Adsorption (2010) 16: 271–277
DOI 10.1007/s10450-010-9226-1

Changes of methylated silica surfaces on ageing

Nora Schreithofer · Janusz S. Laskowski · Kari Heiskanen

Received: 31 March 2010 / Accepted: 28 May 2010 / Published online: 30 June 2010
© Springer Science+Business Media, LLC 2010

Abstract Silica rendered hydrophobic by organosilanes is a widely used model material in colloid chemistry, biological research, catalysis, etc. However, it is often overlooked that the surface properties of silica, and silica made hydrophobic be reacting with silane, change with time when the substrate is immersed in aqueous solution. Therefore the experimental conditions when such model systems are employed have to be carefully assessed.

This paper summarizes the findings of the force measurement tests between air bubbles and silica particles hydrophobized with organosilanes such as trimethylchlorosilane and 1, 1, 1, 3, 3, 3-hexamethyl-disilazane. The results showed that the attractive forces as well as the adhesion between the air bubbles and silica particles decrease with the time of aging in aqueous solution. The silica surfaces rendered hydrophobic with organosilanes become hydrophilic with time due to hydration. The hydrophobicity could be restored by heating the samples at 190 °C.

The atomic force microscopy imaging on silica plates revealed that in addition to hydration, decomposition of the organosilane layer also takes place.

Keywords Silica · Silica surface · Hydration · Methylated silica · AFM

N. Schreithofer · K. Heiskanen
Aalto University School of Science and Technology, Department of Materials Science and Engineering, Research Unit of Mechanical Process Technology and Recycling, P.O. Box 16200, 00076 Aalto, Finland

J.S. Laskowski (✉)
University of British Columbia, N.B. Keevil Institute of Mining Engineering, Vancouver, BC, V6T 1Z4, Canada
e-mail: jsl@apsc.ubc.ca

1 Introduction

The surface chemistry of silica has been more thoroughly investigated than that of almost any other solid. When freshly crushed silica is placed in water the chemisorption of water is a slow process at room temperature and in neutral and acid media. Hydration however greatly speeds up in alkaline solutions, or in the presence of F^- ions. Griot and Kitchener (1965) discovered that while freshly ground silica was sensitive to flocculation in water by polyacrylamide, the fully aged/hydrated silica after long contact with water became completely non-flocculable by polyacrylamide. Using infrared spectroscopy Griot and Kitchener were able to identify free isolated silanol groups on the silica surface that were apparently responsible for adsorption of polyacrylamide by hydrogen bonding.

Such active sites are present on freshly ground silica surfaces, on the aged fully hydrated surfaces they can be generated by heating the hydrated silica to 300 °C or above. In 1969, Laskowski and Kitchener (1969) described their wettability study in which quartz made hydrophobic with trimethylchlorosilane (TMCS) was utilized. These surfaces turned out to be very hydrophobic, but they showed the aging effect similar to those observed by Griot and Kitchener. In alkaline media the wettability strongly depended on pH. In a solution of $\text{pH} > 11.5$ every silica plate was hydrophilic, but if the solution was quickly changed to pH 6 it became hydrophobic again. However, after some time of storage in alkaline solution, the plates became quite hydrophilic independently of pH. The contact angle could, however, be restored by drying at 110 °C.

Silica is a widely used model substrate and it is often rendered hydrophobic by organosilanes and silazanes such as trimethylchlorosilane (TMCS) or hexametyl-disilazane (HMDS). For model systems understanding the effect of aging in water on surface properties is critical and this paper is entirely devoted to this topic.

In the experimental part we used silica surfaces made hydrophobic by organo-silanes, and we studied the surface properties of such systems by particle-bubble interaction force measurements and atomic force microscope (AFM) imaging.

2 Experimental

2.1 Materials

10 µm silica particles (G.KiskerGbR.) and fused silica plates (Finnish Specialglass Oy) were used as substrates in the experiments. The silica spheres were utilized to prepare colloidal probes for the force measurements, while the silica plates were used to estimate the contact angles obtained with different sample preparation techniques as well as for AFM imaging.

All the reagents used in sample preparation and measurements were of analytical grade and were used without further purification. The ultra high purity water used in the measurement was cleaned in five-steps: mechanical removal of the solid particles, ion exchange, active carbon treatment, reverse osmosis and reversed bed ion exchange. The resistivity of the water was higher than 18 MΩcm, and the pH was 5.4 ± 0.2.

