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Surface modification of coated silicon wafer

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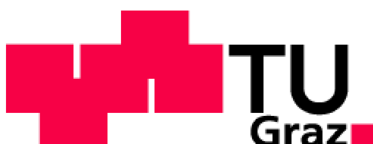

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List of abbreviations

CA	Contact angle
pretr. 1	Pretreatment 1
pretr. 2	Pretreatment 2
LA	Lauric acid
STA	Stearic acid
ODO	1-Octadecanol
DDBSA	4-Dodecylbenzensulfonic acid
ODT	1-Octadecanethiol
TDA	Tetradecylamine
ODA	Octadecylamine
TDPA	Tetradecylphosphonic acid
ODPA	Octadecylphosphonic acid
PFND	*1H,1H,2H,3H,3H*-Perfluorononanoic-1,2-diol
PFNA	Perfluorononanoic acid
PFTDA	Perfluorotetradecanoic acid
SAM	Self-assembled monolayer
LB	Langmuir-Blodgett
THF	Tetrahydrofuran
IPA	Isopropyl alcohol
PVD	Physical vapor deposition
CVD	Chemical vapor deposition
AFM	Atomic force microscopy
XPS	X-ray photoelectron spectroscopy

Inhaltsverzeichnis

1. Introduction 1

2. Literature 2

2.1 State of the art 2

2.1.1 Cleaning and drying 2

2.1.2 Tungsten 3

2.1.3 Titanium nitride 3

2.1.4 Thermal silicon dioxide 4

2.2 Self-assembled monolayers 5

2.2.1 Binding and orientation of SAMs 7

2.2.2 Characterization 8

2.2.2.1 Contact angle goniometry 9

2.2.2.2 Ellipsometry 12

2.3 Langmuir-Blodgett films 13

2.3.1 Comparison of Langmuir-Blodgett films and self-assembled monolayers 14

2.4 Critical micelle concentration 14

3. Results and discussion 16

3.1 Coating experiments 16

3.1.1 Tungsten coated silicon wafer 16

3.1.2 Titanium nitride coated silicon wafer 29

3.1.3 Thermal silicon dioxide coated silicon wafer 33

3.2 Removal 37

3.2.1 Wet chemical removal 37

3.2.1.1 Tungsten coated silicon wafer 37

3.2.1.2 Titanium nitride coated silicon wafer 50

3.2.1.3 Thermal silicon dioxide coated silicon wafer 55

3.2.2 Removal experiments in the tube furnace 58

4. Experimental 61

4.1 General 61

4.2 Coating and wet chemical removal experiments 64

4.2.1 Tungsten coated silicon wafer 64

4.2.1.1 Octadecylphosphonic acid 64

4.2.1.2 Tetradecylphosphonic acid 67

4.2.1.3 4-Dodecylbenzenesulfonic acid 69

4.2.1.4 Tetradecylamine 72

4.2.1.5 1-Octadecanethiol 75
4.2.1.6 Perfluorotetradecanoic acid 77
4.2.1.7 1-Octadecylamine 79
4.2.1.8 1-Octadecanol 83
4.2.1.9 Lauric acid 86
4.2.1.10 Stearic acid 88
4.2.1.11 Perfluorononanoic acid 90
4.2.1.12 *1H,1H,2H,3H,3H*-Perfluorononanoic-1,2-diol 92
4.2.2 Titanium nitride coated silicon wafer 94
4.2.2.1 Octadecylphosphonic acid 94
4.2.2.2 Tetradecylphosphonic acid 97
4.2.2.3 Tetradecylamine 99
4.2.2.4 Octadecylamine 100
4.2.2.5 Lauric acid 101
4.2.2.6 Stearic acid 102
4.2.2.7 1-Octadecanol 104
4.2.2.8 1-Octadecanethiol 105
4.2.2.9 4-Dodecylbenzenesulfonic acid 106
4.2.2.10 *1H,1H,2H,3H,3H*-Perfluorononanoic-1,2-diol 107
4.2.2.11 Perfluorononanoic acid 108
4.2.2.12 Perfluorotetradecanoic acid 110
4.2.3 Thermal silicon dioxide coated silicon wafer 111
4.2.3.1 1-Octadecanethiol 111
4.2.3.2 4-Dodecylbenzenesulfonic acid 112
4.2.3.3 *1H,1H,2H,3H,3H*-Perfluorononanoic-1,2-diol 114
4.2.3.4 Perfluorononanoic acid 115
4.2.3.5 Perfluorotetradecanoic acid 117
4.2.3.6 Tetradecylphosphonic acid 118
4.2.3.7 Octadecylphosphonic acid 120
4.2.3.8 Tetradecylamine 121
4.2.3.9 Octadecylamine 123
4.2.3.10 Lauric acid 124
4.2.3.11 Stearic acid 126
4.2.3.12 1-Octadecanol 127
4.3 Coating and removal experiments in the tube furnace 129

4.3.1 Tungsten coated silicon wafer ... 129
4.3.1.1 Octacylamine ... 129
4.3.1.2 Octadecylphosphonic acid ... 133
4.4 Coating experiments and AFM measurements ... 133
4.4.1 Tungsten coated silicon wafer ... 134
4.4.1.1 Octadecylamine ... 134
4.4.1.2 Octadecanethiol ... 134
4.5 Coating experiments and Raman measurements ... 135
4.6 Coating experiments and X-ray reflectivity measurements ... 135
5. Summary and future prospects ... 136
6. Appendix ... 138
6.1 X-ray reflectivity spectra ... 138
List of literature ... 142
List of figures ... 144
List of tables ... 145

1. Introduction

No matter if they are used as chips in mobile phones or computers, as photodiodes or in other electrical applications life without semiconductors is not imaginable anymore. Because of great demand challenges are increasing in this branch of industry. That further means that smaller structures and higher ratio of the surface to volume fraction are necessary to receive better performances. Therefore requirements on the material are increasing as well. In particular, the surface of wafer is focused on because it is the region which is responsible for interactions both physical and chemical. According to the miniaturization of highly integrated circuits efficient surface modification is more and more attention paid to.

In order to get a fully finished semiconductor wafer, dependent on the area of application, 500 – 800 process steps are required. Most of these steps are carried out as unit processes with the complete wafer before cutting them into smaller chips. About 15 – 20% of the steps are cleaning and drying operations.[1] Great demand is made on these steps because they have to be efficient without destroying the material. Along with the miniaturization of structures these steps are more and more challenging.

Deionized water and isopropyl alcohol are among other liquids state of the art for the cleaning of wafer. During drying – removing of the water – it is possible that the small structures at the wafer surface collapse.

The temporary modification of materials in semiconductor industry is a delicate topic. Self-assembled monolayers (SAM) are more and more the method of choice in silicon technology to modify surfaces. Usually SAM materials are inexpensive, commercial available and easy to handle. Therefore, SAMs are used in electronic applications and nano fabrication as protection layers and to achieve control about parameters like wetting, adhesion or chemical resistance.[44]

The aim of the present thesis is the improvement of the described drying steps. In particular, it was tried to modify different wafer surface materials to get a hydrophobic surface which could make the drying easier. The substrate materials were tungsten, titanium nitride and thermal silicon dioxide silicon wafer. A wide variety of SAM materials has been used.

Of course the introduced hydrophobic layer should be removable again. Therefore, the easy removal of the hydrophobic protection layers is an issue in this thesis. Possibilities and chemicals to achieve a wet chemical hydrophobicity as well as methods to remove the coating of the surface again are described in the present work.

2. Literature

2.1 State of the art

In order to get a fully-finished integrated semiconductor circuit, about 500-800 sequential single processes are necessary. Most of them are carried out on the complete wafer before they are cut into smaller chips. Different methods are established in semiconductor industry to get patterns for the required electrical structure, for example etching or illumination of photo-sensitive material. Among all the required processes about 15-20% of the steps are cleaning and drying operations.[1, 2]

The basic principle for the production of the circuits is the following: Initially, a silicon monocrystal with the desired diameter is drawn. Under clean-room conditions the silicon bar is cut into thin round plates known as 'wafer'. The roughened surface is smoothed via whetting, rounding of the edges, etching and polishing. Now, the blank and pure wafer surface is coated with different materials. What follows are a hundred cleaning and rinsing, etching and coating steps.[2] In the present work titanium nitride, tungsten and thermal silicon dioxide are the used surface materials.

2.1.1 Cleaning and drying

Depending on the application area wafer passes through numerous process steps. These steps can include metallization, deposition processes (PVD, CVD), the removal of layers (etching), or doping. Either wet chemical, dry (physical or chemical etching) or lithographic operations are used. Before the wafer is passed to the next level, it is cleaned to remove residues and excess material. It is important to avoid contaminations without damaging or deleteriously altering the substrate surface in this very sensitive field of work.[1, 2]

Plasma, dry-physical, wet-chemical, vapor phase and supercritical fluid methods are current cleaning methods in semiconductor industries. A distinction has to be made between pre-cleaning and cleaning during the processing. Especially pre-thermal wafer cleaning and surface conditioning are aqueous-based processes. Moreover, post-etch and post-chemical mechanical polishing (post-CMP) are mainly solvent-based cleaning technologies.[1]

Wafer cleaning technology has experienced great interest since the 1970s. Particularly in the years between 1988 and 1992 great increase in development and research was noticed. This trend was observable because of improved analytical methods and instrumentation to characterize impurities

[1] Reinhardt, K. A.; Kern, W. Handbook of Silicon Wafer Cleaning Technology, William Andrew Inc., Second Edition, Norwich, **2008,** page 13-14, 141
[2] http://www.halbleiter.org/waferherstellung/wafer/, 14.06.2013, 09:46

and surface structures. Not just the refinement of semiconductor device architecture, but also miniaturization of the structures let the requirements on cleaning operations increase.[1] Especially in the context of already structured wafer, the cleaning and drying processes are all the more important. Possibly small chambers are not contactable. Furthermore, it could happen during drying that the small patterns collapse because of surface tension and capillary attraction by what the circuit is destroyed.[1]

The possibility to modify the wettability of surfaces, to reduce surface tension or to prevent particle deposition via adding of surface-active agents to cleaning solutions has been known for a long time. These agents are typically organic compounds with a hydrophilic head group and a hydrophobic tail.[3]

2.1.2 Tungsten

The element tungsten is known for its hardness, high melting point, tensile strength and its stability at atmosphere.[4] In semiconductor industry, conductivity and resistance are more important. Tungsten is utilized as barrier metal.

To produce thin tungsten layers on silicon surfaces the chemical vapor deposition (CVD), physical vapor deposition (PVD) or sputtering is often used.[5]

2.1.3 Titanium nitride

Titanium nitride again shows great hardness and a high melting point. It is chemically resistant and has no tendency to form alloys in spite of its metallic character at conventional service temperature. TiN is often used as coating material in the form of thin surface layers to protect other materials from mechanical stress and chemical attack.[6, 7]

In semiconductor fabrication TiN is pretty interesting as gate material.[8] In this application, TiN serves as barrier to avoid diffusion of metal atoms, for example of copper or silicon.[9]

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[3] Reinhardt, K. A.; Reidy, R. F. Handbook of Cleaning for Semiconductor Manufacturing, Scrivener Publishing LLC, New Jersey, **2011**, page 22
[4] Hollemann, A. F.; Wiberg, N. Lehrbuch der Anorganischen Chemie, 102. Auflage, Walter de Gruyter, Berlin und New York, **2007**, page 1583-1584
[5] Yeh, W.-K.; Shiau, Y.-C.; Chen, M.-C. *J. Electrochem. Soc.,* **1997**, 144, 1, 214-217
[6] Münster, A. *Angewandte Chemie*, **1957**, 69, 9, 281-290
[7] Hollemann, A. F.; Wiberg, N. Lehrbuch der Anorganischen Chemie, 102. Auflage, Walter de Gruyter, Berlin und New York, **2007**, S. 1531
[8] http://www.halbleiter.org/lexikon/H/High-k+Metal+Gate/, 14.06.2013, 09:03

Physical vapor deposition is a common method to deposit TiN layers on materials like copper or silicon.[10, 11]

2.1.4 Thermal silicon dioxide

Silicon occurs in nature not elemental because of it's affinity to oxygen.[12] In semiconductor fabrication silicon dioxide is, for example, found as isolator between metal layers as masking for diffusion processes, planarization, or protection layer. The oxide is used because of its resistance and the possibility to produce even and thin layers on wafer surfaces. Silicon dioxide is resistant against water and acids except hydrofluoric acid HF. This property is highly important in semiconductor industry as it is the pre-condition for successful selective etching processes.[13]

Thermal oxidation of silicon is a procedure to get a thin SiO_2 layer on a monocrystal silicon surface. The silicon wafers are, therefore, oxidized in an oxidation oven at temperatures of about 1000 °C. Generally, the oven consists of a silica tube in which the silicon substrate lies as well as a gas inlet pipe. Via the pipe, oxygen is blown into the oven. Silica is the proper material for high temperature processes due to its high melting point of about 1400 °C[12]. Under these conditions the streamed in oxygen reacts with the silicon surface to form SiO_2. Resulting silicon dioxide is glass-like and shows an amorphous modification.[13]

Dry and wet oxidation techniques are to be distinguished. The dry method takes place under pure oxygen atmosphere during which the silicon reacts to the silicon dioxide (Figure 1).

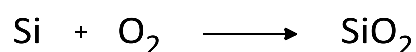

$$Si + O_2 \longrightarrow SiO_2$$

Figure 1: Reaction of silicon to silicon dioxide

Normally, the temperature is between 1000 and 1200 °C. The advantages of dry oxidation are the slow oxide growth, high density and high avalanche voltage that is important for heavy stressed oxides like gate oxides.

[9] Semiconductor Metallization Barrier, US6144099

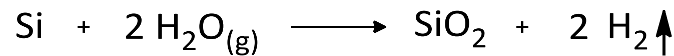
[10] Håkansson, G.; Huitman, L.; Sundgren, J.-E.; Greene, J. E.; Münz, W.-D. *Surface and Coatings Technology*, **1991**, 48, 51-67

[11] http://www.halbleiter.org/abscheidung/pvd/, 14.06.3013, 09:21

[12] Hollemann, A. F.; Wiberg, N. Lehrbuch der Anorganischen Chemie, 102. Auflage, Walter de Gruyter, Berlin und New York, **2007**, page 918-919

[13] http://www.halbleiter.org/oxidation/oxidation/, 14.06.3013, 10:15

For the wet oxidation technique 'wet' oxygen is used. The oxygen is first piped through a 'bubbler-vessel' that contains water (about 95 °C). Therefore, steam is added to the oxygen in the silica tube. Figure 2 shows the resulting reaction equation.



$$Si + 2\,H_2O_{(g)} \longrightarrow SiO_2 + 2\,H_2\uparrow$$

Figure 2: Wet oxidation of silicon to silicon dioxide

The major advantage of this process is the lower temperature of 900 – 1000 °C because the oxide grows faster with lower temperatures. The process is used for the manufacturing of masking layers and field oxides. However, the great disadvantage is the lower quality in comparison to the dry oxidation.

2.2 Self-assembled monolayers

Self-assembling means the formation of monolayers by self-assembly of surfactant molecules at surfaces. A self-assembled monolayer (SAM) is a just a few nanometer thick layer that – as the name implies – is self-contained formed. Usually, they are highly ordered and oriented layers of surface-active agents on solid surfaces. If we are talking about SAMs, a wide range of groups in the chain as well as in the chain termini is addressed. Therefore, it is possible to get a wide scope of surfaces with specific interactions achieved with good chemical control.[14, 15]

SAMs are usually formed by immersing the substrate into a solution that contains the surface-active material. The spontaneous formation of the layer can be traced back to intermolecular interactions and chemical bond formation of molecules with the substrate surface.[14]

The surface-active head group adsorbs at the substrate surface. The alkyl chains in the middle of the molecule rise away from the surface (Figure 3).

[14] Ulman, A. *Chemical Reviews*, **1996**, 96, 4, 1533-1554
[15] Onclin, S.; Ravoo, B. J.; Reinhoudt, D. N. *Angew. Chem. Int. Ed.,* **2005**, 44, 6282-6304

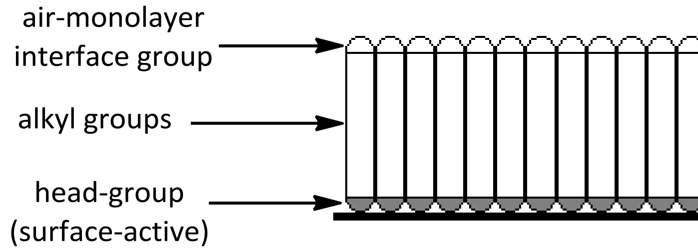


Figure 3: Scheme of a self-assembled monolayer on a solid surface.

The orientation between the chains is controlled by intermolecular interactions. Although, it is more likely that the chains stick out more angulate than straight like in Figure 4.[14]

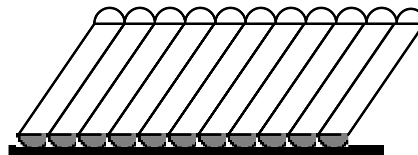


Figure 4: Scheme of an angulate self-assembled monolayer on a solid surface.

Due to SAMs it is possible to increase the understanding of self-organization, interfacial phenomena and structure-property relationships. Nearly all surfactants are able to form self-assembled monolayers at the surfaces. Today, a multitude of self-assembly compounds are known. Probably the best analyzed systems so far are alkanethiolates on gold and alkylsilanes on oxides, in particular SiO_2.[14]

Nowadays, generated monomolecular platforms of SAMs are used in surface structuring and bottom-up nanofabrication techniques. Particularly with regard to special applications in semiconductor industries, nanotechnology and biological arrays the interest in area-wide SAMs grew in the last few years because they are combinable with other state-of-the-art methods like lithography. Especially when the focus is put on the modification of well-defined areas, the right choice of SAM materials can be very helpful on the build-up of layers as well as on further functionalization of already formed layers. In term of the present work, this functionalization is important because it was tried to change wettability of different wafer materials with the help of wet chemical processes.[15]

2.2.1 Binding and orientation of SAMs

Molecular monolayers can be formed either via the Langmuir-Blodgett method (see point 2.3), or chemisorption on metal and oxide surfaces.[15]

SAM formation is based on intermolecular forces between the long molecule chains and molecular forces between the solid surface and molecules. Literature reports agree that the polar head group is the part which binds to the surface. The nonpolar tail, however, sticks – more or less extended – in the surrounding.[14, 16]

In general, the phenomenon of adsorption is in charge for the binding of SAMs on substrate surfaces. Many scientific papers are talking about covalent bindings and, therefore, chemisorption processes. A lot of work has been done so far on different chemicals as well as different surfaces like gold, H-terminated silicon dioxide, silicon or metal oxides. Schlotter et al. proved in their work via IR spectra that the acid head group of arachidic acid chemisorbs at the surface of silver.[17] Covalently bonded organosilanes on chromium oxide surfaces were published by Anac et al..[18] Sergiv reported the covalent binding of octadecyltrichlorosilane to H-terminated SiO_2 surface. First, a hydrolysis reaction of the silane is necessary followed by condensation of the hydrolyzed head group with the surface OH.[19] The P-O bonding of octadecylphosphoric acid on tantalum oxide was proved in the work of Textor et al..[20] After all these are just a few selected examples of chemisorbed SAMs.

SAMs are defined as highly ordered and closely packed layers. Nevertheless, the previous study of Woodward et al. showed that octadecyltrichlorosilanes and phosphonic acids dissolved in THF do not build a homogenous layer but instead aggregate on mica surface. This 'island' building may be caused because of cross-linking of the molecules.[21]

Bain et al. postulated a two-step kinetics for the formation of SAMs. In the first and faster step, the adsorption affects the building; in the second step it is the new orientation of layers which influences it.[22] For simple alkyl chains the second step is not that important. However, for bulky groups

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[16] Bigelow, W. C; Pickett, D. L.; Zisman, W. A. *Journal of Colloid Interface Science*, **1946**, 1, 513
[17] Schlotter, N. E.; Porter M. D.; Bright, T. B.; Allara, D. L. *Chemical Physics Letters*, **1986**, 132, 1, 93-98
[18] Anac, I.; McCarthy, T. J. *Journal of Colloid and Interface Science,* **2009**, 331, 138-142
[19] Sagiv, J. *Journal of the American Chemical Society*, **1980**, 102, 92-98
[20] Textor, M.; Ruiz, L.; Hofer, R.; Rossi, A.; Feldmann, K.; Hähner, G.; Spencer N. D. *Langmuir*, **2000**, 16, 3257-3271
[21] Woodward J. T.; Ulman, A.; Schwartz, D. K. *Langmuir*, **1996**, 12, 3626-3629
[22] Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, I. R. *Journal of the American Chemical Society*, **1989**, 111, 321-335

introduced in the chain the two steps are coupled and so the second step is of great interest because the chemisorption kinetic is greatly hampered by the chain disorder.[23]

Furthermore, it was found that size and chemical properties of surface functionalities affect the structure of SAMs. The introduction of such functionalities reduces the order of monolayers. Steric demanding terminal groups or very polar surface groups like OH or COOH lead to disorder. This introduced 'confusion' has significant effects and is not only limited to the surface.[14]

In conclusion, a lot of facts are already known about the SAM formation.

2.2.2 Characterization

In the last few years, the development in the field of surface analytics and analytics in nanometer scale increased. Nevertheless, characterization of films with a thickness of just a few nanometers is still challenging. To get reliable data more than one technique has to be combined.[15, 24] At this point, just a brief overview is given about SAM and surface characterization methods.

Contact angle goniometry provides information about wettability and, therefore, the polarity of the monomolecular layers. If water is used as liquid conclusions can be drawn about hydrophilic and hydrophobic surface properties (see point 2.2.2.1).

To determine layer thicknesses either ellipsometry or X-ray reflectivity can be used. In semiconductor industry ellipsometry is common, which is an optical technique that uses laser light. It is described more precisely below point 2.2.2.2. X-ray reflectivity uses electron density profile for determination.

Information about the elemental composition can be achieved via X-ray photoelectron spectroscopy (XPS). This technique measures the kinetic energy of electrons that are ejected from the material by an incident photon with known energy. A further method to study the composition of a monolayer is secondary ion mass spectrometry (SIMS). The surface of SAMs is bombarded with primary ions. With the help of a connected mass spectrometer the emitted ions are detected.[15]

Both, Raman spectroscopy as well as Fourier transform infrared spectroscopy (FT-IR), provide data about functional groups of materials. With FT-IR it is possible to determine SAMs on flat substrates[25] and to get information about the bonding of SAMs on substrates. Conventional Raman scattering is not sensitive enough to measure an organic monolayer on semiconductor wafer, but surface-

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[23] Evans, S. D.; Urankar, E.; Ulman, A.; Ferris, N. *Journal of the American Chemical Society*, **1991**, 113, 4121-4131
[24] Functionalization of Semiconductor Surfaces; Edited by Tao, F. F.; Bernasek, S. L. Wiley, New Jersey, **2012**, Chapter 11
[25] Vickerman J. C. Surface Analysis – The Principal Techniques, Wiley, Chichester, **1997**

enhanced Raman methods are.[24] Raman and IR techniques use vibrations for measurements. Differences between the methods are the following: Raman uses the scattering of monochromatically light and the vibrations are generated because of the polarizability change of the irradiated material. FT-IR, on the other hand, uses infrared light of which parts are absorbed by the researched material. In this case, the vibrations are caused by a change of the dipole moment.[26]

Atomic force microscopy (AFM) is the method of choice to determine surface topography. At the cantilever a tip is fixed that scans the surface. Depending on the surface roughness, or in other words deflection of the tip, repulsive and attractive forces are measured.[15]

At this point, just contact angle goniometry and ellipsometry are described more precisely because these are the main analytical methods that are used in the present work.

2.2.2.1 Contact angle goniometry

Contact angle measurements are a good method to receive information about the characteristics of a solid surface. If we are talking about 'contact angle', we usually mean the angle of a liquid where this liquid forms an interface with a vapor and a solid surface (Figure 5). Therefore, the contact angle is a good parameter to determine wettability and surface energy of a solid surface.

