

# Perfluorosilanized Aluminum Oxide Surfaces

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(Received: February 21, 2006 ; Accepted: June 7, 2006)

Hydrophobic, low adhesion, robust aluminum surfaces have useful applications for micro/nano-electromechanical systems (MEMS/NEMS), such as digital micro-mirror devices (DMDs). Substrates of aluminum deposited by physical vapor deposition onto silicon have been reacted with perfluorodecyltrichlorosilane and shown to be very hydrophobic and stable. Perfluorodecyltrichlorosilane modified aluminum surfaces were analyzed by X-ray photoelectron spectroscopy which confirmed the presence of perfluorinated alkyl chains on the surface. The sessile drop static contact angle of pure water on a modified aluminum surface is typically more than 115°. The rms surface roughness of aluminum and modified aluminum, determined by atomic force microscopy, is typically less than 35 nm. Stability tests demonstrate that modified aluminum is able to survive exposure to nitric acid (pH = 1.8, 60°C, 30 min) indicating some degree of robustness.

## 1. Introduction

Aluminum (Al) is a widely used metal due to its interesting properties. Its mechanical strength and light weight make it an ideal construction and/or decorative material for transport vehicles, like airplanes, cars, and trains. It is also useful for the construction of buildings (houses, warehouses, etc.). The high surface energy of hydrated alumina induces the strong adsorption of contaminant molecules which might cause device failure, as shown recently for micro-mirror arrays [1,2] and bonded aluminum pieces.[3,4] Especially for bonding applications, a number of studies have been carried out over the last 30 years to understand how to improve the stability of aluminum against hydrolytic dissolution during pre-treatment [5]. A more simple task, as compared to bonding, is the functionalization of an aluminum surface that will be exposed only to air and/or water with the aim to avoid surface contamination and/or degradation via hydrolysis. Very low energy surface coatings are obtained if perfluoroalkyl-chains are grafted onto the substrate. Robust, hydrophobic, low adhesion Al surfaces have useful applications in a wide range of technical fields, i.e., heat exchanger surfaces, sanitary profiles, architecture, or optics (mirror surfaces for vehicles) to name some. Before commercial application is possible, first the morphological and chemical properties of the modified Al surfaces must be studied. Phosphonate modified Al surfaces have been investigated and the results are already reported in the literature.[6-13] However, 1H,1H,2H,2H-perfluorodecyltrichlorosilane [F<sub>3</sub>C(CF<sub>2</sub>)<sub>7</sub>(CH<sub>2</sub>)<sub>2</sub>SiCl<sub>3</sub>] (PFTS) reacted Al has not yet been investigated thoroughly, although non-perfluorinated organosilanes have been studied.[14-21] Organosilanes are

extensively used as adhesion promoters in order to enhance the durability and adhesion of organic coatings and adhesives to metal surfaces. They are widely employed for many applications, particularly in the aerospace industry.[14] These recipes are based on early works of surface modification by silanization.[22] Different kinds of silanes are considered to result in so called self assembled monolayers,[23] mostly trihalogeno- or trialkoxy-alkylsilanes were studied. The general formula of organohalogenosilanes is RSiX<sub>3</sub>, where R represents an organic functional group and X a hydrolyzable halide group. The idealized organosilane adsorption process proceeds via a condensation type reaction with surface hydroxyl groups.[15,16] However, despite the fact that silanization has been done for over 35 years and many efforts have been undertaken to understand the importance of different reaction steps, the detailed mechanisms of the most intensively studied silanization reactions with silica could not be pinpointed experimentally until now. Very recently, molecular modeling was carried out [24] to understand the importance of pre-hydrolysis and the energy gain from the reaction of polyfunctional silanes with surface hydroxyl groups on monocristalline beta-cristobalite as a model substrate. Recently, the effect of joint failure after bonding of aluminum in different environments has been reported. [3,4] The chemical stability of a  $\gamma$ -glycidopropyl-trimethoxy-silane coating on aluminum has been shown to be reasonably stable when exposed to basic solutions and pure water, but it was observed that the silane coating detached from the alumina surface when exposed to acid solutions (pH = 4) at temperatures as low as 40°C for up to 2 weeks.[3]

