant changes in the snap-in/snap-out positions. These curves demonstrate that, upon oxidation of the monolayer surface, its properties are changed, and that this change is time dependent. Moreover, it can be demonstrated that these changes are irreversible, as shown in Figure 4b, where force curves reveal different surface properties before and after a negative tip bias voltage of –9 V was applied to the surface. The force–distance curves before and after the voltage application (curves 1,3) are not identical any longer, and the force curve on the modified area shows a significantly enhanced adhesion. Nonetheless, the adhesion is not identical within the set of force curves, and a dynamic development of the adhesion properties was observed (Fig. 3b). Namely, the adhesion was reduced within the continuous oxidation cycles. This dynamic characteristic might be induced either by the step-by-step initiation of chemical reactions, or by the continuous injection of charges which are trapped within the monolayer. Recent investigations of oxidized OTS monolayers by means of electrostatic force microscopy (EFM) and Kelvin probe microscopy (KPM)[9] proved the presence of a small amount of charge in these areas, although the total charging remains relatively small, especially for structures which are inscribed at voltages just above the voltage threshold and for short inscription times. This accumulation of surface charge has also been observed for the growth of silicon oxide on bare silicon substrates, where it is suspected to be a limiting factor in the amount of growing silicon oxide.[3] Charges that are trapped within the monolayer and/or the substrate might account for a partial screening of the electrostatic interaction, but it is evident that for such an effect the monolayer first has to be altered, as no charging effect, and thus no shift in the snap-in/snap-out positions, was observed for voltages below the threshold level (as discussed above). Moreover, a spreading of the water meniscus could also account for the shift in the snap-in/snap-out position upon prolonged electro-oxidation time, as it has been demonstrated that the width of the oxidation line depends on the oxidation voltage/time,[9] however it seems to have only a minor effect, as the modified area appears to be rather small in contrast to the large reservoir of water that is expected to be present on the SFM tip. Thus a change in the water layer level of 6 to 8 nm, as was observed, for example, for the snap-out curves, seems unreasonable as the only cause for the diminished adhesion sensed upon the prolonged exposure of the surface to the tip bias voltage.

Blank experiments performed on the same kind of silicon substrates without an OTS monolayer, and thus no barrier to the silicon oxide growth, were conducted, and no influence of the charges trapped in the substrate on the snap-in/snap-out positions was observed (Fig. 5). Even if the successful growth of silicon oxide could be demonstrated by the subsequent inspection of the modified area by means of semicontact-mode SFM imaging (not shown), no time-dependent charge accumulation or water consumption (which are also necessary in this process to initiate the silicon oxide growth) in the modified area, and therefore no time-dependent, dynamic shift in the snap-in/snap-out positions, was observed, at least not with the relatively stiff tapping-mode SFM tips (force constant: 0.6–1.75 N m^{-1}) used to record these data (the same tips were used for the sets of monolayer oxidation).

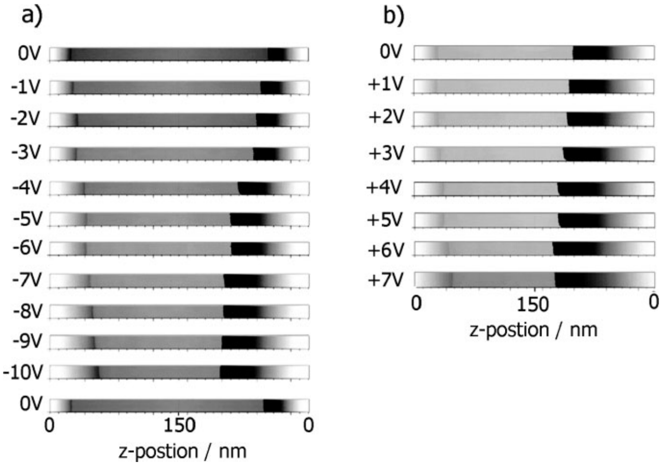

Figure 5. Reference curves obtained during the anodization of bare silicon/silicon oxide substrates with a) negative and b) positive tip bias voltages. A voltage-dependent increase in the adhesion due to the applied voltage was observed, and the snap-in/snap-out positions within each set of continuously recorded curves remained constant.