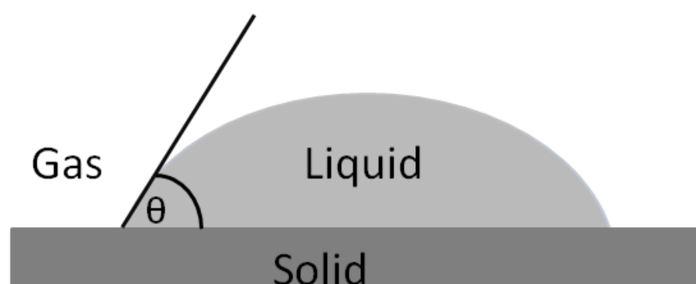

Figure 5: Demonstration of contact angle

The sessile drop analysis is a useful way to get data about the wettability of surfaces. The liquid drop is set on the preferably straight and smooth surface from above via a needle. The less the surface is moistened, the less area of contact exists between the surface and the liquid. That means the drop seems to be rounder and the contact angle gets greater (Figure 6). [27]

[26] Hesse, M.; Meier, H.; Zeeh, B. Spektroskopische Methoden in der organischen Chemie, 7. überarbeitete Auflage, Thieme, Stuttgart, **2005**, Chapter 2
[27] Contact Angle, Wettability, and Adhesion; Edited: Fowkes, F., Advances in Chemistry, 43, Copyright: American Chemical Society, Washington DC, **1964**, Chapter 1

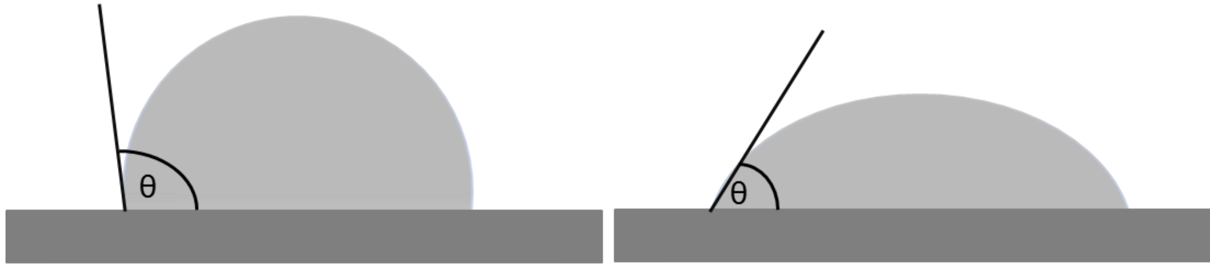

Figure 6: Comparison of more (right) and less (left) wetted contact angles

On the basis of the drop shape and the real drop contour, the angle is calculated via a mathematical model. There are several calculation options. All of them have in common that the contact angle is calculated as the tan θ at the intersection of the contour line and baseline. At this point, only the 'tangent-method' is introduced because it was chosen as calculation scheme in this thesis. The whole profile of the lying drop is conformed to the general conic section equation. The derivation of this equation at the intersection of the contour and baseline leads to the slope in the contact point of the three phases and, therefore, to the contact angle. If water is used as liquid medium, it is possible to make suggestions about the hydrophobicity of the surface material according to the contact angle. Furthermore, it is possible to determine the surface energy of the solid if liquids with known characteristics like surface tension or density are used.[27, 28, 29, 30, 31]

Contact angles can be measured either as static or dynamic angle. In the case of the static drop, the drop is set on the surface and the needle is removed. The drop is created before the measurement and it does not change its volume during the measurement. However, the dynamic drop is measured during increase or decrease of size whereby the interface is continuously new formed. The needle remains in the drop. In this work all of the contact angles were measured via the static angle.

Young's Equation (Equation 1) establishes the connection between the measured contact angle and the surface tension at the 3-phases-contact-line.[28]

$$\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos\theta$$

Equation 1

The indices s and l are standing for 'solid' and 'liquid'. σ_s and σ_l are describing the surface tension of the two phases. The interface tension between the two phases is reflected in the symbol γ_{sl} and θ is the contact angle that equates the angle between the vectors of σ_l and γ_{sl} (Figure 7).

[28] Kwok, D. Y.; Neumann, A. W. *Advanced Colloid Interface Sci.,* **1999**, 81, 167-249
[29] Owens, D. K.; Wendt, R. C. *Journal of Applied Polymer Sciene,* **1969**, 13, 1741-1747
[30] Horsthemke, A.; Schröder J. J.; *Chem. Eng .Process,* **1985**, 19, 277-285
[31] De Gennes, P. G. *Reviews of Modern Physics*, **1985**, 57, 3, 827-863

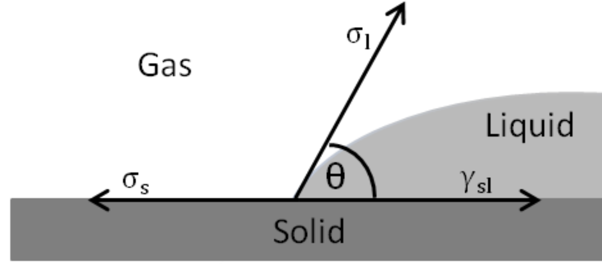

Figure 7: Graphical representation of the vectors

Within the scope of this work the method according to Owens, Wendt, Rabel and Kaelble was chosen to calculate the surface energy of the solids. Hereby surface tensions of all phases are divided into a polar and disperse part (indicated through the indices P and D) (Equation 2, Equation 3).[28, 29, 31]

$$\sigma_l = \sigma_l^P + \sigma_l^D$$

Equation 2

$$\sigma_s = \sigma_s^P + \sigma_s^D$$

Equation 3

Calculation of the interface tension between the surface tension of a solid and a liquid is carried out in one step via Equation 4.

$$\gamma_{sl} = |\sigma_s - \sigma_l|$$

Equation 4

Owens and Wendt took their equation for the interface tension and combined it with Young's equation that leaded to Equation 5.

$$\gamma_{sl} = \sigma_s + \sigma_l - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^P \cdot \sigma_l^P})$$

Equation 5

The system was solved with the help of contact angles of two liquids with known polar and disperse part.

Kaelble achieved results by building liquid pairs and the mean values of the resulting surface energy data. Rabel was able to calculate the polar and disperse part of the surface energy via a regression line that he built out of contact angle data. He linked Equation 4 and Equation 5 and adapted it to the general equation of line (Equation 6).[29, 30, 31]

$$y = mx + b$$

Equation 6

The adapted equation looks as follows:

$$\underbrace{\frac{(1+\cos\theta)\cdot\sigma_l}{2\sqrt{\sigma_l^D}}}_{y} = \underbrace{\sqrt{\sigma_s^P}}_{m}\ \underbrace{\sqrt{\frac{\sigma_l^P}{\sigma_l^D}}}_{x} + \underbrace{\sqrt{\sigma_s^D}}_{b}$$

Equation 7

In the present work water and diiodomethane were chosen as 'pair of liquids'.

2.2.2.2 Ellipsometry

Ellipsometry is a non-invasive, non-destroying routinely used method in semiconductor industry to determine optical properties of materials like refraction indices and layer thicknesses. [32, 33]

This technique basically measures the change in polarization of reflected light. In general, an ellipsometric measurement needs a light source, a polarizer before the light beam strikes the sample and a detector after the reflection. A simple scheme of an ellipsometer is shown in Figure 8.[32, 33]

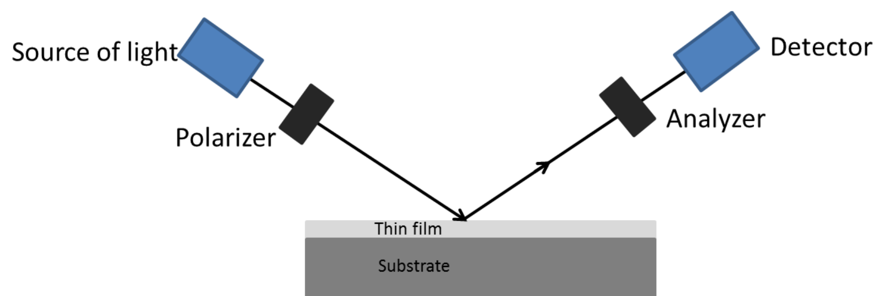

Figure 8: Scheme of an ellipsometer

Incident laser light with a defined wavelength is elliptically polarized and then reflected from the surface of the sample. After the reflection, the polarization state of the light beam is measured. The amplitude ratio ψ and the phase difference Δ between light waves known as s- and p-polarized waves are the crucial parameters for this technique. [32, 33]

The measurement of very thin films (100 Å or less) is possible because of the phase difference between s- and p-waves. With the help of layer models e.g. air/thin film/substrate desired data (e.g. film thickness) can be derived. Optical constants – among others like phase of the light, refractive index or dielectric constant – have to be available to calculate the layer thickness of very thin films. A certain limitation of this method can be traced back to the dependency of the layer model.

[32] Hiroyuki F. Spectroscopic Ellipsometry: Principles and Applications, Wiley, Chichester, **2007**
[33] Tompkins, H. G.; McGahan, W. A. Spectroscopic Ellipsometry and Reflectometry: A User's Guide, Wiley, New York, **1999**

Therefore, no absolute values are achievable. The combination with other methods like IR-spectroscopy provides more accurate data.[24]

In the present thesis, a limitation of the ellipsometric method is reached due to the layer model. Distribution of the values is given because only fixed layers can be chosen. No thought has been given to the carbon or oxygen on the surface layer before the coating. Certainly, there is more than one layer on the surface. Therefore, the reflectivity of polarized light cannot be traced back to the pure surface materials tungsten, titanium nitride and thermal silicon dioxide. An interference of the layer and therefore a falsification of the data is expected.

2.3 Langmuir-Blodgett films

The entire literature cited here is done for aqueous systems.

Langmuir-Blodgett (LB) films are a few nanometer thick layers of one or more levels of an organic material that are formed via the Langmuir-Blodgett method. This means that the solid substrate on which the film should be built is immersed vertically in the solution of the desired chemical. At the interface of liquid and gas, the film is formed either during immersing or extracting the substrate.[34, 35, 36]

The critical micelle concentration (CMC) is important in this field of work because if the CMC is exceeded, the monolayer material is not able to arrange itself at the liquid boundary anymore, but build micelles (see point 2.4).

In technique application it is usual to use mixed monolayers. Therefore, a second substance is often used to stabilize another one that would not build LB-films on its own. Fatty acids, for example, are used as stabilizer. However, it is also possible to get films of two or more separate monolayers if immiscible substances are used.[34]

Again, ellipsometry is a common instrumentation to analyze film thicknesses of the LB-films on solid surfaces. A limitation for this technique is given by the oxide layer probably built between the substrate and LB film. Especially exposure of evaporated metal films or metals after etching processes in semiconductor industry to atmosphere leads to formation of oxide on metals.[34]

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[34] Petty, M.C. Langmuir-Blodgett films: An Introduction, Cambridge University Press, Cambridge u.a., **1996**
[35] Blodgett, K. B. *Journal of the American Chemical Society*, **1935**, 57, 1007-1022
[36] Langmuir, I. *Journal of the American Chemical Society*, **1917**, 39, 9, 1848–1906

Most of the Langmuir-Blodgett materials consist of two parts – a soluble, hydrophilic and an insoluble, hydrophobic one. Among other fatty acids, simple substituted aromatic compounds, dyes, porphyrins and phthalocynines are typical LB materials. The mentioned substances are just a brief list of used organic compounds.[34] Fatty acid derivatives provide an important link between the LB method and the SAM technique.[14]

Today, LB technique is of great interest in aspect of forming patterns on solid substrates with large areas.[37]

2.3.1 Comparison of Langmuir-Blodgett films and self-assembled monolayers

LB films and SAMs have in common that they use the same building blocks and both show organized structures. However, they differ in their procedure and properties. LB films are built at the air/liquid interface during a moving process. SAMs, on the other hand, are formed during immersion in solution.[38]

Experiments with compounds of comparable carbon number and similar head groups done on the same substrate material gave the following results: Contact angle as well as layer thickness of SAMs are higher than those of LB layers. That admits the conclusion that the distribution and the order of the molecular structures differ. It was shown that SAMs are more compact and hydrophobic compared to LB films. Furthermore FT-IR and contact angle measurements lead to the result that the coverage of SAMs is higher.[38]

These results enable an accurate choice of the right material for specific applications.

2.4 Critical micelle concentration

A tenside is an amphiphile molecule that usually consists of a long, nonpolar, hydrophobic carbon hydride residue and a polar, hydrophilic head group. Depending on whether a polar or non-polar environment is used, surfactants are able to build spontaneously micelles with the polar head group inside or outside.[39] Tensides are classified in ionic and nonionic surfactants depending on the head group. Micelles are either spherically or rod shaped.

[37] Chen, X.; Lenhert, S.; Hirtz, M.; Lu, N.; Fuchs H.; Chi, L *Accounts of Chemical Research*, **2007**, 40, 393-401
[38] Meucci, S.; Gabrielli, G.; Caminati, G *Materials Science and Engineering C*, **1999**, 8-9, 135-143
[39] Lucena, I. L.; Canuto, J. D. S., Caroni A. L. P.F.; Fonseca J. L. C.; Dantes Neto, A. A.; Castro Dantas, T. N. *Colloids and Surfaces A: Physiochemical and Engineering Aspects*, **2012**, 408, 48-56

The concentration below surfactants appear in linear form is called critical micelle concentration (CMC). Above this concentration the tensides aggregate to micelles. CMC is of great interest, especially in an issue like SAM or LB-film because the properties of surfactants change according to their form. Of course, micelles are not as qualified to form thin films on a substrate as the linear molecules.

Although, broad literature research was done not much references were found about the CMC of the systems the present thesis deals with. Nevertheless, general trends can be cited for aqueous and even non-aqueous liquids.

CMC of ionic surfactants in organic solvents (octane, decane, dodecane, tetradecane and hexadecane) decreases with increasing number of carbon atoms in the surfactant chain.[40] Li et al. did experiments with non-ionic surfactants in water. Their results proved again that the CMC moves to lower concentrations with increasing hydrophobic chain length. Furthermore, the working group was exploring the influence of bulky groups on the hydrophobic chain of non-ionic surfactants. Bulky groups lead to steric hindrance in the aggregation and, therefore, to a higher CMC. Additionally, it was shown that the location of the introduced bulky group has influence on the hydrophobicity. For example, the further the phenyl ring is next to the head group, the higher is the hydrophobic effect of it.[41]

Another research group studied the influence of alcohol on the CMC. In this case, anionic surfactants were solved in the organic solvent N,N-dimethyl formamide. The used alcohols were n-heptanol, n-octanol, n-nonanol and n-decanol. It was figured out that CMC of the surfactants increases with increasing amount of alcohol and that it decreases with increasing carbon number of the alcohol.[42]

Compared to ionic surfactants nonionic surfactants show lower CMCs, higher efficiency in reducing surface tension and better solubilizing properties.[41]

[40] Zhang X. *Journal of Dispersion Science and Technology*, **2011**, 32, 299-304
[41] Li, Y.; Reeve, J.; Wang, Y.; Thomas R. K.; Wang J.; Yan, H. *J. Phys Chem. B*, **2005**, 109, 16070-16074
[42] Zhang, H.-L.; Kong, Z.; Yan, Y.-M.; Li, G.-Z.; Yu, L. *J. Chem. Eng. Data*, **2008**, 53, 327-330

3. Results and discussion

Aim of the present work was to get intermediate water repellent surfaces on tungsten and titanium nitride coated wafer and thermal silicon dioxide wafer. Industrial requirement was a fast layer formation because otherwise no possibility is given to form a layer in a rinsing process. The SAM formation in a surface/solution interface was favored over the classical LB film formation in regard to the rinsing process. 10 min were chosen as immersion time to observe the fast layer formation. Different SAM materials were tested to receive hydrophobic tungsten, titanium nitride and thermal silicon dioxide surfaces. Their effect on the surfaces, the solvent dependency and the influence of different pretreatments were analyzed. Furthermore, great importance was attached to the removal of the layers. Tetrahydrofuran (THF) was chosen as solvent because of current literature[21, 22, 23] and polarity thoughts, isopropyl alcohol (IPA) with regard to industrial application.

'Rinsed' in all the tables just mean that the coated chip was dipped in pure solvent (rinsed process) before blown dry with either N_2 or compressed air (only for the AFM experiments air was used). If just the substances are mentioned in this chapter, always the coated surface is meant. All the presented values are averaged.

Layer thicknesses for all the experiments were determined on the tungsten and silicon dioxide surfaces via ellipsometric measurements. The data are not presented here because the modeling was not correct for the thin organic layers on the different metal surfaces. The laser beam went through the organic material and was reflected by the W respectively SiO_2. For titanium nitride no recipe was available, not at least because the material was not pure but a mixture of nitride and oxide.

3.1 Coating experiments

3.1.1 Tungsten coated silicon wafer

Initially all experiments were done on tungsten with pretreatment 1. Pretreatment 2 was introduced in adaption to industrial scale (see point 4.1). It equates to pretr. 1, sole exception: there is no drying among the cleaning liquids. Pretreatments are important to achieve clean surfaces.

The contact angle (CA) values for the cleaned wafer chips are between 9 and 25° for water and between 23 and 37° for diiodomethane (see point 4.2.1). Surface energies are between 73 and 78 mN/m. The values vary from preparation to preparation therefore all the data for chips cleaned via pretreatment 1 are averaged. The same was done with the data for pretreatment 2. All the averaged values are presented in Table 1.

Table 1: Averaged contact angle (CA) and surface energy (σ) data of cleaned tungsten surface.

	CA of H_2O [°]	CA of CH_2I_2 [°]	σ [mN/m]
Pretreatment 1	14.7 ± 4.10	28.6 ± 3.48	76.59 ± 1.43
Pretreatment 2	13.4 ± 3.44	30.0 ± 3.06	76.70 ± 1.20

According to the averaged values of Table 1 no significant difference after pretreatment 1 or 2 is recognizable. The difference of maximal 1.4° for the angles and 0.1 mN/m of the surface energy is less than the standard deviation. The standard deviation of about 4° for the water contact angles is because of the measurement difficulties traced back to the small angles. Even the diiodomethane CAs imply a certain measurement inaccuracy.

Table 2 and Table 3 show the contact angle and surface energy values of tungsten wafer chips after the coating with different SAM materials and the differences to the cleaned data. In Table 2 data of the experiments in THF and in Table 3 in IPA are given. Via the wettability of surfaces with water hydrophobic properties can be determined. In general a surface is seen as hydrophobic with a water CA greater than 90°. Therefore, 90° is the lower limit the coated surface should achieve.

In general, with all twelve substances an increase of water and diiodomethane CAs and a decrease of surface energies can be achieved on tungsten. Consequently, all the substances lead to more hydrophobic surfaces in comparison to the uncoated material.

Table 2: Contact angles (CA) and surface energies (σ) on tungsten after the coating with SAM materials solved in THF and the differences to the cleaned value of Table 1.

	coated				Δ		
SAM	**Pretr.**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
LA	**1**	38.2 ± 2.85	41.9 ± 3.03	64.01 ± 1.14	23.5	13.3	-12.58
+ rinsed	**1**	43.9 ± 2.03	42.5 ± 4.34	60.62 ± 1.45	29.2	13.9	-15.97
LA	**2**	37.6 ± 1.83	40.7 ± 3.31	64.63 ± 1.16	24.2	10.7	-12.07
+ rinsed	**2**	41.3 ± 1.14	45.6 ± 5.16	61.35 ± 1.69	27.9	15.6	-15.35
STA	**1**	42.2 ± 2.73	62.2 ± 1.96	57.10 ± 0.78	27.5	33.6	-19.49
+ rinsed	**1**	42.3 ± 3.16	47.8 ± 4.24	60.20 ± 1.48	27.6	19.2	-16.39
STA	**2**	38.3 ± 1.89	67.1 ± 2.47	58.85 ± 0.84	24.9	37.1	-17.85
+ rinsed	**2**	41.3 ± 1.03	53.6 ± 3.84	59.47 ± 1.24	27.9	23.6	-17.23
TDPA	**1**	94.3 ± 0.30	64.6 ± 2.57	27.87 ± 0.54	79.6	36.0	-48.72
+ rinsed	**1**	89.6 ± 3.02	58.4 ± 3.87	31.99 ± 0.91	74.9	29.8	-44.60
TDPA	**2**	97.9 ± 1.67	66.5 ± 4.87	26.14 ± 0.98	84.5	36.5	-50.56
+ rinsed	**2**	87.7 ± 5.41	60.5 ± 4.99	31.60 ± 1.23	74.3	30.5	-45.10
ODPA	**1**	93.9 ± 2.32	72.1 ± 2.27	24.61 ± 0.49	79.2	43.5	-51.98
+ rinsed	**1**	88.6 ± 4.92	59.6 ± 2.82	31.74 ± 0.75	73.9	31.0	-44.85
ODPA	**2**	98.5 ± 0.44	71.7 ± 0.84	23.60 ± 0.16	85.1	41.7	-53.10
+ rinsed	**2**	88.6 ± 3.50	59.4 ± 3.59	31.85 ± 0.87	75.2	29.4	-44.85
TDA	**1**	96.0 ± 1.32	66.4 ± 1.01	26.62 ± 0.22	81.3	37.8	-49.97
+ rinsed	**1**	89.0 ± 3.44	65.0 ± 0.88	29.21 ± 0.31	74.3	36.4	-47.38
TDA	**2**	92.9 ± 3.24	62.1 ± 1.05	29.39 ± 0.30	79.5	32.1	-47.31
+ rinsed	**2**	84.2 ± 3.45	61.3 ± 2.30	32.49 ± 0.63	70.8	31.3	-44.21
ODA	**1**	97.1 ± 1.57	68.3 ± 1.25	25.47 ± 0.27	82.4	39.7	-51.12
+ rinsed	**1**	92.8 ± 1.66	64.6 ± 1.29	28.26 ± 0.30	78.1	36.0	-48.33
ODA	**2**	93.4 ± 1.87	67.3 ± 1.23	26.83 ± 0.29	80.0	37.3	-49.87
+ rinsed	**2**	91.5 ± 1.59	61.6 ± 2.40	30.01 ± 0.54	78.1	31.6	-46.69
ODO	**1**	32.1 ± 2.79	69.3 ± 2.08	62.48 ± 0.85	17.4	40.7	-14.11
+ rinsed	**1**	40.0 ± 1.65	49.1 ± 6.24	61.25 ± 2.04	25.3	20.5	-15.34
ODO	**2**	31.1 ± 2.02	70.4 ± 2.60	62.98 ± 0.91	17.7	40.4	-13.72
+ rinsed	**2**	37.6 ± 2.34	52.0 ± 2.67	62.02 ± 0.97	24.2	22.0	-14.68
DDBSA	**1**	36.5 ± 1.18	46.8 ± 6.41	63.80 ± 0.14	21.8	18.2	-12.79
+ rinsed	**1**	42.9 ± 1.35	49.1 ± 10.19	59.54 ± 0.15	28.2	20.5	-17.05
DDBSA	**2**	29.2 ± 2.39	59.5 ± 2.35	65.27 ± 0.90	15.8	29.5	-11.43
+ rinsed	**2**	37.5 ± 2.98	51.1 ± 3.54	62.33 ± 1.28	24.1	21.1	-14.37
ODT	**1**	58.7 ± 3.63	45.7 ± 1.02	50.98 ± 0.54	44.0	17.1	-25.61
+ rinsed	**1**	59.6 ± 5.21	44.7 ± 0.82	50.79 ± 0.62	44.9	16.1	-25.80
PFND	**1**	63.4 ± 1.35	77.8 ± 2.38	39.42 ± 0.64	48.7	49.2	-37.17
+ rinsed	**1**	68.4 ± 2.80	68.9 ± 1.71	37.93 ± 0.57	53.7	40.3	-38.66
PFNA	**1**	39.7 ± 2.29	81.8 ± 3.30	56.99 ± 1.05	25.0	53.2	-19.60
+ rinsed	**1**	44.7 ± 2.94	74.1 ± 5.99	53.68 ± 1.83	30.0	45.5	-22.91
PFTDA	**1**	40.4 ± 2.17	69.2 ± 2.97	57.23 ± 0.99	25.7	40.6	-19.36
+ rinsed	**1**	43.9 ± 1.37	51.1 ± 6.47	58.40 ±2.06	29.2	22.5	-18.19

Table 3: Contact angles (CA) and surface energies (σ) on tungsten after the coating with SAM materials solved in IPA and differences to the cleaned value of Table 1.