The colloidal probes for force measurements were prepared by gluing silica particles to tipless AFM cantilevers with 5 Minute Super Epoxy (OCI Professional). By specification of the manufacturer, the glue was inert to water and electrolytes, thus it could be used without the danger of contaminating the system.

Trimethylchlorosilane (TMCS) and 1, 1, 1, 3, 3, 3-hexamethyl-disilazane (HMDS) were used to render the tested surfaces hydrophobic as both of these reagents form similar kind of surface groups with the silica (Hair and Hertl 1969; Vasant et al. 1995).

2.2 Methods

2.2.1 Sample cleaning

The same cleaning procedure was strictly followed prior to all experiments. The silica particles were originally suspended in water. As specified by the manufacturer, no further cleaning of the particles was necessary. The cleannliness/hydrophilicity of the particles was checked using the method suggested by Chamerois et al. (2000), which is based on the observation of the behavior of particles sprinkled onto the surface of liquid, in this case water.

The silica plates were cleaned in hot, 37% HCl for 1 hour, then rinsed 10 times with ultrapure water, followed by a 2 minute cleaning in 12 M NaOH and rinsing 10 times in ultrapure water. The cleaned silica plates were stored under ultrapure water prior to the heat treatment and methylation. The cleannliness of the plates was checked with the cling test. If a bubble did not cling to the plate (as observed under microscope), the plate was assumed to be clean and hydrophilic.

2.2.2 Hydrophobization/hydration procedure and contact angle measurements

In order to achieve different degree of hydrophobicity the particles and silica plates were made hydrophobic following the method described by Lamb and Furlong (1982). The particles and silica plates were first heated at 70, 200 and 1050 °C overnight to remove water and control the amount of OH groups on the surface, which serve as reaction sites for the silane (Hair and Hertl 1969). The particles were glued to the AFM cantilevers as described previously. The colloidal probe and the silica plate used as a control substrate were placed on a Teflon block that was put into a small closed jar. Excess amount of TMCS or HMDS were injected and the jar was introduced into a heating chamber at 70 °C for 10 minutes. After methylation in TMCS or HMDS vapor the colloidal probe and the plates were placed in the oven at 110 °C in order to remove the excess amount of hydrophobizing agent. After methylation the substrates were kept in a dessicator over silica gel.

The advancing and receding contact angles were measured on the silica particles with the use of CAM 200 optical contact angle meter (KSV Instruments Ltd.) on the plates treated in the same environment.

The force measurements were conducted in 10^{-3} M aqueous solution of KCl. The time of immersion of the colloidal probe in the electrolyte solution was recorded, as well as the time when the force curves were taken. The time elapsed since immersion into the electrolyte was considered to be the time of hydration.

The silica plates were hydrated in ultrapure water for one hour.

2.2.3 Particle-bubble interaction force measurements

The force measurements were performed with the Colloidal Interaction Force Measurement Apparatus (CIFMA) developed by Schreithofer (2003). The instrument works on the AFM force measurement principle, but it has an extended measurement range and improved measurement capabilities.

For the force measurements an air bubble (with diameter of about 900 µm) was placed on the bottom of the Teflon cuvette with a micropipette. The size of the bubbles was kept as constant as possible. The size of each bubble was measured with the help of a micrometer precision stepper motor.

The colloidal probe was mounted on the piezo translator and moved with nanometer precision towards the bubble and away from it. The deflection of the cantilever was monitored with light lever technique. Cantilever deflection vs. piezo position curves were recorded, and were converted into force vs. piezo position curves by multiplying the cantilever deflection values with the spring constant of the cantilever. The spring constant of the cantilevers was measured with the reference cantilever method described by Tortonese and Kirk (1997). It was observed, that the spring constant of the cantilevers changes with time, thus the cantilevers were calibrated several times during each experiment in order to minimize the error.

The force curves obtained in the measurements were analyzed from attraction (jump-in) and adhesion (jump-off) point of view. The force curves were not converted into force vs. separation curves as some authors do (e.g. Ducker et al. 1994; Assemi et al. 2008) due to uncertainties arising from to the deformation of the bubble on the approach. Thus the curves were analyzed relative to each other.

The jump-in point was taken as a measure of attraction, while the jump-off as a measure of adhesion. As convention, the more negative values mean larger jump-in force. For easier understanding, in the case of the figure comparing adhesion forces, the negative adhesion forces were plotted vs. time, thus in Fig. 4 more positive adhesion values mean larger force.