In this paper, substrates of aluminum deposited by physical vapor deposition onto silicon (Si) [Al/Si] were reacted with trichloroperfluorodecylsilane (PFTS) [PFTS/Al/Si] via a cost effective, wet process which resulted in strongly hydrophobic coatings. We have carried out X-ray photoelectron spectroscopy (XPS) to confirm the presence of a perfluorinated alkyl chain film on untreated PFTS/Al/Si, treated PFTS/Al/Si, and unmodified Al/Si as a control. Atomic force microscopy (AFM) measurements have been made on oxidized Al/Si, PFTS/Al/Si, and treated PFTS/Al/Si to determine the surface roughness and morphology. Using contact angle measurements (CAM), the wetting properties of the PFTS/Al/Si coating has been studied. We have determined the stability of PFTS/Al/Si coatings by treatment in warm nitric acid.

## 2. Experimental

Si pieces of approximately 10x15x0.5 mm were cut from a commercially available Si wafer and ultrasonically cleaned in ethyl acetate, isopropanol and deionized water for 10 minutes each to minimize contamination on the surface. In between each ultrasonic cleaning step, samples were blown dry using argon (Ar) gas. Then, pure Al (99.98%) was DC sputter coated (Edwards Coating System) onto the Si pieces in a high vacuum (HV) chamber (base pressure of  $10^{-6}$  mbar). The sample holder was rotated passing sequentially above the Al target to provide a uniform Al film approximately 1  $\mu\text{m}$  thick. After sputtering, the Al/Si substrates were then oxidized. The bare Al/Si was found to be hydrophilic with a water contact angle  $< 15^\circ$ . The surface modification of Al/Si was performed using fast and simple liquid phase deposition. Commercially available 1H, 1H, 2H, 2H perfluorodecyltrichlorosilane [ $\text{F}_3\text{C}(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCl}_3$ ] (PFTS) [CAS 78560-44-8] solutions were made with a concentration of up to 0.1% (wt) using commercial grade n-pentane [ $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ ] as the solvent. After oxidation, the Al/Si substrates were immersed in the freshly prepared PFTS solution for reaction. The substrates were reacted in the solution with sporadic agitation for approximately 50 minutes at room temperature under ambient conditions. Then, they were taken out and rinsed gently several times with fresh pentane via agitation by hand for approximately 30 seconds each time to remove physisorbed PFTS molecules from the substrate surface. Finally, the samples were blown dry carefully with Ar gas and then heated at  $150^\circ\text{C}$  for one hour in vacuum ( $3.3 \times 10^{-2}$  mbar) giving the final PFTS/Al/Si samples.

The chemical surface composition of Al/Si surfaces before and after PFTS modification were analyzed and determined by XPS (Kratos AXIS ULTRA with a base pressure  $< 10^{-9}$  mbar) using monochromatic Al  $\text{K}_{\alpha}$  radiation at 15.0 kV and 150 W. The angle resolved XPS measurements were done by tilting the sample holder  $90^\circ$ ,  $75^\circ$ ,  $60^\circ$ ,  $45^\circ$ ,  $30^\circ$ , and  $20^\circ$  with respect to the average plane of the substrate sur-

face. The quantitative analysis of the chemical species on the surface is derived from the peak areas of the XPS multiplex. The survey scans were carried out in an energy range of 0 to 1100 eV with a pass energy of 80 eV. The high resolution peaks were measured with a pass energy of 20 eV. The binding energy (BE) of the components of interest was referenced to the binding energy of the C 1s photoelectron peak at 284.8 eV. [25,26] The quantification and curve fitting of high resolution XPS peaks has been carried out by mixed Gaussian-Lorentzian fit after linear-type background subtraction using the CASA XPS processing software. [27] All XPS data used for elemental quantification have an estimated relative error of  $\pm 2\%$ . Sessile drop static and dynamic CAMs were performed with a GBX Digidrop system to determine the wetting properties of the unmodified, oxidized Al/Si and chemically modified Al/Si. All CAMs were done with ultra-pure  $\text{H}_2\text{O}$  (Fluka) at 75% - 90% relative humidity (RH) and  $23^\circ\text{C} - 25^\circ\text{C}$ . The drop of pure water was applied onto the sample surface from a syringe with a teflon tip. All CAM data have an experimental error or uncertainty of  $\pm 3^\circ$ .