		coated			Δ		
SAM	**Pretr.**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
LA	**1**	43.6 ± 0.65	38.4 ± 2.15	61.84 ± 0.71	28.9	9.8	-14.75
+ rinsed	**1**	38.0 ± 1.20	35.7 ± 1.91	65.63 ± 0.68	23.3	7.1	-10.96
STA	**1**	34.3 ± 1.45	40.3 ± 2.04	66.53 ± 0.75	19.6	11.7	-10.06
+ rinsed	**1**	35.2 ± 1.92	40.3 ± 1.04	66.03 ± 0.49	20.5	11.7	-10.56
TDPA	**1**	87.5 ± 3.60	59.7 ± 3.87	32.07 ± 0.94	72.8	31.1	-44.52
+ rinsed	**1**	83.5 ± 3.32	52.0 ± 3.67	36.82 ± 0.95	68.8	23.4	-39.77
ODPA	**1**	94.6 ± 3.55	62.0 ± 3.84	29.04 ± 0.85	79.9	33.4	-47.55
+ rinsed	**1**	87.6 ± 2.94	59.1 ± 5.04	32.29 ± 1.19	72.9	30.5	-44.30
ODPA	**2**	94.4 ± 1.29	64.3 ± 0.94	27.98 ± 0.22	81.0	34.3	-48.72
+ rinsed	**2**	82.9 ± 2.79	58.6 ± 2.11	34.13 ± 0.57	69.5	28.6	-42.57
TDA	**1**	93.2 ± 4.29	68.3 ± 1.55	26.44 ± 0.43	78.5	39.7	-50.15
+ rinsed	**1**	93.6 ± 1.77	66.1 ± 1.22	27.34 ± 0.29	78.9	37.5	-49.25
ODA	**1**	100.1 ± 1.66	70.4 ± 1.34	23.86 ± 0.28	85.4	41.8	-52.73
+ rinsed	**1**	95.0 ± 0.71	69.0 ± 1.12	25.64 ± 0.23	80.3	40.4	-50.95
ODA	**2**	96.5 ± 2.33	68.5 ± 0.67	25.50 ± 0.19	83.1	38.5	-51.20
+ rinsed	**2**	91.6 ± 3.35	64.3 ± 0.94	28.73 ± 0.30	78.2	34.3	-47.97
ODO	**1**	52.8 ± 3.86	48.9 ± 4.52	53.55 ± 1.52	38.1	20.3	-23.04
+ rinsed	**1**	45.3 ± 5.16	37.4 ± 3.14	61.16 ± 1.32	30.6	8.8	-15.43
DDBSA	**1**	19.7 ± 2.36	53.1 ± 2.76	70.54 ± 1.06	5.0	24.5	-6.05
+ rinsed	**1**	25.8 ± 1.28	43.8 ± 1.83	69.84 ± 0.68	11.1	15.2	-6.75
ODT	**1**	45.4 ± 1.29	39.8 ± 1.10	60.45 ± 0.42	30.7	11.2	-16.14
+ rinsed	**1**	44.2 ± 1.11	40.4 ± 3.06	60.98 ± 1.02	29.5	11.8	-15.61
PFND	**1**	51.8 ± 1.62	57.7 ± 3.74	51.77 ± 1.15	37.1	29.1	-24.82
+ rinsed	**1**	56.8 ± 8.82	68.1 ± 11.67	45.93 ± 3.56	42.1	39.5	-30.66
PFNA	**1**	29.9 ± 7.93	87.8 ± 5.45	64.06 ± 2.26	15.2	59.2	-12.53
+ rinsed	**1**	34.2 ± 0.71	70.8 ± 5.53	61.04 ± 1.70	19.5	42.2	-15.55
PFTDA	**1**	28.7 ± 2.68	80.2 ± 3.19	64.18 ± 1.11	14.0	51.6	-12.41
+ rinsed	**1**	28.3 ± 2.56	73.4 ± 1.85	64.42 ± 0.77	13.6	44.8	-12.17

Figure 9 shows the increase of the water CA after the coating with ODA (one example for all the experiments). The right picture shows the ODA coated surface. The drop is rounder than the one on the cleaned surface (left picture). As a result the angle increased. This observation corresponds to the data of Table 2 - ODA has a water CA of 97°.

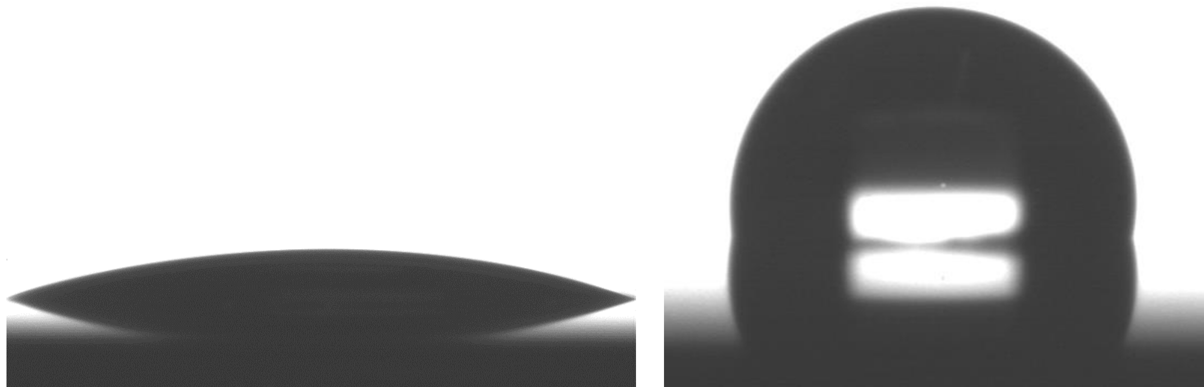

Figure 9: Picture of the water contact angle of a tungsten surface before and after the coating with ODA (pretr. 1, without rinsed process). On the left picture the cleaned surface and on the right the coated one is shown.

For the sake of simplicity, only the results for the experiments in THF are discussed first (Table 2).

For lauric and stearic acid the water contact angle increase is between 24° and 29° respectively 25° and 28°. The highest water CAs can be achieved after pretr. 1 and the rinsed process. Hardly any influence on neither CA nor the surface energy is discernible between the two pretreatments. The rinsed process was carried out to remove any remaining non adsorbed material (after the coating). Without the rinsed process surplus material could falsify the data. Both fatty acids show a small increase with the rinsed process after the coating in THF. The diiodomethane CAs of LA and STA differ more than the water CAs. STA has higher diiodomethane CAs and lower surface energies than LA. The more C-atoms in the chain the higher are the diiodomethane CAs are.

As mentioned in the last preceding paragraph, the rinsed process has an influence on the CAs. Higher water CAs are obtained with the rinsed process for the fatty acids, ODO, DDBSA, ODT and the three fluorinated compounds for the experiments in THF and for DDBSA, PFND and PFNA in IPA. On the one hand, an orientation of the hydrophobic tails occurs with the rinsed process. Due to this orientation effect the chains are more extended and the nonpolar part is accessible. So the water CA increases. On the other hand, the surplus material is removed which explains the decrease of the CAs (no falsification due to not 'confused' layer buildings like not extended chains or double or triple layers).

Only LA and DDBSA show greater diiodomethane CAs with the rinsed treatment. However, DDBSA has a high standard deviation of about 10°. In general, diiodomethane CAs show the trend of increasing angles after the coating for the tests in both solvents. The difference in electronegativity of C to I is about 0.3. Therefore, diiodomethane is not a totally nonpolar solvent, but it is not able to form hydrogen bonds like water. Due to the loss of bridge building ability diiodomethane cannot interact very well with the cleaned surfaces. Furthermore, neither the water nor the diiodomethane

have the ability to interact with the terminal methyl group of the chains. Thus, the increase of both CAs after the coating can be explained.

For TDA, ODA, TDPA and ODPA the water CAs are lower with the rinsed process. These four SAM materials show noticeable greater water CAs than all the other substances. The increase of the water CA is 75 – 85°. Highest water contact angle can be achieved with pretreatment 2 without the rinsed process for the phosphonic acids. Again there is no significant difference between pretreatment 1 and 2. The influence of the chain length is not as obvious as expected. TDPA and ODPA show nearly same water CAs, only the diiodomethane angles differ. With both phosphonic acids water CAs are greater than 90°. Therefore, these surfaces are hydrophobic. Amine coated surfaces achieve the highest water CA with pretr. 1 without the rinsed process. The increase of the water CA and the decrease of the surface energies of TDA and ODA coated surface are in the same range as for the phosphonic acids. Diiodomethane CAs of the amine coated surfaces do not differ as much as for the phosphonic acids coated ones.

Water CA of ODO coated surface increases about 17 – 25°. For the diiodomethane CA the significant difference of about 20° between the treatment with and the one without the rinsed process is discernible. Surface energies are about 62 mN/m and averaged 14° lower than for the uncoated chip. DDBSA values are within the field of ODO. The water CAs increase of the DDBSA coated surface is about 16 – 28°. Highest water CA is achieved with pretreatment 1 and the rinsed process.

ODT coated surfaces show higher water CA with the rinsed process than without the rinsed process although the increase is just about 1°. The total increase of water CAs is about 45°. Also the diiodomethane CA data differ just about 1° for the experiments with and without the rinsed process. According to the CAs the surface energy is about the same for both experiments.

With the fluorinated compounds a “teflon-effect” could have been expected. However, the increase of water CAs is between 25 – 54°. All three substances show the higher water angles with the rinsed process. For all three compounds the diiodomethane CAs are high. Especially PFND and PFNA show higher diidomethane angles than all the other coated surfaces. An explanation for this values is that the C-F chains are ‘lazy’ in their reaction behavior and do not like to interact. The observation of high diiodomethane CAs correlates with literature data of about 70° for *2H*-perfluorodecyltrichlorosilane.[43]

[43] Janssen, D.; De Palma, R.; Verlaak, S.; Heremans, P.; Dehaen, W. *Thin Solid Films*, **2006**, 515, 1433-1438

Table 3 presents the data achieved for the experiments carried out in IPA. STA, DDBSA, PFND and PFNA coated surfaces lead to higher water CA after the rinsed process. The diiodomethane angles increase after the rinsed process for the ODT and PFND coated surfaces. For all the substances an increase of the water CAs, the diiodomethane CAs and a decrease of surface energies are discernible in comparison to the cleaned value of Table 1. Again, no significant influence is seen on the coating for the chips cleaned via pretr. 1 or pretr. 2.

LA coated surface has an increase of the water CA of 23 - 29° and STA coated one of 20 - 21°. The water CA of LA shows inverse behavior than in THF – the water CA decreases after the rinsed process. The diiodomethane CA decreases as well. For STA coated surfaces no difference to the tests in THF are noticed. Consequently the longer hydrocarbon chain stabilizes the SAM formation.

TDPA, ODPA and TDA show smaller increases of the water CA for the immersion in IPA compared to THF. The water CA of the ODA coated surface is averaged about 2° higher for the experiments in IPA. Both phosphonic acids and the amines have a decreasing water CA angle with the rinsed process. This trend is similar for the experiments in both solvents. The influence of the solvent is discussed in the next passages.

In Table 4 and Table 5 the values for THF and IPA are compared. If IPA is used as solvent only ODA and ODO coated surfaces lead to higher water CAs. All the other substances show lower values in IPA. Nevertheless, the water CA of ODPA, TDA and ODA are still above 90° and the differences to the cleaned chips are in the same range for both solvents. Therefore, it is still approvable to say that these substance lead to hydrophobic surfaces and no significant disadvantage results from IPA used as a solvent. So far the phosphonic acids and amines are the most promising SAM materials.

For other substances like STA, DDBSA, ODT and the fluorinated compounds instead, the water CA is clearly lower, if the experiment is carried out in IPA. It seems that the SAM building is not as good in IPA as in THF. In general, a decrease of the surface energy for the experiments in both solvents is discernible. A significant higher decrease of about 10° in THF is seen for DDBSA, ODT and PFND. The influence of the solvent is known in literature. Bain et al. did experiments in different solvents. They found out that for all used solvents SAMs of alkanethiols are formed on gold surfaces but, that some of the built SAMs lead to higher water CAs than others.[22]

Table 4: Comparison of contact angles (CA) and surface energies (σ) of tungsten surfaces coated with SAM materials solved in THF or IPA.

		THF			IPA		
SAM	**Pretr.**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
LA	**1**	38.2 ± 2.85	41.9 ± 3.03	64.01 ± 1.14	43.6 ± 0.65	38.4 ± 2.15	61.84 ± 0.71
+ rinsed	**1**	43.9 ± 2.03	42.5 ± 4.34	60.62 ± 1.45	38.0 ± 1.20	35.7 ± 1.91	65.63 ± 0.68
STA	**1**	42.2 ± 2.73	62.2 ± 1.96	57.10 ± 0.78	34.3 ± 1.45	40.3 ± 2.04	66.53 ± 0.75
+ rinsed	**1**	42.3 ± 3.16	47.8 ± 4.24	60.20 ± 1.48	35.2 ± 1.92	40.3 ± 1.04	66.03 ± 0.49
TDPA	**1**	94.3 ± 0.30	64.6 ± 2.57	27.87 ± 0.54	87.5 ± 3.60	59.7 ± 3.87	32.07 ± 0.94
+ rinsed	**1**	89.6 ± 3.02	58.4 ± 3.87	31.99 ± 0.91	83.5 ± 3.32	52.0 ± 3.67	36.82 ± 0.95
ODPA	**1**	93.9 ± 2.32	72.1 ± 2.27	24.61 ± 0.49	94.6 ± 3.55	62.0 ± 3.84	29.04 ± 0.85
+ rinsed	**1**	88.6 ± 4.92	59.6 ± 2.82	31.74 ± 0.75	87.6 ± 2.94	59.1 ± 5.04	32.29 ± 1.19
ODPA	**2**	98.5 ± 0.44	71.7 ± 0.84	23.60 ± 0.16	94.4 ± 1.29	64.3 ± 0.94	27.98 ± 0.22
+ rinsed	**2**	88.6 ± 3.50	59.4 ± 3.59	31.85 ± 0.87	82.9 ± 2.79	58.6 ± 2.11	34.13 ± 0.57
TDA	**1**	96.0 ± 1.32	66.4 ± 1.01	26.62 ± 0.22	93.2 ± 4.29	68.3 ± 1.55	26.44 ± 0.43
+ rinsed	**1**	89.0 ± 3.44	65.0 ± 0.88	29.21 ± 0.31	93.6 ± 1.77	66.1 ± 1.22	27.34 ± 0.29
ODA	**1**	97.1 ± 1.57	68.3 ± 1.25	25.47 ± 0.27	100.1 ± 1.66	70.4 ± 1.34	23.86 ± 0.28
+ rinsed	**1**	92.8 ± 1.66	64.6 ± 1.29	28.26 ± 0.30	95.0 ± 0.71	69.0 ± 1.12	25.64 ± 0.23
ODA	**2**	93.4 ± 1.87	67.3 ± 1.23	26.83 ± 0.29	96.5 ± 2.33	68.5 ± 0.67	25.50 ± 0.19
+ rinsed	**2**	91.5 ± 1.59	61.6 ± 2.40	30.01 ± 0.54	91.6 ± 3.35	64.3 ± 0.94	28.73 ± 0.30
ODO	**1**	32.1 ± 2.79	69.3 ± 2.08	62.48 ± 0.85	52.8 ± 3.86	48.9 ± 4.52	53.55 ± 1.52
+ rinsed	**1**	40.0 ± 1.65	49.1 ± 6.24	61.25 ± 2.04	45.3 ± 5.16	37.4 ± 3.14	61.16 ± 1.32
DDBSA	**1**	36.5 ± 1.18	46.8 ± 6.41	63.80 ± 0.14	19.7 ± 2.36	53.1 ± 2.76	70.54 ± 1.06
+ rinsed	**1**	42.9 ± 1.35	49.1 ± 10.19	59.54 ± 0.15	25.8 ± 1.28	43.8 ± 1.83	69.84 ± 0.68
ODT	**1**	58.7 ± 3.63	45.7 ± 1.02	50.98 ± 0.54	45.4 ± 1.29	39.8 ± 1.10	60.45 ± 0.42
+ rinsed	**1**	59.6 ± 5.21	44.7 ± 0.82	50.79 ± 0.62	44.2 ± 1.11	40.4 ± 3.06	60.98 ± 1.02
PFND	**1**	63.4 ± 1.35	77.8 ± 2.38	39.42 ± 0.64	51.8 ± 1.62	57.7 ± 3.74	51.77 ± 1.15
+ rinsed	**1**	68.4 ± 2.80	68.9 ± 1.71	37.93 ± 0.57	56.8 ± 8.82	68.1 ± 11.67	45.93 ± 3.56
PFNA	**1**	39.7 ± 2.29	81.8 ± 3.30	56.99 ± 1.05	29.9 ± 7.93	87.8 ± 5.45	64.06 ± 2.26
+ rinsed	**1**	44.7 ± 2.94	74.1 ± 5.99	53.68 ± 1.83	34.2 ± 0.71	70.8 ± 5.53	61.04 ± 1.70
PFTDA	**1**	40.4 ± 2.17	69.2 ± 2.97	57.23 ± 0.99	28.7 ± 2.68	80.2 ± 3.19	64.18 ± 1.11
+ rinsed	**1**	43.9 ± 1.37	51.1 ± 6.47	58.40 ±2.06	28.3 ± 2.56	73.4 ± 1.85	64.42 ± 0.77

Table 5: Comparison of the differences of cleaned and with SAM materials (solved in THF or IPA) coated tungsten surfaces.

		Δ in THF			Δ in IPA		
SAM	**Pretr.**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
LA	**1**	23.5	13.3	-12.58	28.9	9.8	-14.75
+ rinsed	**1**	29.2	13.9	-15.97	23.3	7.1	-10.96
STA	**1**	27.5	33.6	-19.49	19.6	11.7	-10.06
+ rinsed	**1**	27.6	19.2	-16.39	20.5	11.7	-10.56
TDPA	**1**	79.6	36.0	-48.72	72.8	31.1	-44.52
+ rinsed	**1**	74.9	29.8	-44.60	68.8	23.4	-39.77
ODPA	**1**	79.2	43.5	-51.98	79.9	33.4	-47.55
+ rinsed	**1**	73.9	31.0	-44.85	72.9	30.5	-44.30
ODPA	**2**	85.1	41.7	-53.10	81.0	34.3	-48.72
+ rinsed	**2**	75.2	29.4	-44.85	69.5	28.6	-42.57
TDA	**1**	81.3	37.8	-49.97	78.5	39.7	-50.15
+ rinsed	**1**	74.3	36.4	-47.38	78.9	37.5	-49.25
ODA	**1**	82.4	39.7	-51.12	85.4	41.8	-52.73
+ rinsed	**1**	78.1	36.0	-48.33	80.3	40.4	-50.95
ODA	**2**	80.0	37.3	-49.87	83.1	38.5	-51.20
+ rinsed	**2**	78.1	31.6	-46.69	78.2	34.3	-47.97
ODO	**1**	17.4	40.7	-14.11	38.1	20.3	-23.04
+ rinsed	**1**	25.3	20.5	-15.34	30.6	8.8	-15.43
DDBSA	**1**	21.8	18.2	-12.79	5.0	24.5	-6.05
+ rinsed	**1**	28.2	20.5	-17.05	11.1	15.2	-6.75
ODT	**1**	44.0	17.1	-25.61	30.7	11.2	-16.14
+ rinsed	**1**	44.9	16.1	-25.80	29.5	11.8	-15.61
PFND	**1**	48.7	49.2	-37.17	37.1	29.1	-24.82
+ rinsed	**1**	53.7	40.3	-38.66	42.1	39.5	-30.66
PFNA	**1**	25.0	53.2	-19.60	15.2	59.2	-12.53
+ rinsed	**1**	30.0	45.5	-22.91	19.5	42.2	-15.55
PFTDA	**1**	25.7	40.6	-19.36	14.0	51.6	-12.41
+ rinsed	**1**	29.2	22.5	-18.19	13.6	44.8	-12.17

A similar trend for the increasing respectively decreasing after the rinsed process for the experiments in both solvent is discernible for the water CA of STA, DDBSA, PFND, PFNA, TDPA, ODPA and ODA coated surfaces and for the diiodomethane CA of TDPA, ODPA, TDA, ODA, ODO, PFNA and PFTDA coated surfaces.

Below the CMC the SAM materials exist as monomers in solution. The OH group in IPA enables the solvent to build hydrogen bonds for example with the used SAM materials. THF has no such functionality. That’s probably the reason why some of the SAMs are better working in THF than in IPA because in IPA less monomers are available.

As mentioned before, literature agrees with importance of the solvent in the formation of homogenous, highly ordered and oriented layers. Brovelli et al.[48] did experiments with SAM materials

on Ta_2O_5. They achieved the higher water CA of 113° when the ODPA was solved in a mixture of n-heptane and IPA compared to 95° in pure IPA. They attributed the result to lower coverage and/or degree of order. The results of Brovelli et al. correlate with my own observation that the monolayer formation is hindered in pure IPA.

All the results show that the chemicals containing elements of the 15. group of the periodic table are more suitable than sulfur and oxygen of the 16. group. In general, the carboxylic acid group is not binding as good as other functional groups. Neither the fatty acids nor the fluorinated compounds PFNA and PFTDA give very hydrophobic surfaces. Carboxylic groups tend to build dimers in solution via hydrogen bonds. Probably only a part of these compounds exists as monomer in solution. This could be the explanation why the fatty acids and the fluorinated acids are not work as well as other materials.

1-Octadecanol and DDBSA are of limited suitability as SAM material on tungsten. ODO again shows the dimer problem because of the OH functionality. In case of DDBSA the bulky phenyl group has probably an in influence on the results.[14, 22, 23]

The formation of an inverse double layer instead of a single SAM is possible. In this case, the second layer would bind to the first one with the non-polar tail and the polar headgroup is on the outside. This effect can be ruled out for the experiments on the tungsten surfaces because the water CA measurement is a sensitive method towards the terminal functionalities. The polar headgroups are believed to attack the metal respectively metal oxide surface and the methyl chains are pointing towards the environment. If the inverse double layer had been built the polar headgroups would have pointed towards the environment and the water CA would have not increased after the coating experiments.

In addition to the CA measurement AFM analysis was done for ODA and ODT coated surfaces. The root mean squared roughness (Rms) of the uncoated tungsten surfaces was carried out in three orientations without a significant difference (see point 4.4). Rms of the uncoated W is 0.81 nm and the averaged roughness (Ra) is 0.64 nm. Figure 10 shows the uncoated tungsten surface.

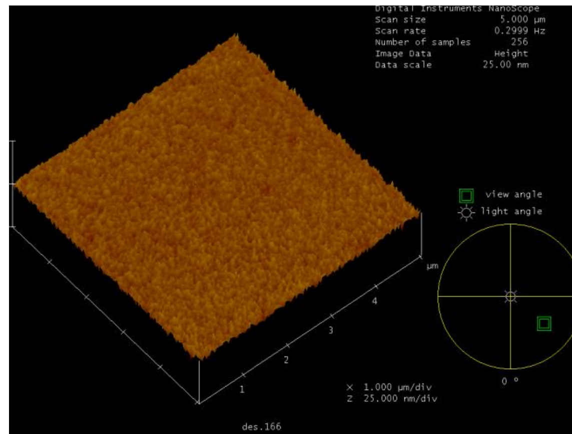

Figure 10: AFM picture of the tungsten surface without coating. Rms = 0.808 nm. Ra = 0.640

All the AFM experiments were done in THF and after pretreatment 1. ODA coated surfaces have an Rms of 1.84 nm and 0.77 nm and a Ra of 1.45 nm and 0.51 nm. Figure 11 shows the ODA coated surface (with the rinsed process). On the picture patterns are discernible. These patterns explain the increase of the roughness. It is possible that the pattern is caused of mechanical influence.