2.2.4 *AFM imaging*

AFM imaging was performed on silica plates heat treated at 70 °C and methylated in HMDS vapors.

Topography and lateral force images were taken with PSIA XE-100 atomic force microscope in contact mode in air. Ultra sharp contact AFM cantilevers (MikroMasch, Spain), typical spring constant 0.03 N/m, tip radius less than 10 nm, were used for imaging. The x, y and z distance scale of the AFM was calibrated using test silicon grating (NT-MDT, TGX and TGG series). The applied loading forces (set point) were kept low ∼3 nN in order to avoid damaging of the deposited silane coating. The images were flattened and displayed with the PSIA XEI image processing software. Line profiles analysis was also performed on the images. The samples were imaged with AFM before oraganosilane treatment, after treatment and after immersion in water.

3 Results

3.1 Force measurements

The contact angle values measured on the silica plates are given in Fig. 1. The contact angle measured on the plates rendered hydrophobic decreases with the temperature of heating the sample prior to methylation. This agrees very well with Lamb and Furlong (1982). The sample heated at 1050 °C becomes slightly hydrophobic even without methylation.

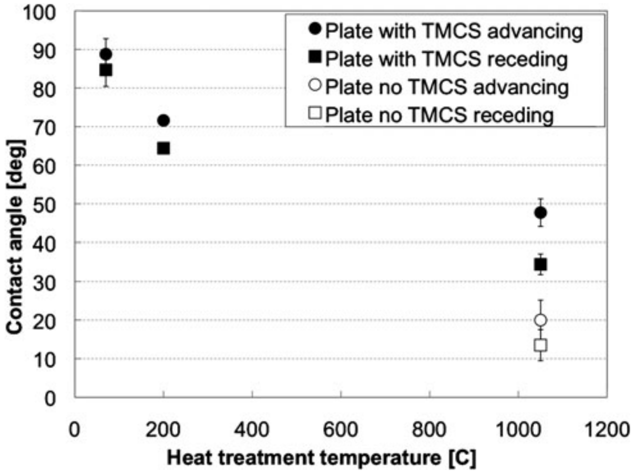


Fig. 1 Advancing and receding contact angles measured on silica plates which were heated at different temperatures and then were subjected to a standard TMCS treatment

Figure 2 shows a set of force curves obtained with a particle approaching an air bubble; the particle was heat treated at 1050 °C and hydrophobized with TMCS. It can be seen from the figure, that the attractive force is highly dependent on the time elapsed since the particle was immersed in the electrolyte. First a strong attractive force acts between the particle and the air bubble, which then decreases with time until it turns into a repulsive force within 5 hours after placing the particle into the electrolyte. Similar results were obtained with particles heat treated at other temperatures (Fig. 3). Contrary to the expectation, the heat treatment temperature and therefore the hydrophobicity did not have a strong effect on the initial jump in force.

The decrease in attractive force can most probably be attributed to the decrease of hydrophobicity with time due to the formation of an ordered hydration layer around the silica particle. The development of a repulsive force as a form of an energy barrier (see curves 265 min and 372 min on Fig. 2a) also confirms this conclusion.

In order to verify the idea of changing attractive force, and therefore hydrophobicity (contact angle decrease) due to hydration, after the disappearance of the attractive force the particles were placed in the oven and re-heated at temperature of 110 °C overnight. The assumption was that this treatment should remove the adsorbed water molecules and restore the hydrophobicity. No change in the surface hydrophobicity could be detected. However, at higher temperature (190 °C) that was also tested, as suggested by Tripp