Surface roughness of Al/Si and PFTS/Al/Si was measured with a Nanosurf Easy Scan AFM at room temperature and atmospheric pressure. High-resolution topographic images were taken of Al/Si and PFTS/Al/Si using a Veeco CP-II AFM operated in contact mode to determine the surface morphology. To verify the stability of PFTS/Al/Si, PFTS modified Al/Si samples were immersed in nitric ( $\text{HNO}_3$ ) acid (pH = 1.8,  $60^\circ\text{C}$ , 30 min).

## 3. Results and Discussion

The rms surface roughness values measured over an area of  $40 \times 40 \mu\text{m}^2$  for unmodified Al/Si, untreated PFTS/Al/Si, and warm nitric acid treated PFTS/Al/Si after 140 days ambient exposure are  $31.8 \pm 0.5$  nm,  $30 \pm 1.5$  nm, and  $32.7 \pm 1.7$  nm, respectively. The rms roughness values are the mean of three values measured on three separate areas of the surface chosen at random. The rms roughness data indicate that PFTS modification does not change significantly the surface roughness of Al/Si. The data also show no significant change in rms surface roughness for PFTS/Al/Si after warm nitric acid treatment.

Fig. 1 shows AFM images of (a) Al/Si and (b) PFTS/Al/Si over an area of  $5 \times 5 \mu\text{m}^2$ . Fig. 1(a) shows clearly grains on the Al surface, while these grains are less obvious in Fig. 1(b) probably due to being almost completely covered with a polysiloxane film after reaction with PFTS.

Table 1 shows the chemical surface composition (at. %) determined from the high resolution core level XPS multiplex performed on oxidized Al/Si (hydrogen (H) is not detected). The elemental quantity is the average of three different values quantified from three different spectra measured at three separate areas (chosen randomly) on the surface. The XPS data confirms the presence of oxide on the Al

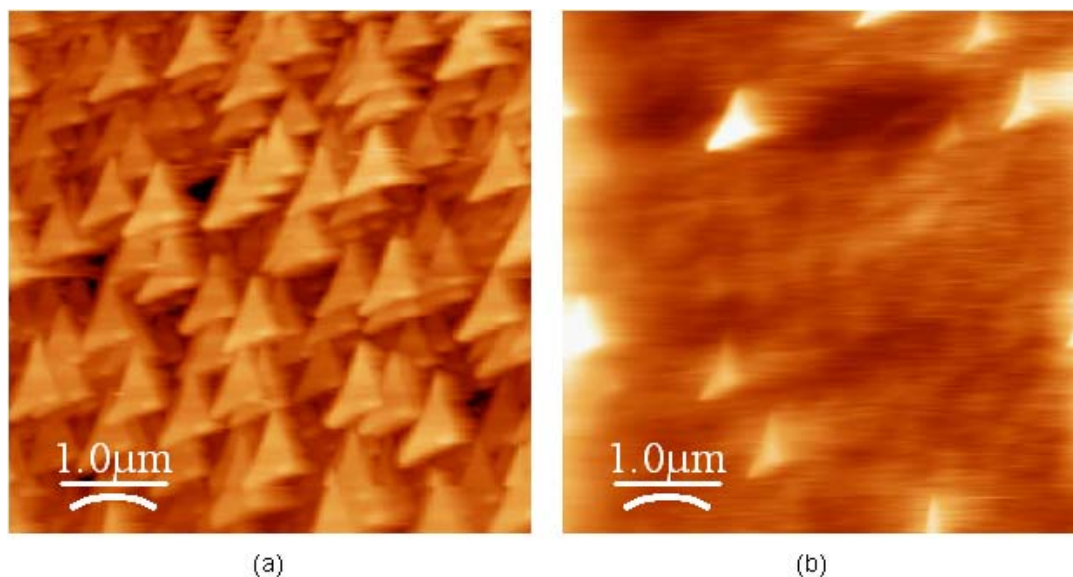


Fig. 1. AFM image of a 5x5 μm<sup>2</sup> area of (a) Al/Si and (b) PFTS/Al/Si.