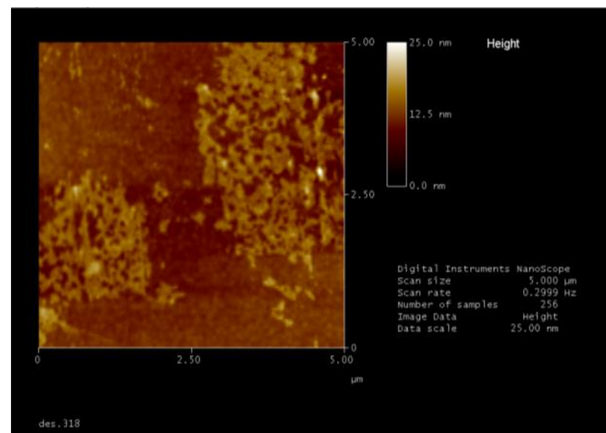

Figure 11: AFM picture of ODA (THF) coated tungsten surface (pretr.1, without rinsed process). Rms = 1.841 nm. Ra = 1.453 nm

Figure 12 shows a more or less smooth ODA coated tungsten surface, instead. Although the surface is not as rough as the uncoated one a few particles are seen. On the one hand, they could be dust particles. On the other hand, they could be aggregates of the SAM material on the substrate. The bright dots are discernible on the right side of the picture in Figure 11 as well. Therefore, the aggregation building is more likely. This observation is supported through light microscopic analysis of an ODPA coated tungsten surface. Crystalline like aggregates were seen. Furthermore, the

phenomenon of aggregation of SAM materials is known in literature.[44, 45] Especially the work of Woodward et al.[21] is interesting because they collected AFM images of samples immersed for different times from 1 to 30 min. The AFM images show clearly the building of ODPA aggregates. These 'islands' increase and grow together with increasing immersion time. According to this work it is likely that a SAM needs a certain time to build a complete layer. A further proof for this observation is the work of Hutchins et al..[46] They achieved a water CA of 110° of an ODPA coated AlO_x surface after the immersion in the solution of the coating material for 16 h. On their AFM pictures no surface aggregation is seen, indicative of true monolayer formation.

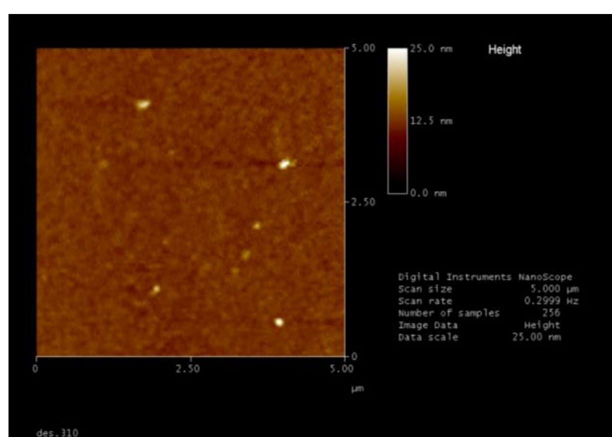

Figure 12: AFM picture of ODA (THF) coated tungsten surface (pretr. 1, with rinsed process). Rms = 0.771 nm. Ra = 0.512 nm

Figure 13 and Figure 14 show the AFM pictures of ODT coated tungsten surface. Both experiments (with and without rinsed process) lead to smoother surfaces compared to the uncoated one because the Rms and the Ra are lower than on pure tungsten. This observation correlates to the CA data of Table 2 and Table 3. An increase of the water CA of about 45° is seen after the coating.

[44] Schwartz, D. K.; Steinberg, S.; Israelachvili, J.; Zasadzinski J. A. N. *Physical Review Letters*, **1992**, 69, 23, 3354-3359

[45] Luzinov, I.; Julthongpiput, D.; Liebmann-Vinson, A.; Cregger, T.; Foster, M. D.; Tsukruk, V. V. *Langmuir*, **2000**, 16, 504-516

[46] Hutchins, D. O.; Weidner, T.; Baio, J.; Polishak, B.; Acton O.; Cernetic, N.; Ma, H.; Jen, A. K.-Y. *Journal of Materials Chemistry C*, **2013**, 1, 101-113

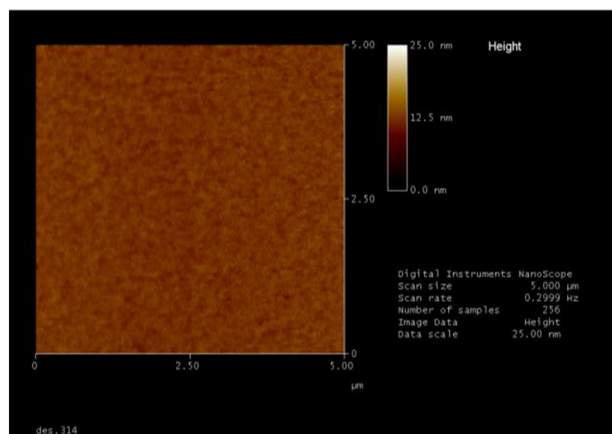

Figure 13: AFM picture of ODT (THF) coated tungsten surface (pretr. 1, without rinsed process). Rms = 0.591 nm. Ra = 0.465 nm

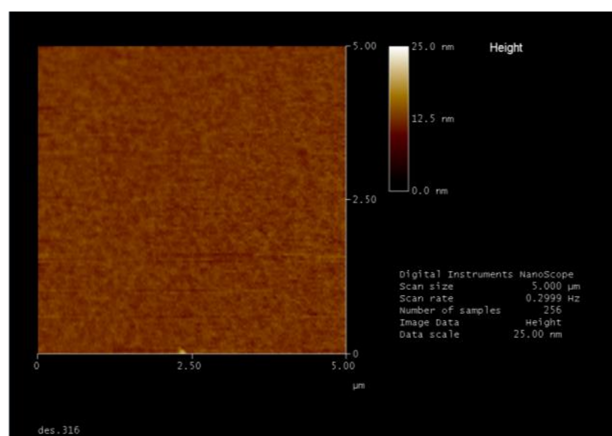

Figure 14: AFM picture of ODT (THF) coated tungsten surface (pretr. 1, with rinsed process). Rms = 0.645 nm. Ra = 0.502 nm

The formation of micelles or crystalline 'islands' on the surface before it is covered completely could be the reason for the differing CA data and high standard deviations of the previous data. SAM materials need a certain time to cover a substrate completely. In literature the immersion time for different substrate materials in the solution of different SAM materials in different solvents is up to 48 h.[20, 47, 48] Therefore, it is possible that the immersion time of 10 minutes was not long enough to receive a highly ordered and homogenous coating on the tungsten surfaces. Nevertheless, both methods, CA and AFM, prove the successful coating of tungsten coated silicon wafer. With both phosphonic acids and both amines the first of two goals of the work was achieved. All four SAM materials lead to hydrophobic surfaces.

[47] Hähner, G.; Hofer, R.; Klingefuss, I. *Langmuir*, **2001**, 17, 7047-7052
[48] Brovelli, D.; Hähner, G.; Ruiz, L.; Hofer, R.; Kraus, G.; Waldner, A.; Schlösser, J.; Oroszlan, P.; Ehrat, M.; Spencer, N. D. *Langmuir*, **1999**, 15, 4324-4327

3.1.2 Titanium nitride coated silicon wafer

The data for the experiments carried out in THF on titanium nitride surfaces are listed in Table 7. The water CAs of the cleaned titanium nitride chips are ranged between 11 and 36°. Diiodomethane CAs of 22° to 36° have nearly the same values than on tungsten. Again a discrepancy of the values is seen from the beginning. Table 6 presents the averaged contact angles after the different pretreatments.[49]

Table 6: Averaged contact angle (CA) and surface energy (σ) data of cleaned titanium nitride surface.

	CA of H_2O [°]	CA of CH_2I_2 [°]	σ [mN/m]
Pretreatment 1	16.7 ± 0.28	25.8 ± 2.94	76.68 ± 0.53
Pretreatment 2	22.5 ± 4.46	30.0 ± 3.07	73.90 ± 1.87
Pretreatment 3	36.0 ± 0.00	28.6 ± 0.00	68.27 ± 0.00

Only a few experiments with different cleaning methods were done. They proved that the used pretreatments have not much influence on the coating. Just like on tungsten the pretreatment is negligible as the data for the phosphonic acids show (Table 7). Even pretreatment 3 (see point 4.1) has not led to a lower water CA. The rinsed process has nearly no effect on the coating as the CAs and surface energies of TDPA and ODPA show. Due to these results and the correlation with industrial procedure pretreatment 2 and the treatment with the rinsed process (also to avoid falsification because of surplus material) were chosen for the following experiments (on TiN and thermal SiO_2 surfaces).

In general, an increase of the CAs and a decrease of the surface energies are discernible for all the SAM materials and experiments done in THF and IPA.

First, the results of the experiments carried out in THF are discussed in detail (Table 7).

[49] Pretreatment 3: Standard deviation is 0.00 because only one experiment with this pretreatment was done (see point 4.1).

Table 7: Contact angles (CA) and surface energies (σ) on titanium nitride after the coating with SAM materials solved in THF and differences to the cleaned values.

		coated			Δ		
SAM	**Pretr.**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
LA + rinsed	**2**	76.8 ± 3.23	54.9 ± 4.59	38.24 ± 1.23	54.3	24.9	-35.64
STA + rinsed	**2**	82.2 ± 2.98	57.9 ± 2.33	34.71 ± 0.63	59.7	27.9	-39.17
TDPA	**1**	92.3 ± 3.69	61.2 ± 2.25	29.98 ± 0.56	75.6	35.4	-46.70
+ rinsed	**1**	93.5 ± 1.77	69.4 ± 1.77	25.88 ± 0.39	76.8	43.6	-50.80
TDPA	**2**	96.6 ± 1.95	69.1 ± 1.02	25.19 ± 0.24	74.1	39.1	-48.69
+ rinsed	**2**	94.9 ± 2.34	64.8 ± 2.51	27.63 ± 0.55	72.4	34.8	-46.25
ODPA	**1**	94.0 ± 2.46	63.6 ± 0.98	28.40 ± 0.26	77.3	37.8	-48.28
+ rinsed	**1**	96.7 ± 0.73	62.6 ± 0.92	28.28 ± 0.20	80.0	36.8	-48.40
ODPA	**2**	96.8 ± 1.70	63.6 ± 1.75	27.78 ± 0.38	74.3	33.6	-46.10
+ rinsed	**2**	95.8 ± 2.90	61.2 ± 1.68	29.15 ± 0.40	73.3	31.2	-44.73
ODPA	**3**	96.1 ± 1.88	65.8 ± 1.08	26.87 ± 0.25	60.1	37.2	-41.40
TDA + rinsed	**2**	83.9 ± 2.02	59.1 ± 2.41	33.54 ± 0.60	61.4	29.1	-40.34
ODA + rinsed	**2**	79.4 ± 3.57	58.1 ± 1.26	35.76 ± 0.45	56.9	28.1	-38.12
ODO + rinsed	**2**	57.8 ± 2.25	46.5 ± 0.95	51.27 ± 0.41	35.3	16.5	-22.61
DDBSA + rinsed	**2**	51.5 ± 1.89	61.7 ± 0.91	50.97 ± 0.40	29.0	31.7	-22.91
ODT + rinsed	**2**	57.0 ± 2.68	47.0 ± 1.75	51.58 ± 0.66	34.5	17.0	-22.30
PFND + rinsed	**2**	74.2 ± 2.05	64.6 ± 4.24	35.90 ± 1.09	51.7	34.6	-37.98
PFNA + rinsed	**2**	73.8 ± 3.17	75.3 ± 6.27	32.89 ± 1.55	51.3	45.3	-40.99
PFTDA + rinsed	**2**	63.8 ± 3.34	69.8 ± 5.41	40.73 ± 1.52	41.3	39.8	-33.15

LA and STA water CAs and diiodomethane angles are clearly higher on titanium nitride than on tungsten and the surface energies are lower as before. Water CA of LA increases 54° and STA of 60° although the 90° border for a hydrophobic layer is not achieved. The diiodomethane CAs increase as well. Again, the increase of the CA is traced back to the absent interaction of the diiodomethane with the terminal methyl groups of the SAMs.

The water CAs of the phosphonic acid coated surfaces are in the same range than on tungsten. The water CAs increase is 72 – 77° for TDPA and 60 – 80° for ODPA. The lowest increase of 60° shows the chip with the pretr. 3. The lower increasing difference is due to higher value for the cleaned chip. Nevertheless, the water CAs are above 90°. Therefore, it is valid to say that hydrophobic titanium nitride surfaces are generated if they will be coated with one of the phosphonic acids.

TDA shows a water CA of 84° for both surface materials – tungsten and TiN – and the diiodomethane angle differs about 2° for TiN and W. The angles result in nearly similar surface energies. However, the water CA of ODA on titanium nitride is 79° and 12° lower on titanium nitride than on tungsten. The diiodomethane CA is just about 4° lower.

With ODO, DDBSA, ODT, PFND, PFNA and PFTDA 3 – 29° higher water CAs than on tungsten can be achieved. The surface energies are lower. For all experiments the same procedure and concentration was used. Therefore, the conclusion is approvable that the used SAM materials operate better on titanium nitride than on tungsten. Especially all the acids (fatty and perfluorinated) lead to higher water CAs and to more hydrophobic surfaces. The titanium nitride surface is not pure but a mixture of nitride and oxide because of its production.[50] Therefore, it is supposed that O and OH groups are at the surface and that the carboxylic head group of the acids can interact with the surface molecules. This statement agrees with literature. More than one working group postulates the binding of SAM materials to metal or metal oxide surface via chemisorption of the functional group on the surface (see point 2.2.1).

Table 8 presents the data for chips cleaned either via pretr. 2 or 1% HF. The chip cleaned via pretr. 2 was stored in a polyethylene bag for one week. The other one was coated immediately after the cleaning (within one minute). It is expected that the coating after the HF treatment leads to lower water CA and higher surface energies because all the surface oxygen should be removed. The opposite result occurs. The chip treated with pretr. 2 leads to a lower water CA although the surface energy is higher because the diiodomethane CA is lower than on the chip treated with HF. Consequently, the surface oxygen is not mandatory necessary for the binding. The oxygen of the phosphonic group is enough. It is proven that the phosphonic head group binds to the surface because otherwise (nonpolar chain binds to the surface and polar head group points towards the environment) the water CA would not be 97°. It is supposable that the surface oxygen even hinders the binding partially because it occupies binding sites for the phosphonic group. Further analysis, like XPS, is necessary to check the real binding situation for the systems used in this thesis.

Huang et al. showed in their work that oxygen is not necessary for the binding of 1-octadecene and 1-octadecanethiol to silicon surfaces.[51] According to this work further experiments with ODT would be interesting.

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[50] Information received from Lam Research®
[51] Huang, Y.-S.; Chen, C.-H.; Chen, C.-H.; Hung W.-H. *ACS Applied Material Interfaces*, **2013**, 5, 5771−5776

Table 8: Contact angles (CA) and surface energies (σ) on titanium nitride after the coating with ODPA solved in THF and differences to the cleaned values. Test of the importance of surface oxygen.

		coated			Δ		
SAM	**Pretr.**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
ODPA	2	92.2 ± 0.80	58.2 ± 2.64	31.41 ± 0.59	69.7	28.2	-42.47
	1% HF	97.0 ± 2.01	36.0 ± 1.21	26.98 ± 0.09	83.1	-29.1	-48.57

Table 9 shows the values for the experiments on TiN immersed in IPA. Compared to the data for coatings in THF all the water CA values are lower in IPA except for ODA, ODO and PFTDA. The ODA coated surfaces has a 4° higher water CA in IPA, ODO a 1° higher water CA and PFTDA has the same angle for the immersion in both solvents. Diiodomethane CAs are higher for the experiments in IPA compared to THF for ODPA, ODA, ODO, PFND and PFTDA coated surfaces. According to the CAs lower surfaces energies are achieved for these materials. Again, all the experiments carried out in IPA lead to an increase of the water and diiodomethane CAs and a decrease of the surface energies as the differences in Table 9 show. Therefore, the coatings in IPA were successful although only the phosphonic acids lead to hydrophobic surfaces.

Table 9: Contact angles (CA) and surface energies (σ) on titanium nitride after the coating with SAM materials solved in IPA and differences to the cleaned values. All values were received after pretreatment 2 and rinsed process.

	coated			Δ		
SAM	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
	H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
LA	72.5 ± 3.49	46.5 ± 2.89	43.49 ± 0.98	50.0	16.5	-30.39
STA	75.6 ± 3.30	51.3 ± 1.22	40.19 ± 0.45	53.1	21.3	-33.69
TDPA	90.7 ± 2.27	61.2 ± 3.12	30.35 ± 0.71	68.2	31.2	-43.53
ODPA	93.7 ± 1.86	63.0 ± 0.88	28.76 ± 0.22	71.2	33.0	-45.12
TDA	78.6 ± 2.87	59.3 ± 1.00	35.66 ± 0.37	56.1	29.3	-38.22
ODA	83.0 ± 2.55	61.3 ± 1.27	32.98 ± 0.38	60.5	31.3	-40.90
ODO	58.6 ± 2.52	49.5 ± 1.00	49.83 ± 0.45	36.1	19.5	-24.05
DDBSA	38.7 ± 1.81	53.6 ± 3.08	60.99 ± 1.05	16.2	23.6	-12.89
ODT	49.9 ± 3.81	40.1 ± 0.84	57.78 ± 0.56	27.4	10.1	-16.10
PFND	67.2 ± 1.73	67.1 ± 2.79	39.22 ± 0.77	44.7	37.1	-34.66
PFNA	51.2 ± 3.50	68.0 ± 2.32	49.88 ± 0.88	28.7	38.0	-24.00
PFTDA	63.8 ± 5.48	73.7 ± 5.85	39.89 ± 1.73	41.3	43.7	-33.99

In comparison to the tungsten surface all the experiments on titanium nitride show higher water contact angle data for the experiments in IPA except TDA and ODA.

3.1.3 Thermal silicon dioxide coated silicon wafer

As mentioned before for all the experiments on the silicon dioxide surface pretr.2 and the rinsed process were chosen (see page 29). The cleaned values are between 20° and 38° for the water CA and 36° and 42° for the diiodomethane CA. In general, the cleaned CAs are higher than on TiN and W. The cleaned SiO_2 surface is more hydrophobic than the other materials. Table 10 shows the averaged data for the cleaned chips.

Table 10: Averaged contact angle (CA) and surface energy (σ) data of cleaned thermal silicon dioxide surface.

	CA of H_2O [°]	CA of CH_2I_2 [°]	σ [mN/m]
Pretreatment 2	32.2 ± 3.70	40.0 ± 2.03	67.58 ± 1.91

In Table 11 the data for the coating experiments carried out in THF are presented. In general, an increase of the CAs and a decrease of the surface energies are recognizable although, the increase of the CAs is not as high as for the other substrate materials. Only DDBSA has a lower water CA after the coating compared to the cleaned value although, the diiodomethane angle increases about 22°. The standard deviation of the DDBSA coated surface is about 6°. Due to the water CA the treatment with DDBSA seems to lead to a more hydrophilic thermal silicon dioxide surface. Nevertheless, in consideration of standard deviations of the cleaned and coated surfaces coating occurs although, the SAM formation seems to be inhomogeneous respectively disordered. Also, the increase of the diiodomethane CA and the decrease of the surface energy agree with this statement.

The fatty acids coated SiO_2 surfaces show higher water CAs than on tungsten but lower ones compared to TiN. The water CA of the coated surfaces has high standard deviations of 8° and 10°. Again, these results lead to the conclusion that the surfaces are not homogenous coated. AFM measurements are necessary to prove the coverage situation of the surface.

Table 11: Contact angles (CA) and surface energies (σ) on thermal silicon dioxide surface after the coating with SAM materials solved in THF and differences to the cleaned values. All values were received after pretreatment 2 and rinsed process.

	coated			Δ		
SAM	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
	H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
LA	50.9 ± 7.54	48.3 ± 0.61	54.89 ± 0.89	18.7	8.3	-12.69
STA	59.5 ± 10.48	49.1 ± 3.39	49.44 ± 1.66	27.3	9.1	-18.14
TDPA	38.7 ± 2.57	46.9 ± 1.47	62.53 ± 0.66	6.5	6.9	-5.05
ODPA	50.6 ± 13.24	51.3 ± 4.78	54.21 ± 2.43	18.4	11.3	-13.37
TDA	67.9 ± 2.04	52.8 ± 2.50	43.40 ± 0.74	35.7	12.8	-24.18
ODA	72.9 ± 3.52	54.7 ± 3.12	40.12 ± 0.93	40.7	14.7	-27.46
ODO	43.7 ± 0.97	43.9 ± 2.63	60.40 ± 0.87	11.5	3.9	-7.18
DDBSA	26.8 ± 5.91	62.2 ± 1.06	66.10 ± 1.05	-5.4	22.2	-1.48
ODT	56.9 ± 6.26	53.8 ± 2.17	49.57 ± 1.06	24.7	13.8	-18.01
PFND	48.1 ± 1.63	67.1 ± 2.54	52.25 ± 0.80	15.9	27.1	-15.33
PFNA	41.6 ± 2.09	70.3 ± 2.21	56.28 ± 0.77	9.4	30.3	-11.30
PFTDA	37.4 ± 2.01	70.8 ± 6.69	59.05 ± 2.07	5.2	30.8	-8.53

The phosphonic acids show different behavior as before – the water CAs of 39° (TDPA) and 51° (ODPA) are clearly lower than tungsten and titanium nitride. ODPA shows high standard deviation. The standard deviation is because of inhomogeneous coating as shown in Figure 15. For TDPA the decrease of the water CA is 49° and 56° compared to tungsten and TiN. ODPA shows decrease of 38° respectively 45°. Diiodomethane CAs are also lower on SiO_2 compared to the other surface materials. The surface energies of the TDPA and ODPA coated surfaces are about 63 and 54 mN/m.

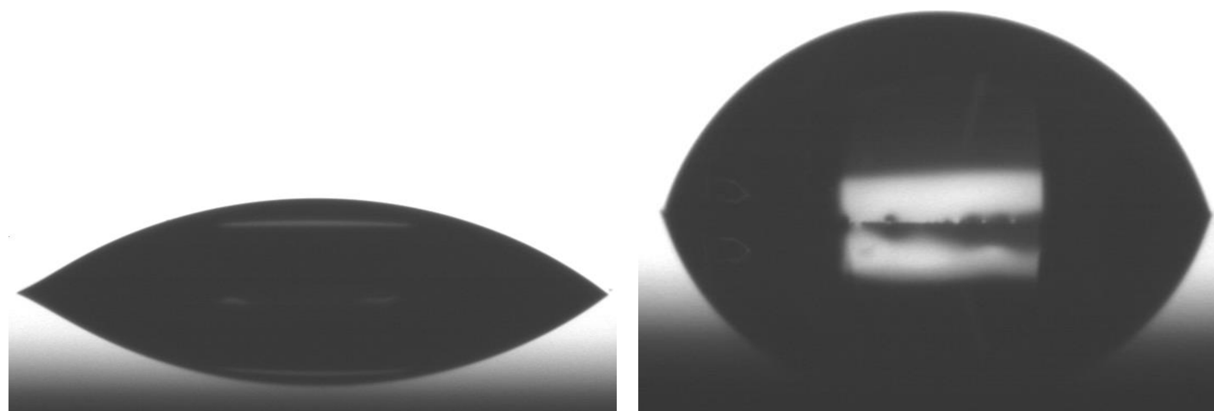


Figure 15: Picture of water contact angle of an ODPA coated silicon dioxide surface (THF, pretr. 2, with rinsed process). Both images were taken from the same chip.

With amines coated SiO_2 surfaces give lower contact angles compared to tungsten and titanium nitride. In the case of TDA the water CA is 68° and 16° lower than on both other substrates. ODA

gives a water CA of 73° and is 19° lower on tungsten and 7° on TiN. Also, the diiodomethane CAs are higher on W and TiN.

With ODO, DDBSA, ODT, PFND, PFNA und PFTDA coated surfaces show lower CA values than the coated titanium nitride although the water CAs and the surface energies lie in the area of the coated tungsten surfaces with a difference of 11° respectively 4 mN/m. The only exception is PFND with a difference of about 20°.

The expected influence of the chain length is discernible on the thermal silicon dioxide surfaces. LA, TDPA and TDA have fewer C atoms in their chains. The water CAs of these materials are lower than with the 18-C chained substances. Therefore, the hydrophobic effect is not as significant with the lower homologous compounds as with the higher ones.

The data of the immersion of thermal silicon dioxide in IPA are listed in Table 12. Water CA decreases for LA, STA, ODPA, ODA, DDBSA, ODT and the fluorinated compounds compared to the experiments done in THF. An increase of 5° is noted for TDPA, 2° for TDA and 3° for ODO. Diiodomethane CAs are higher for the IPA tests with STA, TDPA, ODA, ODO, DDBSA, PFND, PFNA and PFTDA. TDA leads to the same angle on SiO_2 in THF and IPA. In comparison of the 3 surface materials tungsten, titanium nitride and thermal silicon dioxide one trend is discernible: the water CA of ODO is higher for the experiments carried out in IPA compared to THF although, the increase on tungsten and titanium nitride is just about 0.1° respectively 0.8°. The three surface materials have no further trend in common.