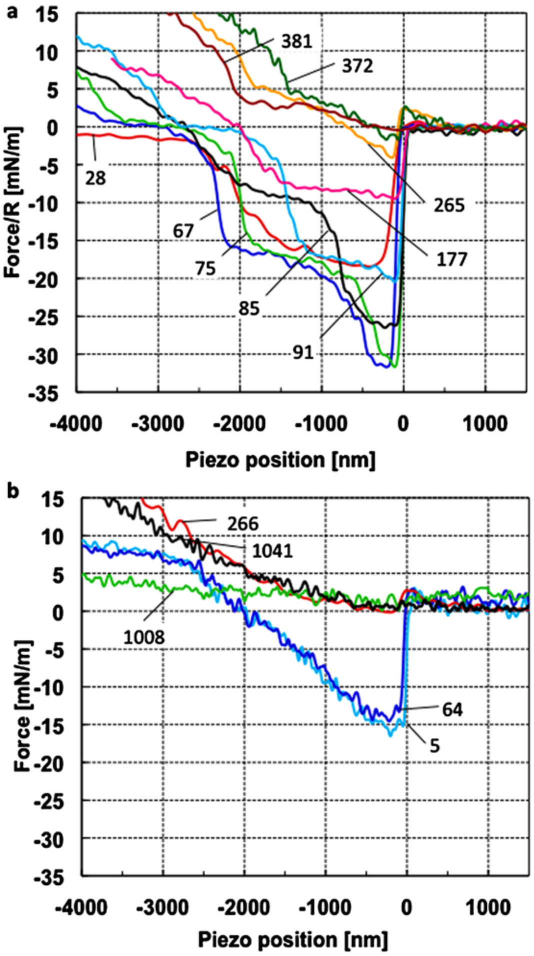


Fig. 2 Approach curves taken with particles heat treated at 1050 °C, hydrophobized with TMCS. The numbers denote time in minutes elapsed since the particles have been immersed in solution: (**a**): after placing the particles in the solution, (**b**) after the particles when the jump-in force disappeared were kept at 190 °C overnight

and Hair (1991), the surface hydrophobicity was indeed restored as shown on Fig. 2b. This serves as a proof that the attraction disappears with time due to a hydration of the silica surfaces. The relatively high noise level of the curves is attributed to the reduced reflectivity of the AFM cantilever caused by the long residence time in electrolyte and heat-treatment.

The values of the adhesion force were plotted as a function of time elapsed since the particle was immersed in electrolyte for the particles treated at different temperatures, as shown in Fig. 4. The dependency of the adhesion force on the time elapsed since the particle was immersed in electrolyte solution was striking. The adhesion decreased significantly during the first 5 hours of the experiment, in some of the experiments the adhesion force decreased as much as 60% within 4 hours of residence time. Nevertheless, the dependence of adhesion as a function of contact angle was not as clear.

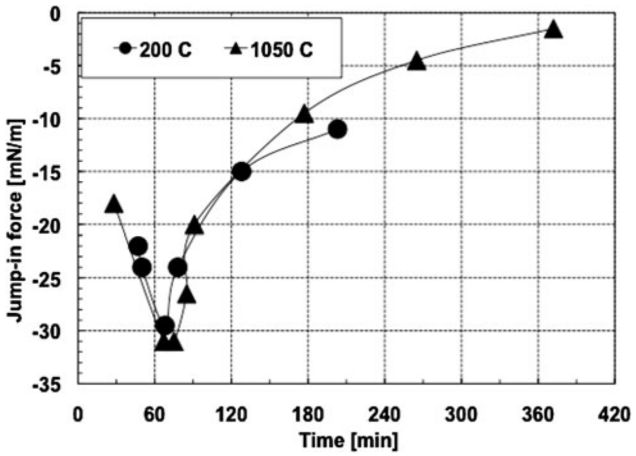


Fig. 3 Attractive forces as function of time with particles treated at different temperatures and hydrophobized with TMCS (more negative jump-in values mean larger jump-in force)

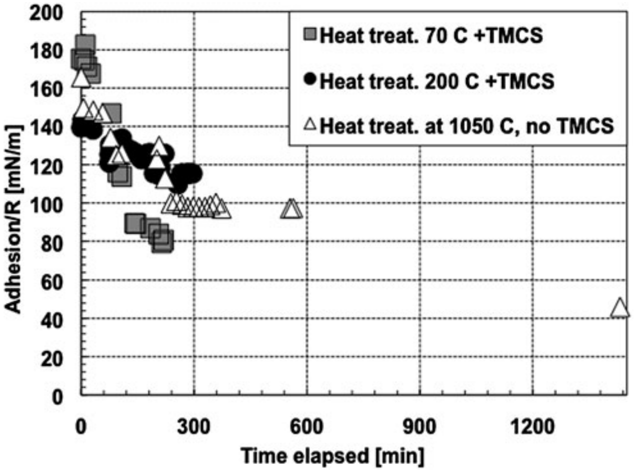


Fig. 4 Maximum adhesion values vs. time between air bubbles and particles treated under different conditions