Table 1 Atomic percent concentration (at. %) ( $\pm 2\%$  relative error) of the elements determined using Al 2p, O 1s, and C 1s spectra taken on unmodified Al/Si. The values are the mean of three different values quantified from three spectra measured on three separate areas (chosen randomly) of the surface.

Substrate	Al (at. %)	O (at. %)	C (at. %)
Al/Si	38	47	15

surface which is required for reaction with silane.

The survey spectra of XPS taken on Al/Si is presented in Fig. 2. This spectra indicates the main elements on the Al/Si surface. The peaks corresponding to O 1s, C 1s, Al 2p, and O KLL (Auger) are observed. C 1s is found in the survey scan due to adventitious organic contamination from atmospheric exposure between sputter deposition and analysis.

Fig. 3 shows the high resolution C 1s core level XPS spectra performed on (a) PFTS reacted Al/Si and (b) warm nitric acid treated PFTS/Al/Si after 140 days ambient exposure. The fitted XPS C 1s spectra obtained for PFTS/Al/Si and treated PFTS/Al/Si is shown as depicted in Fig. 3(a) and 3(b), respectively. The peak component at a binding energy of about 284.8 eV in Fig. 3(a) can be assigned to C-H/C-C groups which arise partly from the CH<sub>2</sub> groups present in the PFTS molecule and from adventitious organic contamination. The binding energy of 285.9 eV is attributed to the

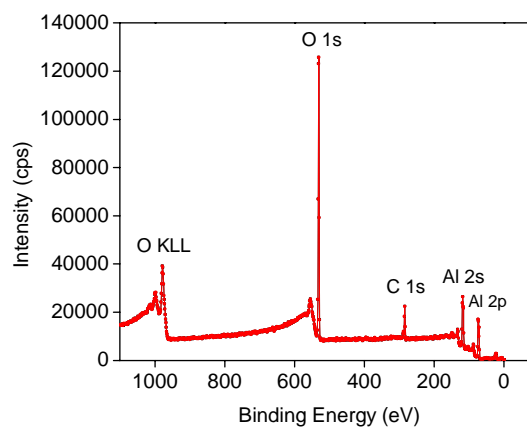


Fig. 2. XPS survey spectra performed on Al/Si in the binding energy range of 0 – 1100 eV with a pass energy of 80 eV.

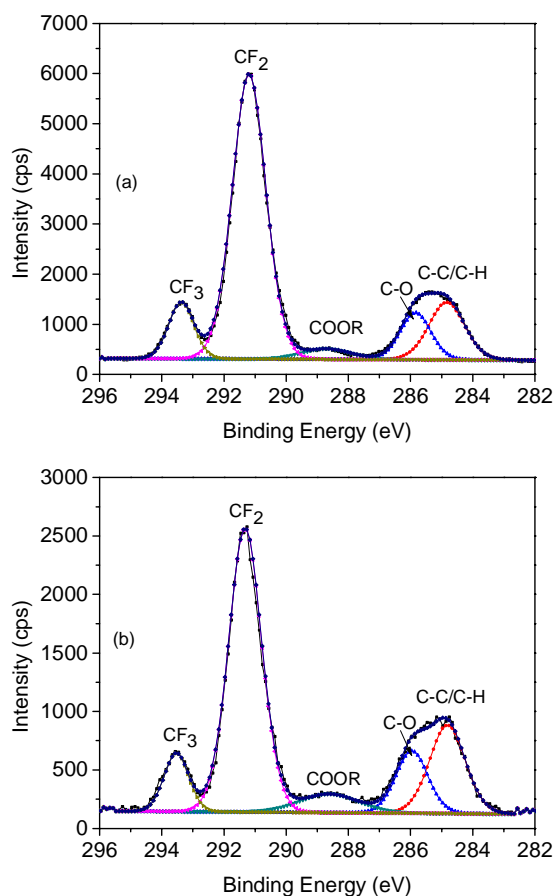


Fig. 3. C 1s core level spectra obtained for (a) PFTS/Al/Si surface and (b) HNO<sub>3</sub> acid treated (pH 1.8, 60°C, 30 min) PFTS/Al/Si after 140 days ambient exposure; FWHM of the fitted peaks are between 0.9 eV and 1.35 eV, except for COOR which is 2.2 eV.