The DDBSA coated surface again shows a negative difference for the water CA for the experiments in IPA as well as PFNA and PFTDA. According to these values the previous conclusion that SAM formation occurs with DDBSA is invalid. The decrease is about 15° and therefore not negligible. Although the diiodomethane angles increase for all three substances, the surface energies remain the same before and after the coating experiment. Consequently, no SAM formation develops as observed before on tungsten and titanium nitride surfaces. The reason for the behavior of DDBSA, PFNA and PFTDA is unknown.

Table 12: Contact angles (CA) and surface energies (σ) on thermal silicon dioxide after the coating with SAM materials solved in IPA and differences to the cleaned values. All values were received after pretreatment 2 and rinsed process.

	coated			Δ		
SAM	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
	H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
LA	40.4 ± 2.70	46.4 ± 1.07	61.68 ± 0.56	8.2	6.4	-5.90
STA	39.6 ± 2.56	54.6 ± 3.59	60.24 ± 1.24	7.4	14.6	-7.34
TDPA	43.6 ± 1.70	52.2 ± 3.10	58.31 ± 1.03	11.4	12.2	-9.27
ODPA	44.9 ± 1.83	49.3 ± 2.38	58.24 ± 0.82	12.7	9.3	-9.34
TDA	69.9 ± 2.65	52.7 ± 2.77	42.41 ± 0.83	37.7	12.7	-25.17
ODA	69.8 ± 5.44	59.1 ± 1.93	40.17 ± 0.80	37.6	19.1	-27.41
ODO	46.4 ± 3.35	49.7 ± 0.86	57.28 ± 0.55	14.2	9.7	-10.30
DDBSA	17.7 ± 4.63	63.3 ± 0.54	69.91 ± 0.80	-14.5	23.3	2.33
ODT	46.7 ± 2.15	45.2 ± 1.53	58.22 ± 0.60	14.5	5.2	-9.36
PFND	37.0 ± 2.81	68.1 ± 4.51	59.53 ± 1.49	4.8	28.1	-8.05
PFNA	22.4 ± 2.08	81.2 ± 1.04	67.62 ± 0.53	-9.8	41.2	0.04
PFTDA	23.8 ± 5.39	71.5 ± 4.59	66.80 ± 1.83	-8.4	31.5	-0.78

To sum up: It can be said that the coating experiments were successful. With all the chosen materials a more or less hydrophobic effect can be achieved on all three substrate materials except with DDBSA, PFNA and PFTDA on the thermal silicon dioxide surface. With the phosphonic acids and the amines hydrophobic tungsten and titanium nitride surfaces are achieved. For the silicon dioxide no surface with a water CA of 90° or above was received. In the present work not much attention was paid to binding mechanism because the goal of the thesis was the hydrophobic coating of coated silicon wafer. It is assumed that on the surface of the tungsten wafer no elemental tungsten is found but tungsten oxide or hydroxide functionalities with which the polar head groups of the organic materials can interact. The same is assumed for titanium nitride and silicon dioxide materials. The data of the titanium nitride experiments (see point 4.2.2.1) show that no surface oxygen was necessary for the chemisorption of the organic compounds although, the binding via an oxygen bond (of the polar head group) is plausible. Nevertheless, further experiments are necessary to achieve an accurate bonding situation, for example XPS measurement.

3.2 Removal

The second goal of this work was to remove the introduced layer again. This was carried out either via wet chemical experiments (serial treatment of the coated chips with 5% NH_3, IPA and 10% HF) or via tube furnace experiments.

3.2.1 Wet chemical removal

3.2.1.1 Tungsten coated silicon wafer

The values of Table 13 to Table 16 show the results for the removal experiments for the in THF coated surfaces. All the values and the differences from step to step are presented. The data prove that the pretreatment has no significant influence on the quality of the coating. With both pretreatments for most of the SAM materials a decrease of the water CA after the treatment with 5% NH_3 is discernible.

The most significant decrease can be achieved for the phosphonic acid coated surfaces. TDPA water CAs decrease between 38° and 48°. The rinsed process has no obvious effect on the removal because the highest and the lowest decrease were received from chips with the rinsed process. ODPA coated surfaces show similar results although the decrease of 9° to 17° is lower than for TDPA. The standard deviations of ODPA coated surfaces are not differing as much as for TDPA. The high standard deviations are a sign of not evenly removing of the thin organic layers. A similar high decrease of the water CA as for TDPA is just seen for PFND coated surfaces. With this material the angle decreases about 31°. Both phosphonic acids have an increase of the water CA and a decrease of the surface energies after the immersion in IPA. This trend is given for all experiments except for ODPA with pretr. 1 and the rinsed process.

Table 13: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 1 without rinsed process.

		coated			Δ		
SAM	Treatment	CA [°]		σ [mN/m]	CA [°]		σ [mN/m]
		H_2O	CH_2I_2		H_2O	CH_2I_2	
LA	coated	38.2 ± 2.85	41.9 ± 3.03	64.01 ± 1.14			
	after NH_3	35.2 ± 3.12	37.6 ± 1.90	66.66 ± 0.85	-3.0	-4.3	2.65
	after IPA	39.4 ± 1.77	28.5 ± 3.04	66.54 ± 1.08	4.2	-9.1	-0.12
	after HF	23.5 ± 2.63	31.2 ± 0.95	73.39 ± 0.57	-15.9	2.7	6.85
STA	coated	42.2 ± 2.73	62.2 ± 1.96	57.10 ± 0.78			
	after NH_3	46.7 ± 5.60	47.5 ± 3.42	57.62 ± 1.41	4.5	-14.7	0.52
	after IPA	43.0 ± 3.49	34.6 ± 2.96	63.17 ± 1.15	-3.7	-12.9	5.55
	after HF	44.8 ± 2.75	34.9 ± 1.93	62.08 ± 0.78	1.8	0.3	-1.09
TDPA	coated	94.3 ± 0.30	64.6 ± 2.57	27.87 ± 0.54			
	after NH_3	48.8 ± 3.30	44.5 ± 2.45	57.18 ± 0.94	-45.5	-20.1	29.31
	after IPA	54.7 ± 2.38	44.1 ± 2.74	53.83 ± 0.92	5.9	-0.4	-3.35
	after HF	49.1 ± 15.68	40.4 ± 8.70	58.19 ± 3.68	-5.6	-3.7	4.36
ODPA	coated	93.9 ± 2.32	72.1 ± 2.27	24.61 ± 0.49			
	after NH_3	76.8 ± 5.77	54.1 ± 2.95	38.53 ± 0.96	-17.1	-18.0	13.92
	after IPA	79.7 ± 6.97	54.7 ± 4.71	37.05 ± 1.37	2.9	0.6	-1.48
	after HF	87.9 ± 4.17	63.0 ± 5.03	30.45 ± 1.19	8.2	8.3	-6.60
TDA	coated	96.0 ± 1.32	66.4 ± 1.01	26.62 ± 0.22			
	after NH_3	88.0 ± 8.08	62.9 ± 1.06	30.47 ± 0.54	-8.0	-3.5	3.85
	after IPA	81.8 ± 3.33	54.0 ± 1.19	36.52 ± 0.41	-6.2	-8.9	6.05
	after HF	75.8 ± 3.38	43.8 ± 2.20	43.11 ± 0.69	-6.0	-10.2	6.59
ODA	coated	97.1 ± 1.57	68.3 ± 1.25	25.47 ± 0.27			
	after NH_3	93.5 ± 0.23	68.6 ± 1.02	26.22 ± 0.01	-3.6	0.3	0.75
	after IPA	91.5 ± 3.41	68.6 ± 2.46	28.56 ± 0.08	-2.0	0.0	2.34
	after HF	92.4 ± 1.42	60.8 ± 1.44	30.10 ± 0.33	0.9	-7.8	1.54
ODO	coated	32.1 ± 2.79	69.3 ± 2.08	62.48 ± 0.85			
	after NH_3	29.1 ± 5.57	37.2 ± 1.41	69.78 ± 1.02	-3.0	-32.1	7.30
	after IPA	40.0 ± 1.99	35.7 ± 1.31	64.57 ± 0.55	10.9	-1.5	-5.21
	after HF	41.6 ± 5.68	32.7 ± 2.56	64.39 ± 1.24	1.6	-3.0	-0.18
DDBSA	coated	36.5 ± 1.18	29.5 ± 0.79	74.80 ± 0.32			
	after NH_3	39.8 ± 4.52	46.8 ± 6.41	63.80 ± 0.14	3.3	17.3	-11.00
	after IPA	42.3 ± 1.99	35.3 ± 3.25	64.73 ± 1.34	2.5	-11.5	0.93
	after HF	29.5 ± 3.11	34.3 ± 1.39	63.64 ± 0.57	-12.8	-1.0	-1.09
ODT	coated	58.7 ± 3.63	45.7 ± 1.02	50.98 ± 0.54			
	after NH_3	44.2 ± 6.21	41.9 ± 4.04	60.64 ± 1.67	-14.5	-3.8	9.66
	after IPA	42.2 ± 4.04	35.6 ± 1.31	63.32 ± 0.75	-2.0	-6.3	2.68
	after HF	41.4 ± 5.17	30.6 ± 0.63	64.98 ± 0.69	-0.8	-5.0	1.66
PFND	coated	63.4 ± 1.35	77.8 ± 2.38	39.42 ± 0.64			
	after NH_3	33.6 ± 2.02	43.3 ± 3.11	66.19 ± 1.12	-29.8	-34.5	26.77
	after IPA	40.8 ± 5.62	35.8 ± 0.87	64.07 ± 0.81	7.2	-7.5	-2.12
	after HF	39.6 ± 1.36	33.5 ± 3.85	65.29 ± 1.32	-1.2	-2.3	1.22
PFNA	coated	39.7 ± 2.29	81.8 ± 3.30	56.99 ± 1.05			
	after NH_3	27.2 ± 2.45	35.6 ± 1.75	70.97 ± 0.77	-12.5	-46.2	13.98
	after IPA	37.6 ± 2.07	31.6 ± 1.43	66.79 ± 0.60	10.4	-4.0	-4.18
	after HF	35.6 ± 6.49	36.8 ± 3.13	66.64 ± 1.53	-2.0	5.2	-0.15
PFTDA	coated	40.4 ± 2.17	69.2 ± 2.97	57.23 ± 0.99			
	after NH_3	39.5 ± 6.15	51.1 ± 8.33	61.07 ± 2.92	-0.9	-18.1	3.84
	after IPA	41.4 ± 3.15	39.0 ± 2.57	62.96 ± 1.01	1.9	-12.1	1.89
	after HF	34.5 ± 6.39	35.3 ± 3.94	67.53 ± 1.76	-6.9	-3.7	4.57

Table 14: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 1 with rinsed process.

		coated			Δ		
SAM	**Treatment**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
LA	coated	43.9 ± 2.03	42.5 ± 4.34	60.62 ± 1.45			
	after NH_3	33.3 ± 2.02	34.0 ± 3.21	68.45 ± 1.17	-10.6	-8.5	7.83
	after IPA	38.6 ± 1.79	27.3 ± 3.93	67.19 ± 1.38	5.3	-6.7	-1.26
	after HF	32.8 ± 2.22	29.2 ± 1.25	69.74 ± 0.58	-5.8	1.9	2.55
STA	coated	42.3 ± 3.16	47.8 ± 4.24	60.20 ± 1.48			
	after NH_3	56.0 ± 7.24	48.2 ± 5.92	51.79 ± 2.10	13.7	0.4	-8.41
	after IPA	42.2 ± 5.12	37.3 ± 5.01	62.91 ± 1.89	-13.8	-10.9	11.12
	after HF	50.3 ± 2.67	34.0 ± 5.61	59.22 ± 1.86	8.1	-3.3	-3.69
TDPA	coated	89.6 ± 3.02	58.4 ± 3.87	31.99 ± 0.91			
	after NH_3	51.4 ± 3.36	44.1 ± 1.23	55.75 ± 0.61	-38.2	-14.3	23.76
	after IPA	56.5 ± 5.32	40.3 ± 0.92	53.91 ± 0.67	5.1	-3.8	-1.84
	after HF	46.0 ± 5.18	38.2 ± 3.91	60.57 ± 1.53	-10.5	-2.1	6.66
ODPA	coated	88.6 ± 4.92	59.6 ± 2.82	31.74 ± 0.75			
	after NH_3	79.9 ± 3.16	54.2 ± 3.29	37.20 ± 0.89	-8.7	-5.4	5.46
	after IPA	77.6 ± 6.06	51.3 ± 3.40	39.34 ± 1.07	-2.3	-2.9	2.14
	after HF	89.4 ± 1.81	60.6 ± 4.62	31.02 ± 1.05	11.8	9.3	-8.32
TDA	coated	89.0 ± 3.44	65.0 ± 0.88	29.21 ± 0.31			
	after NH_3	84.3 ± 6.50	59.4 ± 1.62	33.25 ± 0.62	-4.7	-5.6	4.04
	after IPA	76.5 ± 4.81	48.9 ± 2.27	40.78 ± 0.76	-7.8	-10.5	7.53
	after HF	61.9 ± 8.47	46.6 ± 3.86	48.85 ± 1.57	-14.6	-2.3	8.07
ODA	coated	92.8 ± 1.66	64.6 ± 1.29	28.26 ± 0.30			
	after NH_3	89.4 ± 1.47	61.9 ± 2.95	30.47 ± 0.06	-3.4	-2.7	2.21
	after IPA	86.0 ± 4.58	59.0 ± 4.26	32.86 ± 0.02	-3.4	-2.9	2.39
	after HF	85.6 ± 4.72	56.5 ± 4.16	34.08 ± 1.07	-0.4	-2.5	1.22
ODO	coated	40.0 ± 1.65	49.1 ± 6.24	61.25 ± 2.04			
	after NH_3	31.5 ± 3.82	36.5 ± 2.36	68.79 ± 1.07	-8.5	-12.6	7.54
	after IPA	41.4 ± 3.14	31.5 ± 2.38	64.78 ± 0.96	9.9	-5.0	-4.01
	after HF	51.1 ± 6.41	39.8 ± 2.68	57.18 ± 1.25	9.7	8.3	-7.60
DDBSA	coated	42.9 ± 1.35	49.1 ± 10.19	59.54 ± 0.15			
	after NH_3	34.3 ± 2.39	30.8 ± 3.67	68.64 ± 1.35	-8.6	-18.3	9.10
	after IPA	46.2 ± 2.77	35.5 ± 0.81	61.12 ± 0.47	11.9	4.7	-7.52
	after HF	32.3 ± 2.73	36.2 ± 1.98	68.46 ± 0.84	-13.9	0.7	7.34
ODT	coated	59.6 ± 5.21	44.7 ± 0.82	50.79 ± 0.62			
	after NH_3	37.9 ± 1.12	38.0 ± 2.42	65.16 ± 0.84	-21.7	-6.7	14.37
	after IPA	41.7 ± 2.27	36.1 ± 2.68	63.49 ± 0.98	3.8	-1.9	-1.67
	after HF	39.8 ± 3.44	29.7 ± 4.03	66.04 ± 1.50	-1.9	-6.4	2.55
PFND	coated	68.4 ± 2.80	68.9 ± 1.71	37.93 ± 0.57			
	after NH_3	36.0 ± 3.52	40.4 ± 1.62	65.57 ± 0.81	-32.4	-28.5	27.64
	after IPA	36.9 ± 2.56	36.3 ± 1.19	66.06 ± 0.59	0.9	-4.1	0.49
	after HF	44.6 ± 3.70	38.3 ± 1.93	61.30 ± 0.86	7.7	2.0	-4.76
PFNA	coated	44.7 ± 2.94	74.1 ± 5.99	53.68 ± 1.83			
	after NH_3	42.9 ± 7.19	41.7 ± 4.60	61.44 ± 1.93	-1.8	-32.4	7.76
	after IPA	45.2 ± 6.50	34.2 ± 1.77	62.06 ± 1.08	2.3	-7.5	0.62
	after HF	45.7 ± 6.76	36.0 ± 2.39	61.31 ± 1.26	0.5	1.8	-0.75
PFTDA	coated	43.9 ± 1.37	51.1 ± 6.47	58.40 ±2.06			
	after NH_3	30.7 ± 4.32	34.3 ± 3.40	69.64 ± 1.43	-13.2	-16.8	11.24
	after IPA	34.6 ± 4.45	38.7 ± 1.32	66.71 ± 0.84	3.9	4.4	-2.93
	after HF	35.5 ± 7.12	33.1 ± 4.00	67.56 ± 1.84	0.9	-5.6	0.85

Table 15: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 without rinsed process.

		coated			Δ		
SAM	**Treatment**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
LA	coated	37.6 ± 1.83	40.7 ± 3.31	64.63 ± 1.16			
	after NH_3	36.1 ± 1.82	33.4 ± 4.24	67.19 ± 1.49	-1.5	-7.3	2.56
	after IPA	41.2 ± 1.76	30.7 ± 2.47	65.10 ± 0.89	5.1	-2.7	-2.09
	after HF	34.4 ± 5.02	28.3 ± 2.05	69.11 ± 1.09	-6.8	-2.4	4.01
STA	coated	38.3 ± 1.89	67.1 ± 2.47	58.85 ± 0.84			
	after NH_3	54.5 ± 5.85	52.3 ± 5.42	51.48 ± 1.87	16.2	-14.8	-7.37
	after IPA	58.1 ± 2.52	46.8 ± 5.68	50.98 ± 1.74	3.6	-5.5	-0.50
	after HF	56.1 ± 5.51	51.7 ± 5.90	50.70 ± 1.96	-2.0	4.9	-0.28
TDPA	coated	97.9 ± 1.67	66.5 ± 4.87	26.14 ± 0.98			
	after NH_3	50.9 ± 5.78	45.3 ± 1.20	55.72 ± 0.84	-47.0	-21.2	29.58
	after IPA	59.9 ± 3.81	42.4 ± 2.94	51.34 ± 1.03	9.0	-2.9	-4.38
	after HF	66.6 ± 4.88	50.2 ± 5.71	45.04 ± 1.73	6.7	7.8	-6.30
ODPA	coated	98.5 ± 0.44	71.7 ± 0.84	23.60 ± 0.16			
	after NH_3	84.9 ± 2.74	61.1 ± 1.18	32.30 ± 0.36	-13.6	-10.6	8.70
	after IPA	88.6 ± 1.28	62.9 ± 1.06	30.26 ± 0.26	3.7	1.8	-2.04
	after HF	94.5 ± 1.64	67.6 ± 1.38	26.41 ± 0.31	5.9	4.7	-3.85
TDA	coated	92.9 ± 3.24	62.1 ± 1.05	29.39 ± 0.30			
	after NH_3	82.0 ± 4.08	56.7 ± 1.88	35.27 ± 0.59	-10.9	-5.4	5.88
	after IPA	67.5 ± 5.52	50.5 ± 2.56	44.45 ± 0.97	-14.5	-6.2	9.18
	after HF	79.2 ± 2.01	47.2 ± 2.13	40.39 ± 0.59	11.7	-3.3	-4.06
ODA	coated	93.4 ± 1.87	67.3 ± 1.23	26.83 ± 0.29			
	after NH_3	96.4 ± 1.66	63.2 ± 0.73	28.06 ± 0.18	3.0	-4.1	1.23
	after IPA	84.9 ± 2.97	59.7 ± 0.44	32.92 ± 0.22	-11.5	-3.5	4.86
	after HF	91.8 ± 2.33	60.6 ± 1.56	30.39 ± 0.38	6.9	0.9	-2.53
ODO	coated	31.1 ± 2.02	70.4 ± 2.60	62.98 ± 0.91			
	after NH_3	35.7 ± 1.71	55.2 ± 10.15	62.42 ± 3.29	4.6	-15.2	-0.56
	after IPA	36.3 ± 5.03	36.2 ± 0.40	66.42 ± 0.67	0.6	-19.0	4.00
	after HF	32.9 ± 4.07	36.7 ± 2.95	68.04 ± 1.26	-3.4	0.5	1.62
DDBSA	coated	29.2 ± 2.39	59.5 ± 2.35	65.27 ± 0.90			
	after NH_3	20.8 ± 3.62	34.2 ± 1.69	73.79 ± 0.89	-8.4	-25.3	8.52
	after IPA	32.3 ± 5.65	37.2 ± 2.51	68.21 ± 1.30	11.5	3.0	-5.58
	after HF	32.0 ± 3.67	28.2 ± 1.55	70.33 ± 0.82	-0.3	-9.0	2.12

Table 16: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 with rinsed process.

		coated			Δ		
SAM	**Treatment**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
LA	coated	41.3 ± 1.14	45.6 ± 5.16	61.35 ± 1.69			
	after NH_3	37.9 ± 3.90	36.0 ± 2.70	65.62 ± 1.14	-3.4	-9.6	4.27
	after IPA	41.9 ± 1.64	29.8 ± 3.81	64.91 ± 1.32	4.0	-6.2	-0.71
	after HF	31.2 ± 2.07	26.2 ± 2.91	71.10 ± 1.10	-10.7	-3.6	6.19
STA	coated	41.3 ± 1.03	53.6 ± 3.84	59.47 ± 1.24			
	after NH_3	52.5 ± 8.64	47.3 ± 4.19	54.17 ± 1.81	11.2	-6.3	-5.3
	after IPA	47.3 ± 0.91	42.7 ± 4.97	58.56 ± 1.59	-5.2	-4.6	4.39
	after HF	46.8 ± 6.68	35.7 ± 4.17	60.76 ± 1.72	-0.5	-7.0	2.2
TDPA	coated	87.7 ± 5.41	60.5 ± 4.99	31.60 ± 1.23			
	after NH_3	39.2 ± 5.39	42.1 ± 1.13	63.41 ± 0.87	-48.5	-18.4	31.81
	after IPA	51.9 ± 2.48	33.4 ± 1.14	58.52 ± 0.51	12.7	-8.7	-4.89
	after HF	47.4 ± 10.01	42.5 ± 5.54	58.58 ± 2.37	-4.5	9.1	0.06
ODPA	coated	88.6 ± 3.50	59.4 ± 3.59	31.85 ± 0.87			
	after NH_3	79.6 ± 2.81	59.9 ± 1.43	34.95 ± 0.45	-9.0	0.5	3.1
	after IPA	79.9 ± 4.27	55.7 ± 3.05	36.55 ± 0.88	0.3	-4.2	1.6
	after HF	92.1 ± 2.43	63.2 ± 1.68	29.06 ± 0.41	12.2	7.5	-7.49
TDA	coated	84.2 ± 3.45	61.3 ± 2.30	32.49 ± 0.63			
	after NH_3	81.3 ± 8.74	51.8 ± 3.07	37.63 ± 1.06	-2.9	-9.5	5.14
	after IPA	69.5 ± 5.29	43.6 ± 2.26	45.98 ± 0.86	-11.8	-8.2	8.35
	after HF	70.9 ± 1.98	44.0 ± 1.57	45.15 ± 0.49	1.4	0.4	-0.83
ODA	coated	91.5 ± 1.59	61.6 ± 2.40	30.01 ± 0.54			
	after NH_3	94.8 ± 2.37	62.0 ± 2.00	28.96 ± 0.45	3.3	0.4	-1.05
	after IPA	79.9 ± 8.08	55.9 ± 3.83	36.49 ± 1.22	-14.9	-6.1	7.53
	after HF	87.4 ± 3.46	54.1 ± 2.25	34.62 ± 0.60	7.5	-1.8	-1.87
ODO	coated	37.6 ± 2.34	52.0 ± 2.67	62.02 ± 0.97			
	after NH_3	35.4 ± 4.99	39.8 ± 2.68	66.04 ± 1.25	-2.2	-12.2	4.02
	after IPA	36.9 ± 5.84	33.6 ± 0.58	66.67 ± 0.79	1.5	-6.2	0.63
	after HF	36.4 ± 4.35	32.1 ± 2.43	67.31 ± 1.12	-0.5	-1.5	0.64
DDBSA	coated	37.5 ± 2.98	51.1 ± 3.54	62.33 ± 1.28			
	after NH_3	24.4 ± 1.96	35.9 ± 2.13	72.09 ± 0.84	-13.1	-15.2	9.76
	after IPA	35.3 ± 5.00	33.5 ± 5.52	67.57 ± 2.11	10.9	-2.4	-4.52
	after HF	38.6 ± 3.96	32.4 ± 2.21	66.05 ± 1.00	3.3	-1.1	-1.52

The values of pretr. 1 after the NH_3 step for the amine coated surfaces agree with the values for the phosphonic acids although the decrease of the water CA is 5 – 8° for TDA and 3 – 4° for ODA and therewith lower than with the phosphonic acids. The decrease is higher for both substance classes for the tetradecanoic compounds. This leads to the conclusion that the removal with NH_3 is more hindered the longer the tail chain is.