3.2 AFM imaging

The silica plates made hydrophobic with HMDS vapor were imaged with AFM in contact mode. Several plates were imaged in a number of locations and the results obtained in each point were similar. Figure 5 shows a typical surface structure formed on the silica plate after hydrophobization in vapor (the sample was preheated at 70 °C). The AFM imaging revealed a patch like structure formed by the HMDS on the silica surface. The size of the patches varies between roughly 1 to 5 µm. The line profiling showed the thickness of the adsorbed layers to be 4 to 5 nm. The layer formed by the HMDS vapor on the silica surface was not identified with the use of other experimental procedures like SEM/EDX or TEM/EDX. However since the substrates were thoroughly cleaned and were not exposed to any other substance than

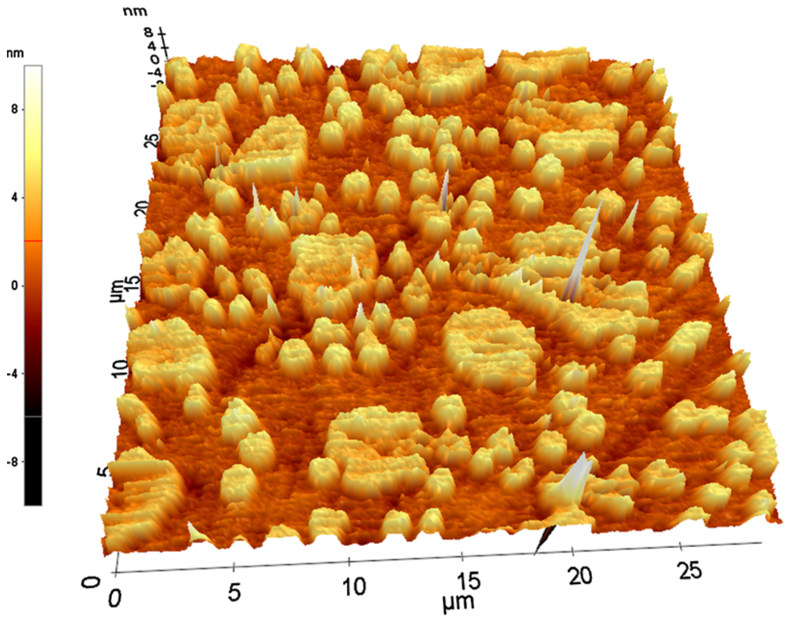


Fig. 5 Typical 3D AFM image of a silica plate hydrophobized in HMDS vapour at 70 °C

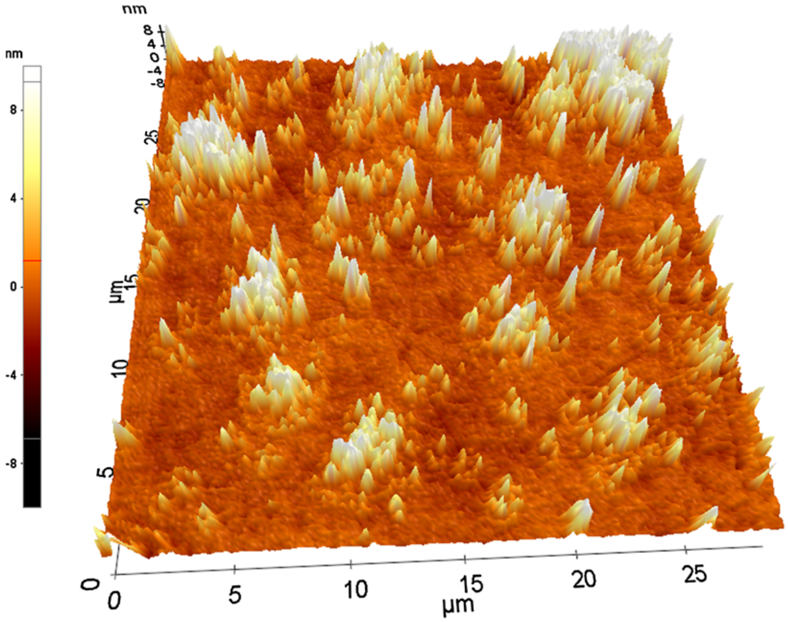


Fig. 6 Typical 3D AFM image of a silica plate hydrophobized in HMDS vapour at 70 °C then kept in ultrapure water for 60 minutes

the organosilane it is clear that the patches observed on the images are the organosilane islands.