oxidized carbon species C-O which also arises from adsorbed contamination. The characteristic oxidized carbon species ester, ketone, or carboxyl type CO-O-C/C-CO-C/CO-O-H (COOR), adsorbed from ambient air, are observed. [28] The high binding energy (BE) peaks [25] of 291.1 eV and 293.4 eV can be unambiguously attributed to the -CF<sub>2</sub> functional backbone groups and -CF<sub>3</sub> tail group present in the PFTS molecule. The ratio of the peak areas for -CF<sub>2</sub> and -CF<sub>3</sub> is 6.7, which is close to the expected value of 7. The same functional groups are observed on the fitted C 1s spectra (Fig. 3(b)) taken on the warm acid treated PFTS/Al/Si after 140 days ambient exposure. The ratio of the peak areas for the two functional groups -CF<sub>2</sub> and -CF<sub>3</sub> for treated PFTS/Al/Si is 6.6, which also remains close to the expected value of 7. The binding energies of all the fitted corresponding functional groups are listed in Table 2. It can be concluded that XPS data confirm growth of a perfluorinated alkyl chain coating on the PFTS reacted, oxidized Al/Si surface and its resistance to harsh treatment (Fig. 3(b)) as well. XPS data reveal

Table 2 The corresponding binding energy values of the functional groups obtained from fitted peaks in the C 1s high-resolution XPS spectra measured for (a) PFTS/Al/Si and (b) warm nitric acid treated PFTS/Al/Si after 140 days ambient exposure.

Functional groups	Binding Energy (eV)	
	PFTS/Al/Si	PFTS/Al/Si (treated)
C-C/C-H	284.8	284.8
C-O	285.9	286.0
COOR	288.7	288.6
CF <sub>2</sub>	291.2	291.3
CF <sub>3</sub>	293.4	293.5

that airborne carbonaceous contaminants (data not shown here) are also present on bare oxidized Al/Si, as bare metal and metal oxide surfaces tend to adsorb adventitious organic materials readily from the atmosphere.

Most of the functional groups which determine the composition of PFTS are also present on the sample surface. Table 3 shows the surface chemical composition (at. %) and elemental ratios of F/Si quantified from the peak areas of high resolution XPS multiplex data taken on PFTS/Al/Si and warm nitric acid treated PFTS/Al/Si after 140 days ambient exposure. The data in Table 3 demonstrate the almost consistent presence of perfluorinated alkyl chain coatings on both surfaces. The elemental ratios of F1s/Si2p for both surfaces are 16.7 and 16.6, respectively, which are very close to the expected value of 17. Thus, based on the atomic percentages illustrated in Table 3, it can be concluded that PFTS/Al/Si survives exposure to the extreme conditions mentioned above. Therefore, a long term stability of PFTS/Al/Si under normal or standard conditions can be expected.

XPS angle resolved measurement data can be used to study the variation in film chemical composition with respect to depth. The depth in the film from which the photoelectrons escape decreases with a decrease of the take-off angle which is defined as the angle between the direction normal to the photoelectron detector and the average surface plane to the substrate. Therefore, angle resolved XPS measurements recorded at different take-off angles with respect to the surface plane were performed on PFTS/Al/Si over a depth of approximately 0 – 6 nm. The estimated depth resolution is approximately 2 nm while the probing depth from which information is obtained is several nm. Fig. 4 shows the variation in chemical composition of PFTS/Al/Si. This plot demonstrates that the signal of all the elements, except carbon, decreases concomitantly with a decrease of take-off angle. The carbon (C) quantity increases because of an over-layer of atmospheric C contamination resulting in a decrease

Table 3 Atomic percent concentration (at. %) (with  $\pm 2\%$  error) of the elements quantified from F 1s, C 1s, O 1s, Si 2p, and Al 2p and elemental ratio of F 1s/Si 2p determined by XPS for untreated PFTS/Al/Si and nitric acid (pH = 1.8, 60°C, 30 min) treated PFTS/Al/Si after 140 days ambient exposure.