With pretr. 2 the water CA decreases for TDA about 3 – 11° but increases for ODA about 3° after the treatment with NH_3. The little increase of the ODA could be a proof for the earlier statement that the layers are not removed evenly. Figure 16 shows a photo of one water CA of TDA coated surface after

the NH_3 step. It is discernible that the removing after NH_3 was not homogenous because the right angle contour is flatter than the left one.

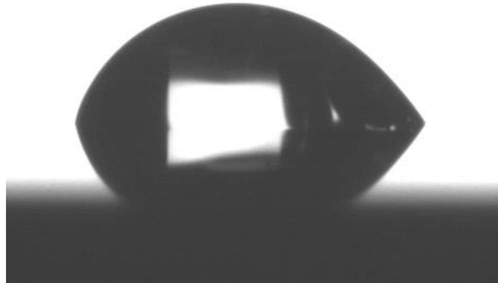


Figure 16: Picture of the water contact angle of a TDA coated tungsten surface (THF, pretr. 2, without rinsed process). Image was taken after the NH_3 removing step.

Water CA of LA coated surfaces show a decrease after the NH_3 step, an increase after the IPA and again, a decrease after the HF step. The water CAs of LA coated surfaces are between 23° and 34° after the last removing step with HF. That is an averaged decrease of 10°. The diiodomethane CAs are decreasing after the treatment with NH_3 and IPA and increasing after HF for pretr. 1. For pretr.2 the diiodomethane CA decreases after the HF step as well. Removal of the layers is not complete but partially because the cleaned values (Table 1) are not achieved but a total decrease after the last removing step with HF is discernible.

Notably interest should be paid to the STA layer. With all pretreatments and treatments the water CA after the NH_3 step increases. Without rinsed process the values increasing about 5° or 16° and with the rinsed process 14° or 11°. Standard deviations are between 6 and 9°. The results are traced back to the reorientation of long chains before the attack of the aqueous ammonia. This could be the explanation for the higher water CAs because the reorientation leads to straightened nonpolar chains and therefore the more hydrophobic behavior especially for longer chains (orientation needs longer). Additionally, as mentioned before, a hindrance because of the longer carbon chain is possible. After IPA the water CAs decrease and increase again after the HF step. Only the experiment with pretreatment 2 and without rinsed process does not agree with these observations. The total decrease of the water CA and the high standard deviation can be explained through a partially removing of the coating.

DDBSA and ODO show no trend except the increase of the water CA after the IPA step. The increase of the CAs is perhaps because IPA is able to diffuse between the chains and interact with the nonpolar part. Furthermore, the orientation effect could occur again.

ODT shows a decrease after the NH_3 and the HF step for both angles and therefore, an increase of the surface energy. The treatment with IPA differs. One time the water CA decreases about 2° and the second time it increases about 4°. The diiodomethane angles decrease for both experiments (Table 13 and Table 14).

PFND shows, as mentioned before, a high decrease of the water CA after the NH_3 step. PFND, PFNA and PFTDA have the increase of the water CA after the IPA step in common. It is discernible that for the chips treated without rinsed process after the coating the water CA after HF decreases whereas the chips treated with the rinsed process increase after the HF treatment whereby the increase for PFNA and PFTDA is just about 1° and for PFND 8°. The diiodomethane CA of all three fluorinated substances decreases after the NH_3 removal. PFND further, shows a decrease after IPA step. Only the behavior after the HF step differs for the PFND chips with and without the rinsed. For PFNA coated surfaces the behavior of the diiodomethane CA is the same for the experiments with and without rinsed process: decrease, decrease, increase. PFTDA instead shows different behavior after the treatment with IPA.

For most of the experiments the treatment with 5% NH_3 leads to a partially removing. Only STA shows constant increase of the water CA after the NH_3 step. ODA, ODO and DDBSA show only two times respectively one time an increase after NH_3. The removal cannot be complete after the treatment with NH_3 because the values for the cleaned chips are not achieved neither for the CAs nor the surface energies. IPA instead leads to an increase of the water CA for LA, TDPA, ODPA, ODO, DDBSA and the three fluorinated compounds. ODPA has just one time a lower CA.

For the treatment with HF no trend is discernible. The only exception is ODPA. All 4 experiments show an increase of the water CA after the HF step compared to the values after the IPA step. In Figure 17 two water contact angles of the same chip after the removing with HF from different parts of the chip are shown, exemplarily for all experiments. Again (like in Figure 16), it is clearly discernible that removing is not homogenous. The right picture shows still a drop contour whereas in the left picture the water moistens the surface.

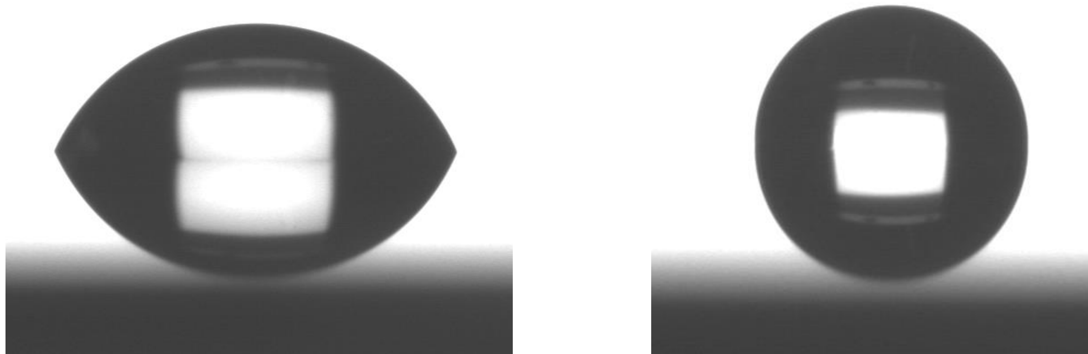


Figure 17: Picture of water contact angle of an ODA coated tungsten surface (THF, pretr. 2, without rinsed process) after the HF removing step. Both images were taken from the same chip.

The images correspond to the data of Table 13 to Table 16 and prove the inhomogeneous and not complete removing of the layers. According to these results the lack of any trend is explainable. These results lead to the conclusion that the removing liquids are not strong enough respectively the immersion time in the removing liquids was not adequate. Furthermore, the inhomogeneity of the removing can be traced back to the inhomogeneous coating and aggregation building of the SAM materials. This observation correlates to the AFM pictures in the previous chapter (Figure 10 to Figure 14).

A possible explanation for the increase after the removing step with HF could be that the layers encapsulate and the acid is not able to diffuse between the layers. Instead of the removing an order occurs. The differing of the values agrees with this statement because the layers are not homogenous affected by the previous removal liquids. Further experiments are necessary to prove this theory. The behavior of the diiodomethane CAs is not analog to that of the water angles. However, no clear trend is discernible. Partially the angle increase and partially they decrease. The factor human can't be ruled out because the removing out of the beaker could have an influence on the orientation and the removal of the layers.

The averaged cleaned value (Table 1) for the water CA is achieved after the last removing step with HF just for the LA (pretr. 1, without rinsed process; pretr. 2, with rinsed process) and DDBSA (pretr. 1, without rinsed process) coated surfaces. The starting diiodomethane CA is received for LA, ODO, DDBSA, ODT and PFTDA for different experiments. Among this substances no trend, except for LA (all four experiments) is discernible. Therefore, removing occurs but only a part of the coating is removed.

The comparison of LA with STA, TDA with ODA and TDPA with ODPA shows that the longer chains are more stable.

Woodward et al.[21] proved in their work that the water CA of an ODPA coated surface decreases after the water CA remained on the mica surface for 5 min. The rinsed process (with the same solvent than the experiment was done in) removes surplus material but the aqueous liquid attacks the coating layer. Therefore, it is possible that the immersion time in the aqueous ammonia and HF was not long enough to lead to a complete removing of the SAM.

If it is assumed that after the NH_3 step the SAM is removed partially it is supposable that after the treatment with IPA an orientation effect (reorientation of the long chains) occurs. This effect leads to the increase of the water CAs and the decrease of the surface energies after the IPA removing step. Further experiments are necessary to prove this statement.

The results of the similar experiments for the coating done in IPA are presented in Table 17 to Table 20.

After the immersion in NH_3 all the substances show a decrease of the water and diiodomethane CAs. Only for ODO and STA coated surfaces the CAs are differing: ODO shows an increase of 0.4° of the water CA for the chip treated with pretr. 1 and the rinsed process and STA an increase of 0.5° of the diiodomethane CA for the chip treated with pretr. 1 without the rinsed process. The highest decrease of 55° is discernible for the PFNA coated surface.

An increase of the water CA after the IPA step is discernible for DDBSA, ODT and the fluorinated compounds. The water CA of the STA, TDPA and ODPA coated surfaces is not constantly increasing for all the experiments. No trend compared to the experiments in THF can be found for the IPA removal. The increase of the angle is explainable via the ordering of the long chains. Probably, the treatment with the aqueous NH_3 leads to the removal of a part of the binding molecules (this statement agrees with the decreasing CAs which do not achieve the cleaned starting values). Not all the remaining methyl chains are pointing in the same direction respectively are tilted in the same angle. Then the IPA orders the molecules. Further analysis, like X-ray reflectivity, is necessary to prove this statement. The fact that there is no consistent behavior within one SAM material is traced back to the inhomogeneous coating.

Table 17: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in IPA) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 1 without rinsed process.

		coated			Δ		
SAM	Treatment	CA [°]		σ [mN/m]	CA [°]		σ [mN/m]
		H_2O	CH_2I_2		H_2O	CH_2I_2	
LA	coated	43.6 ± 0.65	38.4 ± 2.15	61.84 ± 0.71			
	after NH_3	32.3 ± 1.61	27.4 ± 1.11	70.33 ± 0.49	-11.3	-11.0	8.49
	after IPA	26.0 ± 1.88	31.3 ± 3.13	72.37 ± 1.17	-6.3	3.9	2.04
	after HF	36.7 ± 2.80	31.1 ± 3.25	67.36 ± 1.22	10.7	-0.2	-5.01
STA	coated	34.3 ± 1.45	40.3 ± 2.04	66.53 ± 0.75			
	after NH_3	31.8 ± 1.35	37.8 ± 0.96	68.30 ± 0.41	-2.5	-2.5	1.77
	after IPA	37.0 ± 3.25	32.0 ± 2.02	66.99 ± 0.89	5.2	-5.8	-1.31
	after HF	40.7 ± 6.09	35.0 ± 4.93	64.31 ± 1.96	3.7	3.0	-2.68
TDPA	coated	87.5 ± 3.60	59.7 ± 3.87	32.07 ± 0.94			
	after NH_3	38.9 ± 3.99	33.3 ± 2.44	65.71 ± 1.07	-48.6	-26.4	33.64
	after IPA	39.4 ± 5.90	39.8 ± 0.52	63.87 ± 0.78	0.5	6.5	-1.84
	after HF	54.0 ± 6.04	43.6 ± 3.89	54.37 ± 1.50	14.6	3.8	-9.5
ODPA	coated	94.6 ± 3.55	62.0 ± 3.84	29.04 ± 0.85			
	after NH_3	77.7 ± 6.35	48.7 ± 1.37	40.39 ± 0.63	-16.9	-13.3	11.35
	after IPA	70.1 ± 12.39	49.6 ± 2.84	43.49 ± 1.45	-7.6	0.9	3.1
	after HF	86.7 ± 2.72	58.5 ± 2.66	32.85 ± 0.66	16.6	8.9	-10.64
TDA	coated	93.2 ± 4.29	68.3 ± 1.55	26.44 ± 0.43			
	after NH_3	85.5 ± 6.59	58.9 ± 2.63	33.07 ± 0.81	-7.7	-9.4	6.63
	after IPA	80.0 ± 2.81	54.2 ± 1.61	37.14 ± 0.49	-5.5	-4.7	4.07
	after HF	68.1 ± 3.57	42.8 ± 3.21	46.95 ± 1.02	-11.9	-11.4	9.81
ODA	coated	100.1 ± 1.66	70.4 ± 1.34	23.86 ± 0.28			
	after NH_3	88.5 ± 3.76	67.3 ± 1.57	28.38 ± 0.46	-11.6	-3.1	4.52
	after IPA	86.5 ± 1.41	59.4 ± 2.25	32.48 ± 0.54	-2.0	-7.9	4.1
	after HF	90.2 ± 1.39	62.5 ± 0.72	29.94 ± 0.19	3.7	3.1	-2.54
ODO	coated	52.8 ± 3.86	48.9 ± 4.52	53.55 ± 1.52			
	after NH_3	53.2 ± 4.62	48.1 ± 6.43	53.47 ± 2.10	0.4	-0.8	-0.08
	after IPA	43.7 ± 2.01	32.1 ± 1.98	63.35 ± 0.74	-9.5	-16.0	9.88
	after HF	30.3 ± 1.76	37.0 ± 3.08	69.25 ± 1.12	-13.4	4.9	5.9
DDBSA	coated	19.7 ± 2.36	53.1 ± 2.76	70.54 ± 1.06			
	after NH_3	16.3 ± 3.78	36.1 ± 3.53	74.89 ± 1.48	-3.4	-17.0	4.35
	after IPA	23.5 ± 3.99	32.1 ± 0.57	73.24 ± 0.63	7.2	-4.0	-1.65
	after HF	21.2 ± 4.43	32.4 ± 0.57	74.02 ± 0.70	-2.3	0.3	0.78
ODT	coated	45.4 ± 1.29	39.8 ± 1.10	60.45 ± 0.42			
	after NH_3	31.7 ± 4.94	36.8 ± 2.34	68.59 ± 1.18	-13.7	-3.0	8.14
	after IPA	39.0 ± 3.72	35.0 ± 1.65	65.28 ± 0.82	7.3	-1.8	-3.31
	after HF	46.3 ± 6.85	39.0 ± 4.63	60.13 ± 1.87	7.3	4.0	-5.15
PFND	coated	51.8 ± 1.62	57.7 ± 3.74	51.77 ± 1.15			
	after NH_3	30.6 ± 3.68	37.0 ± 2.87	69.12 ± 1.20	-21.2	-20.7	17.35
	after IPA	30.6 ± 3.05	31.2 ± 1.86	70.38 ± 0.85	0.0	-5.8	1.26
	after HF	32.7 ± 3.16	31.9 ± 0.91	69.22 ± 0.59	2.1	0.7	-1.16
PFNA	coated	29.9 ± 7.93	87.8 ± 5.45	64.06 ± 2.26			
	after NH_3	24.1 ± 1.96	32.8 ± 2.55	72.84 ± 0.98	-5.8	-55.0	8.78
	after IPA	33.9 ± 4.45	36.2 ± 1.45	67.65 ± 0.87	9.8	3.4	-5.19
	after HF	31.6 ± 3.57	36.1 ± 1.53	68.85 ± 0.81	-2.3	-0.1	1.2
PFTDA	coated	28.7 ± 2.68	80.2 ± 3.19	64.18 ± 1.11			
	after NH_3	22.6 ± 4.33	41.3 ± 2.67	71.68 ± 1.25	-6.1	-38.9	7.5
	after IPA	32.4 ± 3.17	37.3 ± 0.67	68.17 ± 0.54	9.8	-4.0	-3.51
	after HF	31.8 ± 6.19	42.0 ± 8.01	67.43 ± 2.98	-0.6	4.7	-0.74

Table 18: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in IPA) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 1 with the rinsed process.

		coated			Δ		
SAM	**Treatment**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
LA	coated	38.0 ± 1.20	35.7 ± 1.91	65.63 ± 0.68			
	after NH_3	32.8 ± 1.60	29.4 ± 2.06	69.70 ± 0.78	-5.2	-6.3	4.07
	after IPA	29.3 ± 2.61	31.7 ± 3.38	70.87 ± 1.29	-3.5	2.3	1.17
	after HF	39.1 ± 1.12	30.8 ± 1.80	66.19 ± 0.64	9.8	-0.9	-4.68
STA	coated	35.2 ± 1.92	40.3 ± 1.04	66.03 ± 0.49			
	after NH_3	34.4 ± 2.40	40.8 ± 2.44	66.36 ± 0.94	-0.8	0.5	0.33
	after IPA	30.3 ± 2.46	32.5 ± 1.86	70.21 ± 0.79	-4.1	-8.3	3.85
	after HF	36.4 ± 7.04	38.1 ± 2.29	65.93 ± 1.36	6.1	5.6	-4.28
TDPA	coated	83.5 ± 3.32	52.0 ± 3.67	36.82 ± 0.95			
	after NH_3	45.3 ± 5.75	39.8 ± 2.69	60.51 ± 1.25	-38.2	-12.2	23.69
	after IPA	54.4 ± 4.14	39.7 ± 2.25	55.29 ± 0.92	9.1	-0.1	-5.22
	after HF	70.7 ± 6.13	36.3 ± 4.77	48.01 ± 1.53	16.3	-3.4	-7.28
ODPA	coated	87.6 ± 2.94	59.1 ± 5.04	32.29 ± 1.19			
	after NH_3	62.3 ± 12.25	40.7 ± 5.47	50.60 ± 2.23	-25.3	-18.4	18.31
	after IPA	63.7 ± 13.04	45.2 ± 3.15	48.35 ± 1.70	1.4	4.5	-2.25
	after HF	65.5 ± 12.73	49.4 ± 5.86	45.94 ± 2.28	1.8	4.2	-2.41
TDA	coated	93.6 ± 1.77	66.1 ± 1.22	27.34 ± 0.29			
	after NH_3	86.8 ± 6.29	60.8 ± 2.75	31.82 ± 0.81	-6.8	-5.3	4.48
	after IPA	79.2 ± 2.29	76.5 ± 4.81	38.97 ± 0.73	-7.6	15.7	7.15
	after HF	64.5 ± 3.54	48.1 ± 5.39	46.94 ± 1.62	-14.7	-28.4	7.97
ODA	coated	95.0 ± 0.71	69.0 ± 1.12	25.64 ± 0.23			
	after NH_3	92.0 ± 2.79	68.1 ± 1.46	26.88 ± 0.37	-3.0	-0.9	1.24
	after IPA	86.6 ± 2.01	59.8 ± 2.87	32.27 ± 0.69	-5.4	-8.3	5.39
	after HF	89.5 ± 1.36	62.1 ± 1.24	30.32 ± 0.30	2.9	2.3	-1.95
ODO	coated	45.3 ± 5.16	37.4 ± 3.14	61.16 ± 1.32			
	after NH_3	28.7 ± 3.41	30.8 ± 3.68	71.29 ± 1.45	-16.6	-6.6	10.13
	after IPA	38.1 ± 2.19	34.1 ± 0.65	65.92 ± 0.40	9.4	3.3	-5.37
	after HF	29.0 ± 3.00	38.2 ± 1.48	69.63 ± 0.74	-9.1	4.1	3.71
DDBSA	coated	25.8 ± 1.28	43.8 ± 1.83	69.84 ± 0.68			
	after NH_3	14.6 ± 3.18	34.7 ± 3.58	75.64 ± 1.44	-11.2	-9.1	5.80
	after IPA	26.6 ± 1.52	31.2 ± 1.44	72.15 ± 0.59	12.0	-3.5	-3.49
	after HF	24.2 ± 5.12	33.2 ± 1.50	72.71 ± 1.01	-2.4	2.0	0.56
ODT	coated	44.2 ± 1.11	40.4 ± 3.06	60.98 ± 1.02			
	after NH_3	38.3 ± 3.98	37.9 ± 2.03	64.97 ± 0.95	-5.9	-2.5	3.99
	after IPA	41.1 ± 1.85	36.3 ± 1.23	63.82 ± 0.52	2.8	-1.6	-1.15
	after HF	32.0 ± 4.47	30.5 ± 1.96	69.81 ± 1.02	-9.1	-5.8	5.99
PFND	coated	56.8 ± 8.82	68.1 ± 11.67	45.93 ± 3.56			
	after NH_3	30.2 ± 2.30	37.0 ± 3.04	69.30 ± 1.14	-26.6	-31.1	23.37
	after IPA	30.4 ± 1.75	35.5 ± 1.41	69. 54 ± 0.59	0.2	-1.5	0.24
	after HF	27.8 ± 4.46	32.8 ± 2.30	71.28 ± 1.14	-2.6	-2.7	1.74
PFNA	coated	34.2 ± 0.71	70.8 ± 5.53	61.04 ± 1.70			
	after NH_3	19.1 ± 3.49	30.9 ± 1.43	75.04 ± 0.81	-15.1	-39.9	14.00
	after IPA	28.7 ± 1.84	35.4 ± 2.14	70.35 ± 0.83	9.6	4.5	-4.69
	after HF	29.4 ± 12.31	30.9 ± 3.84	70.99 ± 2.42	0.7	-4.5	0.64
PFTDA	coated	28.3 ± 2.56	73.4 ± 1.85	64.42 ± 0.77			
	after NH_3	25.7 ± 6.15	36.7 ± 8.51	71.40 ± 3.22	-2.6	-36.7	6.98
	after IPA	33.7 ± 6.36	33.6 ± 3.90	68.34 ± 1.75	8.0	-3.1	-3.06
	after HF	26.5 ± 3.00	35.4 ± 2.82	71.32 ± 1.15	-7.2	1.8	2.98

Table 19: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in IPA) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 without rinsed process.

		coated			Δ		
SAM	**Treatment**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
ODPA	coated	94.4 ± 1.29	64.3 ± 0.94	27.98 ± 0.22			
	after NH_3	79.3 ± 4.27	59.3 ± 1.83	35.33 ± 0.61	-15.1	-5.0	7.35
	after IPA	84.8 ± 3.87	55.6 ± 2.44	34.74 ± 0.67	5.5	-3.7	-0.59
	after HF	84.6 ± 8.75	57.4 ± 4.18	34.02 ± 1.24	-0.2	1.8	-0.72
ODA	coated	96.5 ± 2.33	68.5 ± 0.67	25.50 ± 0.19			
	after NH_3	94.9 ± 2.80	65.3 ± 2.37	27.39 ± 0.53	-1.6	-3.2	1.89
	after IPA	86.7 ± 5.25	57.6 ± 1.42	33.24 ± 0.50	-8.2	-7.7	5.85
	after HF	78.4 ± 7.31	54.0 ± 2.87	37.90 ± 1.00	-8.3	-3.6	4.66

Table 20: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in IPA) and removing steps with 5% NH_3, IPA and 10% HF. All coated values are received after pretreatment 2 with the rinsed process.

		coated			Δ		
SAM	**Treatment**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
ODPA	coated	82.9 ± 2.79	58.6 ± 2.11	34.13 ± 0.57			
	after NH_3	65.6 ± 5.04	51.0 ± 2.75	45.29 ± 1.00	-17.3	-7.6	11.16
	after IPA	68.2 ± 7.93	47.5 ± 2.07	45.17 ± 1.01	2.6	-3.5	-0.12
	after HF	77.4 ± 5.36	48.0 ± 1.90	40.77 ± 0.69	9.2	0.5	-4.40
ODA	coated	91.6 ± 3.35	64.3 ± 0.94	28.73 ± 0.30			
	after NH_3	91.4 ± 3.30	63.7 ± 2.21	29.06 ± 0.54	-0.2	-0.6	0.33
	after IPA	85.4 ± 1.69	53.6 ± 2.66	35.44 ± 0.66	-6.0	-10.1	6.38
	after HF	80.8 ± 8.09	51.4 ± 4.55	38.03 ± 1.37	-4.6	-2.2	2.59

After the treatment with HF LA, STA, ODPA, ODA, ODO, DDBSA and PFTDA coated surfaces show the same behavior for pretr. 1 with and without the rinsed process. For LA the water CA increase and the diiodomethane CA decreases after the treatment with HF compared to the values after the IPA step. For ODO, DDBSA and PFTDA coated surfaces the diiodomethane CA increases. For the STA and ODA coated surface the both angles increase. ODPA follows this last trend except for the experiment done with pretr. 2 without the rinsed process – a decrease of water CA of 0.2° occurs although the standard deviation of about 9° is quite high. This high standard deviation for the ODPA coated surface agrees with the values of the chips coated in THF. Therefore, again, an inhomogeneous removal is probably.