In order to determine what causes the decrease of hydrophobicity of the silica surface, the AFM imaging was repeated after the silica plates were kept in ultrapure water for 60 minutes. Figure 6 shows the results obtained with these plates. These images reveal that the HMDS layer decays with time. The clear 1–5 µm patches observed after the HMDS vapor treatment disintegrated when the plates were kept in water. The patches could still be observed, but they form a far less homogeneous coverage and even structure observed in the previous case is clearly disrupted by the water penetrating into the surface layer.

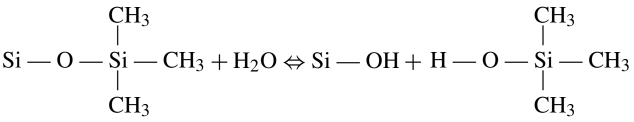
4 Discussion

The tests with silica conducted in surfactant free electrolyte solutions revealed that the changes occurring in the silica-water-air bubble system are much more complex than thought before. The time dependent behavior of both attraction and adhesion forces probably results from the slow changes occurring on silica surface, caused by hydration of the hydrophobic surface. Changes of the silica surface properties on aging was first reported by Griot and Kitchener (1963, 1965). When pure silica is heated to remove most of the chemisorbed water (650–850 °C) its surface becomes hydrophobic. Evidently a surface siloxane groups (Si-O-Si) are intrinsically hydrophobic. In contact with water (or with water vapor) the final equilibrium condition corresponds to a hydrophilic surface. The rates of change caused by aging were apparently related to the concentration of OH^- ions. Laskowski and Kitchener (1969) worked with silica surfaces made hydrophobic using TMCS. It was estimated that only 54% of the surface was covered with methyl groups and rehydration of the areas lying between the methyl groups was apparently slow. The changes in wettability of such surfaces caused by aging/hydration were similar to those described by Griot and Kitchener, the more alkaline the solution, the greater was the change of the contact angle with time. Vigil et al. (1994) in their measurements performed with the use of SFA also reported changes with time of aging.

We would like to emphasize that this study shows for the first time such time dependent phenomena in the experiments carried out using AFM type of equipment.

As Fig. 4 demonstrates, the silica plate made hydrophobic by pre-heating at 1050 °C and without the treatment with silane, undergoes wettability changes on aging similar to what is observed with the samples rendered hydrophobic by the treatment with silane. This is a very strong indication that the aging effect results from the hydration of the silica surface. Since these measurements were conducted at a pH of 5.4 ± 0.2 aging takes place not only in alkaline solutions.

In addition, the results reported in this paper imply as well that the changes in the hydrophobicity of the silica substrates treated with silanes and silazanes to some extent can also be attributed to the decay of the hydrophobic silane layer. On the silane treated surface the breakdown of the silane coverage appears inevitable, although it has been shown (Takach et al. 1988) that stability of the silane coating on the surfaces can be improved by vapour-phase silanization. Even so, the coating still breaks down, but after longer time. Menawat et al. (1984) examined the air-water and xylene-water contact angles on silane-treated surfaces. They found a time dependent behavior of xylene-water contact angles, which were explained by two mechanisms: rehydrolyzation and desorption of weakly adsorbed molecules. The rehydrolyzation reaction of silane-treated surfaces with water is possible due to the penetration of water molecules in between the small methyl groups, as shown by the reaction below:



$$\mathrm{Si-O-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3 + H_2O \Leftrightarrow Si-OH + H-O-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3}$$

Wei and coworkers (1993) studied the effect of water, air and oil on wettability of the silane treated glass surfaces. They have shown that the advancing and receding contact angles measured on the slides treated with TMCS and stored in water significantly decrease with time. The contact angle started to decrease immediately after placing the slide in water. In experiments carried out with quartz and silica plates the deterioration was comparable with the data obtained on glass surfaces. They ruled out the possibility of removal of the silane molecules as suggested by Menawat et al. (1984), because the contact angle values did not deteriorate when the substrates were kept in air or oil. Our results however confirm the findings of Menawat et al. (1984), and they show that actually even the chemical bonding between the silane and silica can be affected by water. Our tests were carried out at pH 5.4 ± 0.2 and so they do not address the issue of the effect of pH on silica hydration.

The results of this study demonstrate that the hydration of the silica surface and the disintegration phenomena of the silane or silazane layer are parallel processes taking place at the same time. While the loss of hydrophobicity due to hydration can be reversed by heating the sample, the decomposition of the hydrophobic silane or silazane layer cannot.