Substrate	F (at.%)	C (at.%)	O (at.%)	Si (at.%)	Al (at.%)	F/Si
PFTS/Al/Si	56.8	33.1	6.3	3.4	0.4	16.7
PFTS/Al/Si + 140 days + acid	54.7	34.6	7.1	3.3	0.3	16.6

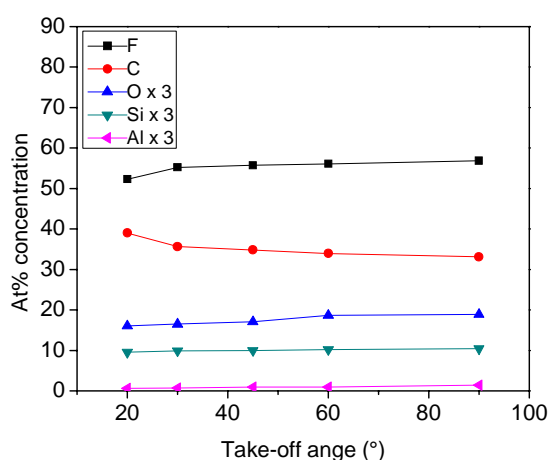


Fig. 4. Angle resolved XPS on PFTS/Al/Si: plot of at. % concentration (quantified from elemental spectral peaks of F 1s, C 1s, O 1s, Si 2p, and Al 2p) versus take-off angle; measurements were performed at take-off angles of 90°, 60°, 45°, 30°, and 20°; please note that the actual at. % concentration of O, Si, and Al is one third of that shown in the graph.

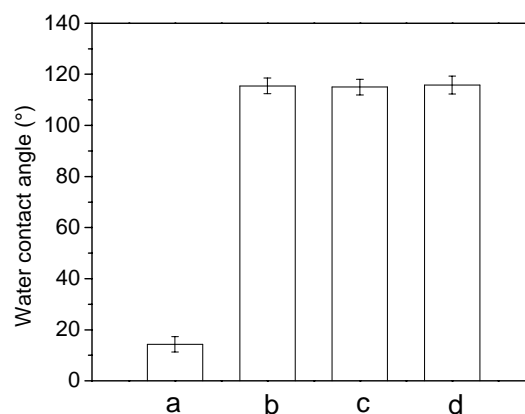


Fig. 5 Water sessile drop static contact angles ( $\pm 3^\circ$  error) measured at 75% - 90% RH and 23 - 25 °C on (a) bare, oxidized Al/Si, (b) untreated PFTS/Al/Si, (c) 140 day ambient exposed PFTS/Al/Si, and (d) nitric acid treated PFTS/Al/Si after 140 days ambient exposure.

in the quantity of F detected with a decrease in take-off angle. C/Si ratios increase with a decrease of take-off angle. Table 4 shows that F/Si ratios remain almost constant thus, indicating a molecularly non-oriented film. Tri-functional organosilane molecules, such as PFTS, can form a complex polymer structure depending on the reaction conditions, which usually results in an organopolysiloxane film that is neither homogeneous nor a monolayer. Thus, PFTS/Al/Si is also an inhomogeneous and polysiloxane perfluorinated alkyl chain film which is not a self-assembled monolayer (SAM).

Fig. 5 shows a histogram of the sessile drop static CAM data measured for pure water at 75% - 90% RH and 23 - 25 °C on unmodified Al/Si, freshly modified PFTS/Al/Si, 140 day ambient exposed PFTS/Al/Si, and nitric acid treated PFTS/

Al/Si after 140 days ambient exposure. Water CAMs were taken as a measure of comparative characteristic hydrophobicity of the modified and non-modified surfaces. The measured values are compared between the samples as presented in Fig. 5. A significant improvement in hydrophobicity was observed for PFTS/Al/Si compared to bare, oxidized Al/Si. The sessile drop static water contact angle on PFTS/Al/Si is  $>115^\circ$  whereas it is  $<15^\circ$  for bare, oxidized Al/Si. The water contact angle generally increases as surface energy decreases.[29] From the above observation, it can be concluded that the surface wettability dramatically changes from hydrophilic to hydrophobic after reaction of PFTS with Al/Si. A water contact angle  $>115^\circ$  was also observed on PFTS/Al/Si after 140 days ambient exposure and warm acid treated

Table 4 The elemental ratios of F/Si quantified from the angle (90°, 75°, 60°, 45°, 30°, and 20°) resolved XPS high resolution multiplex spectra for F 1s and Si 2p.