For ODA coated surfaces both angles show a decrease for the experiments done with pretr. 2 (Table 19 and Table 20). The differences between pretr. 1 and pretr. 2 are lower than 10°. Again, these results lead to the conclusion of inhomogeneous removal which correlates with the observation of Figure 17.

For LA coated surfaces the data do not agree for the experiments done in IPA and THF. In IPA water CA increases after the HF step although, in summary an angle decrease of 7° occurs (15° in THF). That means that in summary a part of the layer is removed. The tests with LA in IPA lead to water CAs of 37° and 39° after the last removal steps. For LA the second value is even higher after removing than after the coating. The surface energy is also higher after removing because the diiodomethane angle decreases. Compared to THF the surface energies are in the same range. The results for STA do not agree in IPA and THF although for both solvents the water CA after the last removing step is higher than after the coating. The surface energies are higher in IPA than in THF. Diiodomethane CAs show also an increase after HF and no analogy to the THF values. The fatty acids, within the functional group, neither show a trend in IPA nor in THF compared to each other. For example STA coated surfaces have a water CA increase of 5° after the removing step with IPA and LA has a decrease of 6°. Also diiodomethane CAs and surface energies show no trend. These results are attributed to the difference in the chain length.

TDPA experiments in IPA and THF do not correlate. Only the little increase of the water CA after the IPA removing step is noticed in both cases. Diiodomethane angles again have no trend in common. Surface energies are averaged 15° higher for the tests in IPA. Also ODPA solved in IPA shows no similarities to the one solved in THF. The high standard deviation of the water CA after the IPA step leads to the conclusion that there are parts removed but not homogenously. Again an increase of the water CA after the HF step is seen. For both phosphonic acids the surface energies increase analogous to the decrease of the water CA.

Again, the wet chemical removing of the surface layers (coated in IPA) is partially successful. The cleaned water CA values (Table 1) are achieved for DDBSA, PFND, ODO, ODT, PFNA and PFTDA after the treatment with HF and the cleaned values of diiodomethane CA are achieved for LA, ODT, PFND and PFNA.

The differences and the lack of trends is traced back to inhomogeneous removal (see Figure 16 and Figure 17) because of inhomogeneous coating. This assumption correlates with the observation of aggregation of SAM materials and therefore, with the AFM measurements of the coated surfaces (see Figure 10 to Figure 14). Furthermore, it could be that the immersion time in the removal liquids was not long enough for complete removal.

3.2.1.2 Titanium nitride coated silicon wafer

Again, the pretreatment has no significant influence on the coating respectively the removing of the thin organic layers. Compared to the experiments done on tungsten surfaces the data are more homogenous on titanium nitride. In Table 21 to Table 26 the data for the removing experiments on the titanium nitride surfaces are presented.

All the coated surfaces (THF and IPA), except DDBSA in THF, show a decrease of the water CA after the treatment with NH_3. The diiodomethane CA decreases for all SAM materials, except ODA (THF and IPA), after the NH_3 immersion.

A decrease of the water and the diiodomethane CA after IPA is discernible for the amine coated surfaces for the experiments done in THF and IPA. No trend is noticed for TDPA, ODPA and ODT. TDPA decreases in three of five experiments, ODPA just in one experiment out of six and ODT in one out of two. For the other SAM materials the water CA increases after the IPA step compared to the angle after the treatment with NH_3. This increase leads again to conclusion that IPA is able to diffuse into the layers and interact with the nonpolar chains respectively lead to an ordering effect of the not removed monomers.

The diiodomethane CA decreases for all substance, except PFND and PFTDA, after the IPA removal for the experiments in THF. For the coatings received in IPA the angle decreases for STA, both amines and PFTDA after the IPA step.

Within the compounds containing the carbonyl group the values are differing. LA on the one hand, shows once a decrease of 42° in THF and once an increase of 5° in IPA for the water CA after the HF step. STA on the other hand, shows two times a decrease of 22° and 36°.

The water CA of the amine coated surfaces decreases in THF and IPA after the HF step. For TDA the water CA decreases 26° in THF and 28° in IPA and for ODA 15° in THF and 10° in IPA.

For TDPA coated surfaces the water CA decreases after the HF removal whereas (exception: THF, pretr. 2, with rinsed process) ODPA shows always an increasing water CA. The diiodomethane CA increases for both phosphonic acids after this removal step, except for the TDPA coated surface after pretr. 2 (IPA). The ODPA behavior correlates to the data received from tungsten.

All the other SAM materials show a decrease of the water and the diiodomethane CA and an increase of the surface energies after the treatment with HF, except ODO (THF), LA (IPA) and ODT (IPA) although the water CA of the cleaned surface (Table 6) is achieved only for ODT in THF. The diiodomethane CA of the cleaned surface is received for PFND and PFTDA after the HF step.

As a consequence, of these data the wet chemical removing of the organic layers was not complete – it seems that fragments are removed but not the whole layer.

Table 21: Contact angles (CA), surface energies (σ) and differences on titanium nitride after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All coated values are received after pretreatment 1 without rinsed process.

		coated			Δ		
SAM	**Treatment**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
TDPA	coated	92.3 ± 3.69	61.2 ± 2.25	29.98 ± 0.56			
	after NH_3	66.0 ± 1.04	47.2 ± 0.61	46.45 ± 0.22	-26.3	-14.0	16.47
	after IPA	64.5 ± 1.34	44.8 ± 1.94	48.06 ± 0.59	-1.5	-2.4	1.61
	after HF	50.4 ± 8.21	49.0 ± 4.44	54.99 ± 1.87	-14.1	4.2	6.93
ODPA	coated	94.0 ± 2.46	63.6 ± 0.98	28.40 ± 0.26			
	after NH_3	91.5 ± 2.03	61.4 ± 1.33	30.07 ± 0.33	-2.5	-2.2	1.67
	after IPA	88.6 ± 2.90	59.8 ± 1.11	31.64 ± 0.33	-2.9	-1.6	1.57
	after HF	96.0 ± 4.52	67.6 ± 2.91	26.02 ± 0.67	7.4	7.8	-5.62

Table 22: Contact angles (CA), surface energies (σ) and differences on titanium nitride after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All coated values are received after pretreatment 3 without rinsed process.

		coated			Δ		
SAM	**Treatment**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
ODPA	coated	96.1 ± 1.88	65.8 ± 1.08	26.87 ± 0.25			
	after NH_3	82.3 ± 3.53	54.9 ± 0.38	45.33 ± 0.93	-13.8	-10.9	18.46
	after IPA	88.7 ± 2.79	57.2 ± 1.83	32.80 ± 0.47	6.4	2.3	-12.53
	after HF	89.7 ± 1.33	60.5 ± 3.18	31.01 ± 0.72	1.0	3.3	-1.79

Table 23: Contact angles (CA), surface energies (σ) and differences on titanium nitride after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 1 with the rinsed process.

		coated			Δ		
SAM	**Treatment**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
TDPA	coated	93.5 ± 1.77	69.4 ± 1.77	25.88 ± 0.39			
	after NH_3	70.1 ± 3.58	45.0 ± 2.82	45.17 ± 0.90	-23.4	-24.4	19.29
	after IPA	68.7 ± 5.08	44.1 ± 1.50	46.17 ± 0.68	-1.4	-0.9	1.00
	after HF	59.9 ± 16.73	49.2 ± 3.97	48.15 ± 2.31	-8.8	5.1	1.98
ODPA	coated	96.7 ± 0.73	62.6 ± 0.92	28.28 ± 0.20			
	after NH_3	86.9 ± 1.38	59.5 ± 2.24	32.34 ± 0.53	-9.8	-3.1	4.06
	after IPA	90.8 ± 0.93	57.0 ± 1.33	32.32 ± 0.31	3.9	-2.5	-0.02
	after HF	92.0 ± 2.96	64.5 ± 1.76	28.49 ± 0.44	1.2	7.5	-3.83

Table 24: Contact angles (CA), surface energies (σ) and differences on titanium nitride after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 without rinsed process.

		coated			Δ		
SAM	**Treatment**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
TDPA	coated	96.6 ± 1.95	69.1 ± 1.02	32.93 ± 1.39			
	after NH_3	69.2 ± 2.86	48.3 ± 3.91	44.35 ± 1.14	-27.4	-20.8	11.42
	after IPA	63.0 ± 4.13	46.6 ± 2.02	48.24 ± 0.79	-6.2	-1.7	3.89
	after HF	51.5 ± 5.80	47.0 ± 4.01	54.84 ± 1.54	-11.5	0.4	6.6
ODPA	coated	96.8 ± 1.70	63.6 ± 1.75	27.78 ± 0.38			
	after NH_3	83.6 ± 2.47	59.8 ± 0.98	33.37 ± 0.32	-13.2	-3.8	5.59
	after IPA	87.6 ± 0.99	57.8 ± 1.06	32.87 ± 0.26	4.0	-2.0	-0.5
	after HF	92.0 ± 3.56	63.5 ± 1.50	28.95 ± 0.41	4.4	5.7	-3.92

Comparison of Table 25 and Table 26 leads to following observations: increase or decrease of water CA after the treatment with different removing liquids is the same for the coating experiments in THF and IPA, except for LA, STA and TDPA after the HF step, DDBSA after the NH_3 step and ODT after the IPA one. The increase and decrease of DDBSA coated surfaces differs about 1° and is negligible. ODT on the other hand, shows a difference of 12° from a decrease of 1.5° in THF and an increase of 10.5 in IPA. However, the most significant difference is seen for the fatty acids. The LA coated surface decreases about 42° after the HF for the experiment done in THF and increases about 5° for the chip coated in IPA. STA shows the inverted effect – an increase of 36° for the experiment in THF and a decrease of 22° for the coating in IPA.

All the other substance follow the same trend of increasing or decreasing within a range of 10° difference for experiments in THF and IPA. Only for the ODT after HF, PFND after IPA and PFNA after NH_3 the difference is higher.

Table 25: Contact angles (CA), surface energies (σ) and differences on titanium nitride after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 with the rinsed process.

		coated			Δ		
SAM	**Treatment**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
LA	coated	76.8 ± 3.23	54.9 ± 4.59	38.24 ± 1.23			
	after NH_3	53.2 ± 6.28	46.9 ± 4.15	53.89 ± 1.60	-23.6	-8.0	15.65
	after IPA	67.7 ± 5.64	41.4 ± 2.42	47.62 ± 0.94	14.5	-5.5	-6.27
	after HF	26.0 ± 1.83	37.0 ± 2.41	71.19 ± 0.92	-41.7	-4.4	23.57
STA	coated	82.2 ± 2.98	57.9 ± 2.33	34.71 ± 0.63			
	after NH_3	69.6 ± 3.24	56.1 ± 2.83	41.35 ± 0.87	-12.6	-1.8	6.64
	after IPA	74.8 ± 2.12	51.9 ± 2.75	40.34 ± 0.76	5.2	-4.2	-1.01
	after HF	39.3 ± 6.37	42.9 ± 5.25	63.15 ± 2.07	-35.5	-9.0	22.81
TDPA	coated	94.9 ± 2.34	64.8 ± 2.51	27.63 ± 0.55			
	after NH_3	71.1 ± 3.79	50.6 ± 2.63	42.57 ± 0.84	-23.8	-14.2	14.94
	after IPA	75.9 ± 2.99	47.8 ± 2.74	41.44 ± 0.80	4.8	-2.8	-1.13
	after HF	82.9 ± 8.91	61.5 ± 4.72	32.93 ± 1.39	7.0	13.7	-8.51
ODPA	coated	95.8 ± 2.90	61.2 ± 1.68	29.15 ± 0.40			
	after NH_3	82.5 ± 3.71	59.0 ± 2.28	34.14 ± 0.65	-13.3	-2.2	4.99
	after IPA	87.6 ± 1.72	57.4 ± 0.69	33.07 ± 0.20	5.1	-1.6	-1.07
	after HF	94.8 ± 1.93	64.1 ± 1.95	27.97 ± 0.43	7.2	6.7	-5.10
TDA	coated	83.9 ± 2.02	59.1 ± 2.41	33.54 ± 0.60			
	after NH_3	68.9 ± 3.84	53.5 ± 4.50	42.64 ± 1.33	-15.0	-5.6	9.10
	after IPA	57.2 ± 3.34	46.2 ± 3.18	51.67 ± 1.08	-11.7	-7.3	9.03
	after HF	31.3 ± 6.63	31.9 ± 2.02	69.85 ± 1.28	-25.9	-14.3	18.18
ODA	coated	79.4 ± 3.57	58.1 ± 1.26	35.76 ± 0.45			
	after NH_3	76.6 ± 2.41	61.1 ± 2.74	35.88 ± 0.74	-2.8	3.0	0.12
	after IPA	74.7 ± 2.92	50.0 ± 3.09	41.07 ± 0.89	-1.9	-11.1	5.19
	after HF	59.6 ± 7.24	45.4 ± 5.22	50.57 ± 1.86	-15.1	-4.6	9.50
ODO	coated	57.8 ± 2.25	46.5 ± 0.95	51.27 ± 0.41			
	after NH_3	55.0 ± 2.83	40.7 ± 2.67	54.67 ± 0.93	-2.8	-5.8	3.40
	after IPA	56.1 ± 4.57	37.8 ± 1.11	54.91 ± 0.65	1.1	-2.9	0.24
	after HF	32.4 ± 11.16	41.1 ± 3.06	67.29 ± 2.07	-23.7	3.3	12.38
DDBSA	coated	51.5 ± 1.89	61.7 ± 0.91	50.97 ± 0.40			
	after NH_3	51.2 ± 4.93	40.6 ± 3.83	56.91 ± 1.44	-0.3	-21.1	5.94
	after IPA	55.1 ± 3.20	39.5 ± 2.24	54.98 ± 0.84	3.9	-1.1	-1.93
	after HF	30.0 ± 3.52	33.4 ± 2.93	70.16 ± 1.22	-25.1	-6.1	15.18
ODT	coated	57.0 ± 2.68	47.0 ± 1.75	51.58 ± 0.66			
	after NH_3	55.2 ± 2.81	42.6 ± 4.20	53.97 ± 1.37	-1.8	-4.4	2.39
	after IPA	53.7 ± 2.33	40.3 ± 1.01	55.55 ± 0.45	-1.5	-2.3	1.58
	after HF	21.1 ± 3.95	37.9 ± 2.79	72.97 ± 1.25	-32.6	-2.4	17.42
PFND	coated	74.2 ± 2.05	64.6 ± 4.24	35.90 ± 1.09			
	after NH_3	56.0 ± 4.89	39.6 ± 1.55	54.39 ± 0.79	-18.2	-25.0	18.49
	after IPA	60.0 ± 4.19	43.9 ± 2.63	50.82 ± 0.97	4.0	4.3	-3.57
	after HF	29.5 ± 4.53	33.7 ± 3.21	70.32 ± 1.40	-30.5	-10.2	19.50
PFNA	coated	73.8 ± 3.17	75.3 ± 6.27	32.89 ± 1.55			
	after NH_3	56.4 ± 2.88	42.9 ± 0.97	53.21 ± 0.48	-17.4	-32.4	20.32
	after IPA	58.3 ± 3.91	41.3 ± 1.48	52.60 ± 0.67	1.9	-1.6	-0.61
	after HF	40.7 ± 3.04	38.9 ± 4.32	63.36 ± 1.54	-17.6	-2.4	10.76
PFTDA	coated	63.8 ± 3.34	69.8 ± 5.41	40.73 ± 1.52			
	after NH_3	45.9 ± 8.78	50.4 ± 11.54	57.33 ± 3.95	-17.9	-19.4	16.60
	after IPA	54.8 ± 2.96	52.4 ± 9.41	51.25 ± 2.85	8.9	2.0	-6.08
	after HF	29.0 ± 2.04	30.5 ± 2.22	71.22 ± 0.87	-25.8	-21.9	19.97

Table 26: Contact angles (CA), surface energies (σ) and differences on titanium nitride after the coating (done in IPA) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 with the rinsed process.

		coated			Δ		
SAM	**Treatment**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
LA	coated	72.5 ± 3.49	46.5 ± 2.89	43.49 ± 0.98			
	after NH_3	44.1 ± 4.11	36.1 ± 2.25	62.19 ± 0.99	-28.4	-10.4	18.70
	after IPA	55.1 ± 3.11	40.8 ± 0.79	54.58 ± 0.46	11.0	4.7	-7.61
	after HF	60.3 ± 9.94	47.2 ± 1.64	49.59 ± 1.19	5.2	6.4	-4.99
STA	coated	75.6 ± 3.30	51.3 ± 1.22	40.19 ± 0.45			
	after NH_3	63.2 ± 5.13	47.0 ± 3.40	48.02 ± 1.20	-12.4	-4.3	7.83
	after IPA	66.6 ± 1.76	45.3 ± 1.59	46.81 ± 0.51	3.4	-1.7	-1.21
	after HF	44.9 ± 8.64	41.4 ± 2.41	60.37 ± 1.47	-21.7	-3.9	13.56
TDPA	coated	90.7 ± 2.27	61.2 ± 3.12	30.35 ± 0.71			
	after NH_3	67.0 ± 6.01	50.0 ± 2.67	44.87 ± 1.03	-23.7	-11.2	14.52
	after IPA	78.9 ± 2.81	51.5 ± 2.57	38.71 ± 0.72	11.9	1.5	-6.16
	after HF	70.1 ± 6.25	50.1 ± 3.89	43.29 ± 1.30	-8.8	-1.4	4.58
ODPA	coated	93.7 ± 1.86	63.0 ± 0.88	28.76 ± 0.22			
	after NH_3	83.2 ± 2.99	59.4 ± 0.79	33.69 ± 0.30	-10.5	-3.6	4.93
	after IPA	87.3 ± 3.02	59.4 ± 1.24	32.24 ± 0.37	4.1	0.0	-1.45
	after HF	91.1 ± 1.79	61.5 ± 2.13	30.12 ± 0.49	3.8	2.1	-2.12
TDA	coated	78.6 ± 2.87	59.3 ± 1.00	35.66 ± 0.37			
	after NH_3	72.6 ± 1.30	55.7 ± 1.52	39.94 ± 0.43	-6.0	-3.6	4.28
	after IPA	69.2 ± 1.51	45.6 ± 1.38	45.36 ± 0.43	-3.4	-10.1	5.42
	after HF	41.4 ± 6.71	37.5 ± 1.52	63.31 ± 1.08	-27.8	-8.1	17.95
ODA	coated	83.0 ± 2.55	61.3 ± 1.27	32.98 ± 0.38			
	after NH_3	77.7 ± 3.75	61.6 ± 2.64	35.17 ± 0.77	-5.3	0.3	2.19
	after IPA	75.6 ± 3.22	48.6 ± 2.41	41.24 ± 0.73	-2.1	-13.0	6.07
	after HF	65.6 ± 3.66	37.1 ± 3.56	50.12 ± 1.15	-10.0	-11.5	8.88
ODO	coated	58.6 ± 2.52	49.5 ± 1.00	49.83 ± 0.45			
	after NH_3	45.5 ± 4.68	36.5 ± 1.45	61.29 ± 0.83	-13.1	-13.0	11.46
	after IPA	55.2 ± 5.55	38.9 ± 1.22	55.08 ± 0.77	9.7	2.4	-6.21
	after HF	31.8 ± 5.05	37.2 ± 2.16	68.46 ± 1.14	-23.4	-1.7	13.38
DDBSA	coated	38.7 ± 1.81	53.6 ± 3.08	60.99 ± 1.05			
	after NH_3	39.6 ± 5.35	37.6 ± 1.32	64.28 ± 0.90	0.9	-16.0	3.29
	after IPA	52.0 ± 4.74	39.4 ± 0.97	56.75 ± 0.67	12.4	1.8	-7.53
	after HF	21.2 ± 2.14	32.0 ± 2.24	74.10 ± 0.91	-30.8	-7.4	17.35
ODT	coated	49.9 ± 3.81	40.1 ± 0.84	57.78 ± 0.56			
	after NH_3	43.8 ± 4.33	37.7 ± 2.59	61.91 ± 1.11	-6.1	-2.4	4.13
	after IPA	54.3 ± 5.49	40.1 ± 1.44	55.22 ± 0.83	10.5	2.4	-6.69
	after HF	39.9 ± 1.91	41.0 ± 0.62	63.27 ± 0.36	-14.4	0.9	8.05
PFND	coated	67.2 ± 1.73	67.1 ± 2.79	39.22 ± 0.77			
	after NH_3	46.9 ± 3.39	41.2 ± 1.13	59.22 ± 0.61	-20.3	-25.9	20.00
	after IPA	68.9 ± 2.41	46.9 ± 2.19	45.07 ± 0.68	22.0	5.7	-14.15
	after HF	37.2 ± 2.86	30.4 ± 2.63	67.24 ± 1.04	-31.7	-16.5	22.17
PFNA	coated	51.2 ± 3.50	68.0 ± 2.32	49.88 ± 0.88			
	after NH_3	45.5 ± 5.18	35.9 ± 1.02	61.40 ± 0.77	-5.7	-32.1	11.52
	after IPA	56.0 ± 4.66	44.5 ± 1.06	52.90 ± 0.66	10.5	8.6	-8.50
	after HF	31.1 ± 3.70	32.4 ± 2.04	69.89 ± 0.97	-24.9	-12.1	16.99
PFTDA	coated	63.8 ± 5.48	73.7 ± 5.85	39.89 ± 1.73			
	after NH_3	47.8 ± 7.93	51.5 ± 6.74	55.88 ± 2.48	-16.0	-22.2	15.99
	after IPA	57.4 ± 3.95	46.8 ± 5.51	51.41 ± 1.76	9.6	-4.7	-4.47
	after HF	34.2 ± 4.88	35.3 ± 3.63	67.69 ± 1.52	-23.2	-11.5	16.28

3.2.1.3 Thermal silicon dioxide coated silicon wafer

The rinsed process has not much influence on the coating and the removing of the thin organic layers. A decrease of the water CA after the treatment with 5% NH_3 is discernible for all substances, except, the ODPA covered surface (Table 27, coating experiment done in THF) and the DDBSA coated surface (Table 28, coating done in IPA). Also, the diiodomethane CAs decrease after the NH_3 step, except for the ODT coated surface (THF).

After the IPA removing step the water CAs increase, only STA (THF), TDA (THF) and ODA (THF and IPA) differ from this trend. The water CA of the STA coated surface shows no difference after the removing compared to the value after the NH_3 removing for the coating carried out in THF. The increase of the water CA is about 6° for the coating done in IPA.

The diiodomethane CA differs from the water CA behavior. An increase of the angle after the IPA removing step is seen for STA, both phosphonic acids and PFND for the experiments done in THF. The angle of the PFNA coated surface does not change after the treatment with IPA. If IPA was used as solvent for the coating the diiodomethane CA decrease for LA, TDPA and ODT coated surfaces after the removing step with IPA (Table 28).

An increase of the water CA is discernible only for PFTDA coated surface (THF) after the treatment with HF. All the other SAM materials show a decrease of the water CA after the HF step for the coating experiments in THF and IPA. An increase of the surface energy is seen for all the materials after the HF step except, for PFTDA after the treatment with HF. This observation correlates with the water CA behavior of all materials. The diiiodomethane CAs increase after the HF step except, for the phosphonic acids for the coating experiments in THF. In general, the surface energy data correlates to the water CA increase respectively decrease, except for the ODPA and ODT surfaces (THF) and TDA surface (IPA).

The water CA values are all either lower or about the same than the cleaned value of 32° (in account of the standard deviation) after the HF step. The diiodomethane CAs are lower than the coated ones although the cleaned value of 40° is not achieved. In general, the coating on the thermal silicon dioxide surface did not lead to the same hydrophobic effect than on the other two surface materials tungsten and titanium nitride (water CAs are lower, see point 3.1.3). The chemical removing seems to be more effective on the thermal silicon dioxide than on the other surface materials although this observation could just occur because the coating was no proper on the silicon dioxide surface.