On the other hand, one can observe also in these datasets the voltage dependence of the adhesion properties. Also, in this case, an adhesion increase with higher voltages was detected. The reproducibility of the datasets recorded at 0 V before (set of measurements on the top row, Fig. 5a) and after (bottom set of measurements, Fig. 5a) recording the intermediate voltage datasets shows the dependence of the surface adhesion on the applied voltage is very reproducible, as both datasets show the same adhesion strength, and the snap-in/snap-out events occur almost at the same z-piezo position. This nicely demonstrates the reproducibility of the measurements, excludes massive influences due to piezo drift during the measurements, and suggests that the tip shape was not significantly changed, which would certainly result in a different contact area and therefore a different adhesion force. For positive applied tip bias voltages, it was difficult to obtain a complete set of force curves, as a dramatic degradation of the tip quality was observed. Therefore, only data sets up to +7 V are depicted in Figure 5b; nonetheless, they show the same tendency.

This correlation of force-curve recording experiments on OTS-covered and bare silicon oxide substrates leads to the conclusion that charging effects are not a major reason for the dynamic shift in the force curves, which was observed for successful oxidation experiments where voltages more negative than the threshold level were applied; however, it is likely that a chemical modification is also involved in the change in the surface properties, and therefore for the change in the adhesion characteristics. More investigations on this phenomenon have to be performed, preferably with spectroscopic techniques that can be applied in the nanometer dimensions range, to explore the nature of the created chemical species.

All datasets presented up to now focussed on the investigation of the oxidation of the OTS monolayer. As described earlier, longer oxidation times and/or higher voltages are also sufficient to initiate the site-selective growth of silicon oxide once the monolayer has broken down. The transition between both phenomena is certainly interesting to study, but requires more demanding conditions in terms of z-resolution, as usually only 1–5 nm high silicon oxide structures are formed (the height of the OTS monolayer is 2.5–2.7 nm). Therefore, investigations have been performed that allow improved z-resolution because of a higher number of measurement points per force-curve cycle, and the possibility of applying higher voltages. These investigations were also performed with a stiff tapping-mode cantilever, to reduce the width of the force curves in order to obtain sufficient resolution in the z-direction. Moreover, it is easier to investigate the growth of the silicon oxide with a stiff cantilever, as the influence of the adhesion on the cantilever snap-in is less pronounced. Therefore, significantly stiffer tips were used (force constant ~5.5 N m^{-1}). From Figure 3a (voltages between –8 to –10 V), it can be seen that the snap-in curve is generally less sensitive to the changes of the surface properties than the snap-out curve. Therefore, it is more likely that changes in the surface topography—which was, up to now, negligible, as the monolayer oxidation is not correlated with a significant change in the surface topography[9,15]—will be observable by referring to this characteristic reference point of the individual force curves. Figure 6

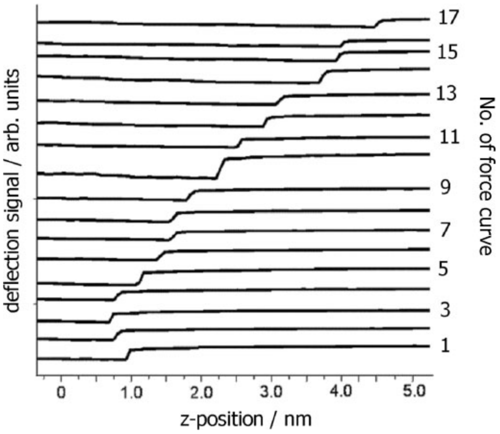

Figure 6. Magnification of the snap-in area of continuously recorded force–distance curves during an electro-oxidation performed at –12 V tip bias voltage, which leads to the breakdown of the monolayer, and the subsequent silicon oxide growth is recorded. The numbers to the right indicate the oxidation cycle.