Over the last several years, silica has been often used as a model substrate in the systems studied in different fields, from paper industry to biology. The results of the present study reveal that the use of silica as a model material in AFM force measurements and other applications has to be reassessed.

The changes of the surface properties of silica over time that might be attributed either to the slow hydration of the surface or to structural changes of silica surface can significantly affect the results of the force measurements and can lead to misleading conclusions. Therefore, when using silica as a model material in AFM and other measurements that are conducted over a longer time period (several hours), one has to be aware of the dynamic processes taking place at the silica/water interface.

5 Conclusions

1. The use AFM allows the effect of time of immersion in aqueous solution of the silica samples made hydrophobic by methylation to be tested. These measurements confirm early contact angle results by Laskowski and Kitchener (1969), which showed slow changes of wettability of initially hydrophobic methylated silica surfaces when placed in water.
2. The time dependent changes of the silica surfaces observed on immersion in water are caused by two parallel phenomena: hydration and decomposition of the organosilane layer.
3. While AFM imaging confirmed early conclusions that silane covers only some parts of the silica surface, these tests also indicate that some silane molecules are removed from the surface when these samples are immersed in water.

References

Assemi, S., Nguyen, A.V., Miller, J.D.: Direct measurement of particle-bubble interaction forces using atomic force microscopy. Int. J. Mineral. Process. **89**, 65–70 (2008)

Chamerois, M., Francois, M., Villiéras, F., Yvon, J.: Modification of calcium carbonate surface properties: macroscopic and microscopic investigations. In: Drelich, J., Laskowski, J.S., Mittal, K.L. (eds.) Apparent and Microscopic Contact Angles, pp. 405–417. VSP, Cologne (2000)

Ducker, W.A., Xu, Z., Isrealachvili, J.N.: Measurements of hydrophobic and DLVO forces in bubble-surface interactions in aqueous solutions. Langmuir **10**(9), 3279–3289 (1994)

Griot, O., Kitchener, J.A.: 'Ageing' of silica suspensions in water and its influence on flocculation by polyacrylamide. Nature **200**(4910), 1004–1005 (1963)

Griot, O., Kitchener, J.A.: Role of surface silanol groups in the flocculation of silica suspensions by polyacrylamide. Part 2.—Surface changes of silica suspensions on ageing. Trans. Faraday Soc. **61**, 1032–1038 (1965)

Hair, M.L., Hertl, W.: Reactions of chlorosilanes with silica surfaces. J. Phys. Chem. **73**(7), 2372–2378 (1969)

Lamb, R.N., Furlong, D.N.: Controlled wettability of quartz surfaces. J. Chem. Soc. Faraday Trans. **1**(78), 61–73 (1982)

Laskowski, J.S., Kitchener, J.A.: The hydrophilic-hydrophobic transition of silica J. Colloid Interface Sci. **29**, 670–679 (1969)

Menawat, A., Henry, J., Siriwardane, R.: Control of surface energy of glass by surface reactions: contact angle and stability. J. Colloid Interface Sci. **101**, 110–119 (1984)

Schreithofer, N.: Investigation of particle-bubble interactions with a new experimental setup. Ph.D. Thesis, Helsinki University of Technology (2003)

Takach, N.E., Benett, L.B., Douglas, C.B., Andersen, M.A., Thomas, D.C.: Wettability alteration of model sandstone surfaces by vapor-phase treatment with organosilanes. J. Am. Chem. Soc. **33**, 525–529 (1988)

Tortonese, M., Kirk, M.: Characterization of application specific probes for SPMs. SPIE **3009**, 53–60 (1997)

Tripp, C.P., Hair, M.L.: Reaction of chloromethylsilanes with silica: a low-frequency infrared study. Langmuir **7**, 923–927 (1991)

Vasant, E.F., Van Der Voort, P., Vrancken, K.C.: Characterization and Chemical Modification of the Silica Surface. Elsevier, Amsterdam (1995)

Vigil, G., Xu, Zh., Steinberg, S.I., Israelachvili, J.: Interactions of silica surfaces. J. Colloid Interface Sci. **165**, 367–385 (1994)

Wei, M., Bowman, R.S., Wilson, J.L., Morrow, N.R.: Wetting properties and stability of silane-treated glass exposed to water, air, and oil. J. Colloid Interface Sci. **157**, 154–159 (1993)