Take-off angle	90 °	75 °	60 °	45 °	30 °	20 °
F/Si	16.6	16.4	16.6	16.4	16.3	16.2

Table 5 Water sessile drop dynamic contact angles ( $\pm 3^\circ$  error) measured at 75% - 90% RH and 23 - 25 °C on (a) PFTS/Al/Si, (b) untreated, 140 day ambient exposed PFTS/Al/Si, and (c) warm nitric acid treated PFTS/Al/Si after 140 days ambient exposure. The advancing angle, receding angle, and hysteresis values are the average from at least 3 measurements.

Substrate	Advancing angle (°)	Receding angle (°)	Wetting hysteresis (°)
PFTS/Al/Si	120	95	25
PFTS/Al/Si(140 days exposed)	121	93	28
PFTS/Al/Si(nitric acid after 140 days)	123	92	31

PFTS/Al/Si after 140 days ambient exposure, as illustrated in Fig. 5, thus confirming the stability of PFTS/Al/Si to aggressive treatment.

It appears that there is only one thermodynamic contact angle from Young's equation:

$$\gamma_{SL} + \gamma \cos \theta_0 = \gamma_{SV}$$

where  $\gamma_{SL}$ ,  $\gamma$ , and  $\gamma_{SV}$  are the interfacial tensions between the liquid and the solid, the liquid and the vapor, and the solid and the vapor, respectively, and  $\theta_0$  is the equilibrium contact angle the drop makes with the surface. However, daily experience shows that drops have a spectrum of contact angles ranging from the so-called advancing contact angle up to the so-called receding contact angle which are the maximal and minimal values that can be obtained.[30] Imperfections or defects (either chemical or structural) on the solid surface act to pin the contact line between the water drop and surface and it is this pinning effect that gives rise to contact angle wetting hysteresis. Hence, the same surface defect may pin it in an advancing or receding direction. Thus, the surface defects determine the maximal deviation from the equilibrium Young contact angle (maximal advancing and minimal receding contact angles).[30,31] The advancing and

receding contact angles found for (a) PFTS/Al/Si, (b) untreated, 140 day ambient exposed PFTS/Al/Si, and (c) nitric acid (pH = 1.8, 60°C, 30 min) treated PFTS/Al/Si after 140 days ambient exposure are listed in Table 5. The data show an almost consistent water drop wetting hysteresis (difference between the advancing and receding contact angles) for all 3 cases, thus indicating some degree of robustness for PFTS/Al/Si.

#### 4. Conclusion

The stability of perfluorodecyltrichlorosilane (PFTS) reacted Al/Si (PFTS/Al/Si) surface has been investigated using X-ray photoelectron spectroscopy (XPS) and contact angle measurements (CAM). XPS confirms the presence of a perfluorinated alkyl chain coating on PFTS/Al/Si, 140 day ambient exposed PFTS/Al/Si, and nitric acid treated PFTS/Al/Si after 140 days ambient exposure. CAM carried out on the untreated, ambient exposed, and nitric acid treated PFTS/Al/Si show that the static water contact angle is  $>115^\circ$  and wetting hysteresis remains almost constant, thus demonstrating the highly hydrophobic nature and good resistance, i.e., stability, of PFTS/Al/Si to nitric acid (pH  $\leq 1.8$ , 60°C, 30 min). The AFM data show no significant difference in surface roughness for PFTS/Al/Si before and after warm nitric

acid treatment which also indicates the stability of the PFTS/Al/Si film.

#### Acknowledgements

Financial support for this work was provided by the Swiss Technology Oriented Program of TOP Nano 21 (Contract CTI5824.4), Bern.

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