shows the result of such an oxidation experiment performed with an applied voltage of –12 V in this particular sample. Moreover, much longer oxidation times between two force-curve measurements were applied by increasing the contact time of the tip with the sample during the repulsive part of the force-curve after the snap-in event. Therefore, the monolayer oxidation is observed for only three oxidation cycles. A small change in the force curve is also observed here, which results in a 0.2–0.3 nm shift in the snap-in position of the force curve to the left. After this, apparently correlated to the onset of the silicon oxide growth, a rapid shift in the snap-in to the right is observed, which is believed to be triggered by the growing silicon oxide underneath the tip. These shifts of 0.3–0.4 nm for each oxidation cycle resemble the rapid growth of the silicon oxide on the one hand, and the fast transition between the OTS monolayer oxidation and the silicon oxide growth on the other, and reflects, therefore, the rapid breakdown of the OTS monolayer induced by electro-oxidative probe lithography.

3. Conclusions

Scanning force microscopy studies could be used to follow the kinetics of the electrochemical oxidation of *n*-octadecyltrichlorosilane (OTS) self-assembled monolayers, and represent a powerful tool for investigating surface properties on the nanometer scale, even if some experimental uncertainties have to be taken into account to separate surface-property effects and topographic features. Information on the change in surface properties during the electro-oxidation process of an OTS self-assembled monolayer on silicon substrates was extracted from force-spectroscopic measurements, and a decrease in the hydrophilic surface properties upon the prolonged exposure of the bias voltage was observed. This suggests the fast formation of hydrophilic –COOH groups, which are later gradually rendered less hydrophilic. This might be induced by further chemical change of the surface functions, which would certainly have a large influence on the wettability of the nanostructures. This result may have a significant impact on subsequent derivatization processes and their optimization, which have been demonstrated to contribute to the application of this kind of surface structure as chemically addressable surface templates for nanofabrication.

Moreover, the transition between the oxidation of the self-assembled monolayer and the start of the growth of silicon oxide is an interesting point for further investigation. Therefore, improved experimental setups are required that will allow the recording of more than 50 force–distance curves, and certainly with higher z- and time-resolution. Careful attention should also be paid to the exclusion of adhesion properties that screen the observation of the growth of real topographic features, for example, use of stiffer tips or recording of additional oxidation parameters such as the patterning current (as recently reported by Martín and co-workers and Pellegrino et al., where force curves were simultaneously recorded with corresponding current curves).[16–18]

4. Experimental

Silicon wafers (p-type, boron doped, <1–0–0>, 10–20 $\Omega\,\mathrm{cm}^{-1}$, single-side polished) were purchased from Silicon Quest Intl., and were cleaned in a UV/ozone atmosphere for about one hour. Pre-cleaned substrates were immediately used to perform oxidation experiments, or were coated with a self-assembled monolayer of OTS (Sigma Aldrich) prepared from dry biscyclohexane (Fluka) solution. Careful rinsing of the coated substrates with toluene (BIOSOLVE) and repeating the OTS coating procedure up to three times gradually increased the water-contact angle of such monolayer substrates to ≥115°. Prior to use, contaminants were removed from the substrate by attaching and peeling-off commercially available Scotch Tape (3M).

Oxidation experiments were either performed on a Solver P47H (NT-MDT) SFM, or on a Nanoscope IIIa Multimode (Digital Instruments) with commercially available, Pt–Ir-coated SFM cantilevers (μmasch). The individual force constants of the levers are mentioned in the context of the experiments. All sets of experiments were performed at 70–75 % humidity, which was kept constant by a home-built humidity control-system, that uses wet and dry nitrogen to adjust the humidity within a closed SFM measurement chamber.

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