Table 27: Contact angles (CA), surface energies (σ) and differences on thermal silicon dioxide after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 with the rinsed process.

		coated			Δ		
SAM	Treatment	CA [°]		σ [mN/m]	CA [°]		σ [mN/m]
		H_2O	CH_2I_2		H_2O	CH_2I_2	
LA	coated	50.9 ± 7.54	48.3 ± 0.61	54.89 ± 0.89			
	after NH_3	35.0 ± 2.87	41.4 ± 0.80	65.87 ± 0.53	-15.9	-6.9	10.98
	after IPA	40.5 ± 2.43	40.4 ± 1.92	63.09 ± 0.76	5.5	-1.0	-2.78
	after HF	35.7 ± 4.05	46.3 ± 0.96	64.39 ± 0.71	-4.8	5.9	1.30
STA	coated	59.5 ± 10.48	49.1 ± 3.39	49.44 ± 1.66			
	after NH_3	37.8 ± 7.38	43.4 ± 1.53	63.88 ± 1.21	-21.7	-5.7	14.44
	after IPA	37.8 ± 5.14	43.6 ± 3.49	63.82 ± 1.47	0.0	0.2	-0.06
	after HF	27.5 ± 4.72	47.0 ± 1.23	68.40 ± 0.89	-10.3	3.4	4.58
TDPA	coated	38.7 ± 2.57	46.9 ± 1.47	62.53 ± 0.66			
	after NH_3	38.0 ± 3.27	42.7 ± 0.49	63.94 ± 0.49	-0.7	-4.2	1.41
	after IPA	46.2 ± 6.98	47.6 ± 5.68	57.93 ± 2.15	8.2	4.9	-6.01
	after HF	39.5 ± 8.77	44.9 ± 2.84	62.58 ± 1.67	-6.7	-2.7	4.65
ODPA	coated	50.6 ± 13.24	51.3 ± 4.78	54.21 ± 2.43			
	after NH_3	52.6 ± 6.04	45.6 ± 4.21	54.62 ± 1.60	2.0	-5.7	0.41
	after IPA	54.9 ± 7.91	51.2 ± 2.68	51.53 ± 1.35	2.3	5.6	-3.09
	after HF	37.6 ± 3.52	48.2 ± 2.06	62.89 ± 0.92	-17.3	-3.0	11.36
TDA	coated	67.9 ± 2.04	52.8 ± 2.50	43.40 ± 0.74			
	after NH_3	54.2 ± 6.42	43.4 ± 1.35	54.30 ± 0.90	-13.7	-9.4	10.90
	after IPA	49.1 ± 4.25	42.5 ± 2.17	57.60 ± 0.95	-5.1	-0.9	3.30
	after HF	31.7 ± 5.03	44.1 ± 1.03	66.99 ± 0.86	-17.4	1.6	9.39
ODA	coated	72.9 ± 3.52	54.7 ± 3.12	40.12 ± 0.93			
	after NH_3	52.5 ± 4.69	49.2 ± 4.44	53.62 ± 1.55	-20.4	-5.5	13.50
	after IPA	49.5 ± 3.71	42.2 ± 2.11	57.41 ± 0.88	-3.0	-7.0	3.79
	after HF	35.0 ± 3.77	46.3 ± 0.21	64.73 ± 0.51	-14.5	4.1	7.32
ODO	coated	56.9 ± 6.26	53.8 ± 2.17	49.57 ± 1.06			
	after NH_3	40.8 ± 5.87	44.6 ± 2.17	61.87 ± 1.17	-16.1	-9.2	12.30
	after IPA	47.5 ± 5.77	43.2 ± 1.97	58.35 ± 1.05	6.7	-1.4	-3.52
	after HF	27.7 ± 3.20	46.3 ± 1.24	68.47 ± 0.70	-19.8	3.1	10.12
DDBSA	coated	26.8 ± 5.91	62.2 ± 1.06	66.10 ± 1.05			
	after NH_3	26.3 ± 4.07	42.5 ± 2.03	69.89 ± 1.02	-0.5	-19.7	3.79
	after IPA	40.3 ± 1.92	38.8 ± 1.09	63.63 ± 0.49	14.0	-3.7	-6.26
	after HF	22.4 ± 2.65	44.8 ± 2.05	71.05 ± 0.88	-17.9	6.0	7.42
ODT	coated	43.7 ± 0.97	43.9 ± 2.63	60.40 ± 0.87			
	after NH_3	40.3 ± 4.13	44.1 ± 1.32	62.29 ± 0.77	-3.4	0.2	1.89
	after IPA	40.4 ± 3.07	41.4 ± 1.39	62.92 ± 0.68	0.1	-2.7	0.63
	after HF	34.0 ± 1.94	45.3 ± 0.24	65.51 ± 0.29	-6.4	3.9	2.59
PFND	coated	48.1 ± 1.63	67.1 ± 2.54	52.25 ± 0.80			
	after NH_3	29.1 ± 1.77	39.5 ± 2.35	69.27 ± 0.88	-19.0	-27.6	17.02
	after IPA	40.0 ± 2.37	39.8 ± 1.48	63.55 ± 0.64	10.9	0.3	-5.72
	after HF	24.8 ± 2.05	43.9 ± 0.67	70.27 ± 0.43	-15.2	4.1	6.72
PFNA	coated	41.6 ± 2.09	70.3 ± 2.21	56.28 ± 0.77			
	after NH_3	33.1 ± 2.59	41.6 ± 1.75	66.82 ± 0.76	-8.5	-28.7	10.54
	after IPA	34.6 ± 3.10	41.6 ± 0.27	66.03 ± 0.43	1.5	0.0	-0.79
	after HF	21.6 ± 1.66	45.4 ± 1.15	71.26 ± 0.52	-13.0	3.8	5.23
PFTDA	coated	37.4 ± 2.01	70.8 ± 6.69	59.05 ± 2.07			
	after NH_3	21.0 ± 2.74	43.1 ± 2.51	71.93 ± 1.03	-16.4	-27.7	12.88
	after IPA	30.2 ± 2.18	41.7 ± 0.71	68.28 ± 0.44	9.2	-1.4	-3.65
	after HF	35.9 ± 5.62	46.1 ± 4.40	64.30 ± 1.79	5.7	4.4	-3.98

Table 28: Contact angles (CA), surface energies (σ) and differences on thermal silicon dioxide after the coating (done in IPA) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 with the rinsed process.

		coated			Δ		
SAM	**Treatment**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
		H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
LA	coated	40.4 ± 2.70	46.4 ± 1.07	61.68 ± 0.56			
	after NH_3	36.2 ± 2.69	41.3 ± 1.31	65.29 ± 0.63	-4.2	-5.1	3.61
	after IPA	39.1 ± 1.70	42.1 ± 1.15	63.50 ± 0.48	2.9	0.8	-1.79
	after HF	28.0 ± 4.20	45.2 ± 0.99	68.54 ± 0.76	-11.1	3.1	5.04
STA	coated	39.6 ± 2.56	54.6 ± 3.59	60.24 ± 1.24			
	after NH_3	36.9 ± 1.99	42.2 ± 1.42	64.66 ± 0.59	-2.7	-12.4	4.42
	after IPA	43.1 ± 1.59	41.1 ± 0.96	61.46 ± 0.41	6.2	-1.1	-3.20
	after HF	36.3 ± 5.72	48.0 ± 1.70	63.62 ± 1.08	-6.8	6.9	2.16
TDPA	coated	43.6 ± 1.70	52.2 ± 3.10	58.31 ± 1.03			
	after NH_3	35.2 ± 1.76	42.9 ± 1.04	65.41 ± 0.47	-8.4	-9.3	7.10
	after IPA	38.7 ± 1.53	43.1 ± 1.51	63.48 ± 0.57	3.5	0.2	-1.93
	after HF	25.8 ± 1.11	48.1 ± 0.62	68.98 ± 0.30	-12.9	5.0	5.50
ODPA	coated	44.9 ± 1.83	49.3 ± 2.38	58.24 ± 0.82			
	after NH_3	36.9 ± 4.18	47.3 ± 1.45	63.46 ± 0.84	-8.0	-2.0	5.22
	after IPA	39.1 ± 0.61	44.2 ± 1.19	62.96 ± 0.41	2.2	-3.1	-0.50
	after HF	28.0 ± 2.18	48.3 ± 1.41	67.92 ± 0.63	-11.1	4.1	4.96
TDA	coated	69.9 ± 2.65	52.7 ± 2.77	42.41 ± 0.83			
	after NH_3	40.5 ± 3.04	43.1 ± 1.82	62.43 ± 0.79	-29.4	-9.6	20.02
	after IPA	41.0 ± 2.03	41.0 ± 1.97	62.68 ± 0.74	0.5	-2.1	0.25
	after HF	33.4 ± 2.23	49.6 ± 0.26	64.89 ± 0.34	-7.6	8.6	2.21
ODA	coated	69.8 ± 5.44	59.1 ± 1.93	40.17 ± 0.80			
	after NH_3	64.6 ± 5.44	52.2 ± 4.23	45.46 ± 1.40	-5.2	-6.9	5.29
	after IPA	49.4 ± 3.82	41.6 ± 2.08	57.65 ± 0.88	-15.2	-10.6	12.19
	after HF	28.8 ± 1.66	48.6 ± 0.51	67.48 ± 0.33	-20.6	7.0	9.83
ODO	coated	46.7 ± 2.15	45.2 ± 1.53	58.22 ± 0.60			
	after NH_3	31.6 ± 1.91	41.8 ± 0.80	67.56 ± 0.43	-15.1	-3.4	9.34
	after IPA	39.7 ± 1.92	41.5 ± 1.09	63.22 ± 0.49	8.1	-0.3	-4.34
	after HF	31.7 ± 5.68	46.6 ± 1.57	66.42 ± 1.07	-8.0	5.1	3.20
DDBSA	coated	17.7 ± 4.63	63.3 ± 0.54	69.91 ± 0.80			
	after NH_3	27.9 ± 2.00	43.1 ± 1.44	69.05 ± 0.62	10.2	-20.2	-0.86
	after IPA	43.8 ± 3.84	42.0 ± 1.18	60.82 ± 0.69	15.9	-1.1	-8.23
	after HF	19.7 ± 2.86	42.7 ± 0.54	72.50 ± 0.51	-24.1	0.7	11.68
ODT	coated	46.4 ± 3.35	49.7 ± 0.86	57.28 ± 0.55			
	after NH_3	31.2 ± 1.25	40.3 ± 1.74	68.10 ± 0.64	-15.2	-9.4	10.82
	after IPA	40.0 ± 3.45	41.1 ± 1.42	63.20 ± 0.73	8.8	0.8	-4.90
	after HF	27.2 ± 2.97	47.1 ± 1.43	68.54 ± 0.43	-12.8	6.0	5.34
PFND	coated	37.0 ± 2.81	68.1 ± 4.51	59.53 ± 1.49			
	after NH_3	24.8 ± 4.29	44.7 ± 1.59	70.09 ± 0.94	-12.2	-23.4	10.56
	after IPA	36.9 ± 1.89	42.3 ± 0.93	64.66 ± 0.45	12.1	-2.4	-5.43
	after HF	34.5 ± 3.02	45.1 ± 0.82	65.31 ± 0.56	-2.4	2.8	0.65
PFNA	coated	22.4 ± 2.08	81.2 ± 1.04	67.62 ± 0.53			
	after NH_3	22.1 ± 2.72	42.5 ± 1.04	71.66 ± 0.61	-0.3	-38.7	4.04
	after IPA	38.4 ± 0.47	42.2 ± 1.54	63.82 ± 0.52	16.3	-0.3	-7.84
	after HF	22.8 ± 3.65	44.1 ± 1.34	71.04 ± 0.80	-15.6	1.9	7.22
PFTDA	coated	23.8 ± 5.39	71.5 ± 4.59	66.80 ± 1.83			
	after NH_3	23.4 ± 2.85	44.1 ± 2.08	70.80 ± 0.91	-0.4	-27.4	4.00
	after IPA	34.4 ± 2.72	42.1 ± 1.41	66.04 ± 0.67	11.0	-2.0	-4.76
	after HF	19.8 ± 2.56	42.5 ± 0.85	72.50 ± 0.54	-14.6	0.4	6.46

The behavior for the removing of organic layer is similar on silicon dioxide than on titanium nitride and tungsten - most of the coated surfaces show a decrease of the water CAs after the NH_3 step, an increase after IPA and again a decrease after HF.

3.2.2 Removal experiments in the tube furnace

The experiments in the tube furnace were carried out to remove the coated SAM of tungsten surfaces. Table 29 lists the contact angles and the surface energies of the cleaned and coated chips and after the tube furnace treatment. In addition, the differences between the treatments are given.

Table 29: Contact angles (CA), surface energies (σ) and differences of coated and uncoated tungsten surfaces before and after the tube furnace experiments. All the tungsten chips were treated with pretreatment 2 and the rinsed process (after coating). The experiments were carried out under oxygen flow and 450 °C.

						Δ		
SAM	**Time in Oven [min]**	**Treatment**	**CA [°]**		**σ [mN/m]**	**CA [°]**		**σ [mN/m]**
			H_2O	**CH_2I_2**		**H_2O**	**CH_2I_2**	
Blank	2	pretr. 2	14.4 ± 1.27	30.2 ± 1.87	76.52 ± 0.73			
		after oven	32.9 ± 1.84	32.3 ± 2.64	69.02 ± 0.98	18.5	2.1	-7.50
ODA	2	pretr. 2	18.8 ± 5.50	36.7 ± 0.84	74.00 ± 0.91			
		coated	80.2 ± 2.95	53.1 ± 1.58	37.53 ± 0.48	61.4	16.4	-36.47
		after oven	70.3 ± 2.29	38.8 ± 1.81	47.36 ± 0.58	-9.9	-14.3	9.83
Blank	6	pretr. 2	27.7 ± 4.25	34.2 ± 5.21	71.05 ± 2.00			
		after oven	12.1 ± 1.83	30.7 ± 1.86	76.95 ± 2.04	-15.6	-3.5	5.90
ODA	6	pretr.2	23.8 ± 3.12	37.9 ± 4.30	71.92 ± 1.64			
		coated	73.3 ± 1.97	48.7 ± 0.64	42.18 ± 0.26	49.5	10.8	-29.74
		after oven	30.1 ± 3.69	30.0 ± 1.86	70.83 ± 0.92	-43.2	-18.7	28.65
Blank	10	pretr. 2	17.8 ± 2.63	29.6 ± 3.09	75.69 ± 1.24			
		after oven	17.1 ± 2.35	43.6 ± 3.11	73.15 ± 1.20	-0.7	14.0	-2.54
ODA	10	pretr.2	22.0 ± 1.30	38.6 ± 3.09	72.47 ± 1.12			
		coated	69.5 ± 1.61	48.3 ± 2.49	44.22 ± 0.72	47.5	9.7	-28.25
		after oven	34.2 ± 3.72	52.0 ± 2.24	63.98 ± 1.00	-35.3	3.7	19.76
Blank	20	pretr. 2	22.4 ± 3.19	40.7 ± 1.90	71.91 ± 0.90			
		after oven	-	28.6 ± 6.33	-	-	-12.1	-
ODA	20	pretr.2	24.0 ± 1.41	29.8 ± 3.35	73.50 ± 1.23			
		coated	62.5 ± 3.65	56.7 ± 2.11	45.25 ± 0.78	38.5	26.9	-28.25
		after oven	-	29.8 ± 2.49	-	-	-26.9	-
Blank	10	pretr. 2	19.4 ± 0.55	26.2 ± 1.12	75.79 ± 0.42			
		after oven	17.0 ± 3.17	28.9 ± 0.74	76.04 ± 0.59	-2.4	2.7	0.25
ODPA	10	pretr.2	19.6 ± 1.24	27.0 ± 1.41	75.59 ± 0.57			
		coated	72.8 ± 2.70	48.4 ± 3.30	41.89 ± 0.93	53.2	21.4	-33.70
		after oven	16.8 ± 1.84	31.2 ± 2.36	75.68 ± 0.93	-56.0	-17.2	33.79

The experiments were carried out with ODA and ODPA because these two SAM materials were the most promising one after the coating experiments.

Neither on the blank nor on the ODA coated surface an optical change was recognizable after the treatment of 2 minutes in the oven. Interesting is the increase of the water CA on the blank surface because it is seen only for the 2 minutes experiment, for all the other times the water CA decreases or remains the same after the treatment in the oven.

ODA coated surface shows that 2 minutes are too short to give complete removal because the water CA of 70° is still higher than after the pretreatment although it seems that partial removing occurs. After 6 min in the oven at 450 °C the water and the diiodomethane CA of the blank surface decrease. Again, no optical change is recognizable, neither on the blank nor on the coated surface. Surface energy after pretreatment and after 6 min in the oven differ about 1 mN/m. ODA layer is nearly completely removed as the surface energy and the water CA of 30° shows.

The ODA coated surface after 10 min in the oven at 450 °C led to following results: the blank surface turned golden yellow and the coated surface remains silver. The explanation of color change on the uncoated surface is the oxidation to W-O bonds. The diiodomethane CA increases because the diiodomethane is not able to interact with the oxygen at the surface because it is not able to form hydrogen bonds. The decrease of the water CA after the heating shows partial removing although it is possible that partial oxidation already occurs because the diiodomethane CA increases again. Further experiments are necessary to prove this observation. Especially the treatment with (more) different heating times is interesting.

Nevertheless, 10 min are not enough to remove the complete ODA layer because the CAs have not reached the starting values although a part is removed as for the 6 min experiment.

After 20 min in the oven (10 min during heating up and 10 min at 450°) the uncoated surface is golden yellow and the ODA coated blue purple instead of silver. The water CA was not measurable because the drop moistened the surface nearly complete as shown in Figure 18. Diiodomethane CA decreases on the uncoated and coated surface. Both angles are smaller than for the cleaned substrate surface. The ODA layer is destroyed and tungsten oxides are formed in different stoichiometric and non-stoichiometric bonds (yellow and purple are indicative for different tungsten oxides[52]) also depending on the oxidation state of the tungsten. As a consequence 20 min are too long because also the substrate is attacked.

[52] Hollemann, A. F.; Wiberg, N. Lehrbuch der Anorganischen Chemie, 102. Auflage, Walter de Gruyter, Berlin und New York, **2007**, page 1590-1591

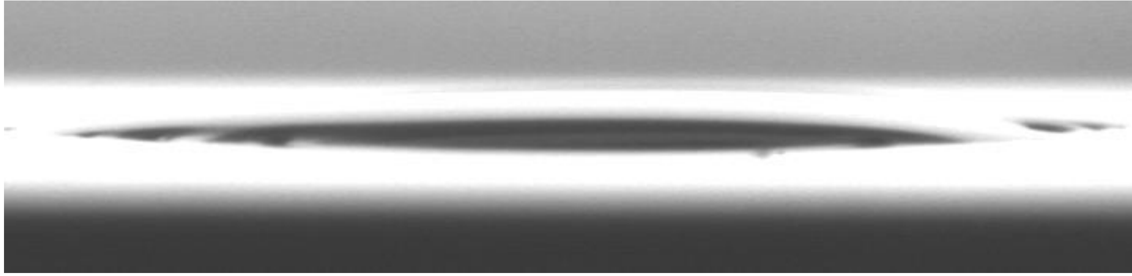


Figure 18: Water CA of the ODA coated surface after 30 min in the tube furnace.

For the ODPA coated surface no further modification except the removal of the layer is noticed after 10 min in the oven. In contrast to the blank of the ODA experiment the blank of the ODPA experiment did not change the color. It remained silver. This can be traced back to the different temperature distribution in the oven. The angles of the blank surface are nearly the same before and after the heating in the oven. So the surface was not affected. The ODPA coated surface achieves the cleaned CA and surface energy values after the treatment in the oven. Therefore, 10 min are enough to remove the organic ODPA layer without affecting the substrate as all CAs and the surface energies show. As a consequence, the thermal removing was successful.

4. Experimental

4.1 General

In this thesis, following chemicals and materials were used. The chemicals were purchased and used without further purification. The wafer were received from Lam RESEARCH®.

Lauric acid, ≥ 98%, FCC, FG SAFC Batchno.: 02796MH CAS: 143-07-7	Stearic acid, reagent grade 95% Sigma Aldrich LOT: MKBJ9505V CAS: 57-11-4
Tetradecylphosphonic acid, 97% Sigma Aldrich LOT: MKBK1477V CAS: 4671-75-4	Octadecylphosphonic acid, 97% Sigma Aldrich LOT: MKBJ8197V CAS: 4724-47-4
1-Octadecanol, 97% Alfa Aesar LOT:10169648 CAS: 112-92-5	1-Octadecanethiol, 96% Alfa Aesar LOT: 5001A13A CAS: 2885-00-9
Tetradecylamine 95% Aldrich LOT: MKBB8670V CAS: 2016-42-4	1-Octadecylamine, 98% Alfa Aesar LOT: 10106823 CAS: 124-30-1
1H,1H,2H,3H,3H-Perfluorononanoic-1,2-diol, 95% Alfa Aesar LOT: 10123113 CAS: 107650-06-6	Perfluorononanoic acid, 97% Alfa Aesar LOT: 10153238 CAS: 375-95-1
4-Dodecylbenzenesulfonic acid mixture of isomers, ≥ 95% Sigma Aldrich LOT: BCBG0649V CAS: 121-65-3	Perfluorotetradecanoic acid, 96% Alfa Aesar LOT: 10153757 CAS: 376-06-7
Hydrofluoric acid 40% VWR BatchNo: 11H120501 CAS: 7664-39-3	Ammonia solution 32% Merck LOT: B0791326 CAS: 7664-41-7
Propan-2-ol VWR BatchNo: 12B030509 CAS: 67-63-0	2-Propanol VLSI Selectipur BASF LOT: 09935013K0 CAS: 67-63-0
Hydrogen peroxide about 50% VWR BatchNo: 12A160508 CAS: 7722-84-1	water deionized In-house installation without further microfiltration
Contact angle liquids Diiodomethane, Reagent Plus®, 99% (GC) Sigma Aldrich CAS: 75-11-6	Tungsten wafer 500 Å thick W layer PVD deposited Purchased from Wafernet
Titanium nitride wafer 330 Å thick TiN layer PVD deposited Purchased from Novellus	Thermal silicon dioxide wafer 1050 Å thick SiO_2 layer Purchased from Wafernet

Table 30: Molecular formulas and molecular weights [g/mol] of the used SAM materials.

Substance	Molecular formula	Molecular weight [g/mol]
Lauric acid	$C_{12}H_{24}O_2$	200.32
Stearic acid	$C_{18}H_{36}O_2$	284.48
Tetradecylamine	$C_{14}H_{31}N$	213.41
1-Octadecylamine	$C_{18}H_{39}N$	269.51
Tetradecylphosphonic acid	$C_{14}H_{31}O_3P$	278.37
Octadecylphosphonic acid	$C_{18}H_{39}O_3P$	334.48
1-Octadecanol	$C_{18}H_{38}O$	270.50
1-Octadecanethiol	$C_{18}H_{38}S$	286.57
4-Dodecylbenzenesulfonic acid	$C_{18}H_{30}O_3S$	326.50
***1H,1H,2H,3H,3H*-Perfluorononanoic-1,2-diol**	$C_9H_7F_{13}O_2$	394.13
Perfluorononanoic acid	$C_9HF_{17}O_2$	464.08
Perfluorotetradecanoic acid	$C_{14}HF_{27}O_2$	714.12

General procedure for all the coating experiments: The wafer materials were cut into pieces with the size of 4x4 cm. For all the coating experiments the SAM materials were solved in polytetrafluoroethylene beaker to avoid competing reaction with beaker glass wall. If not mentioned different in all the tests and intermediate steps compressed N_2 was used to blow the chips dry. The nitrogen came from the in-house pipeline.

Before the chips were coated they were cleaned via a pretreatment (abbr.: pretr.) to remove impurities like fatty residue, fingerprints or dust particles. Due to appropriate literature[53, 54]following pretreatments were used:

Pretreatment 1: Chips were dipped in 1 min in 1% NH_3, 1 min in deionised water and 1 min in isopropyl alcohol. Between every new solution the chips were blown dry with compressed N_2.

Pretreatment 2: Chips were dipped 1 min in 1% NH_3, 1 min in deionised water and 1 min in isopropyl alcohol. Only after the isopropyl alcohol step they were dried with compressed N_2.

Pretreatment 3: Chips were dipped 1 min in 1% H_2O_2, 1 min in deionised water and 1 min in isopropyl alcohol. Between every new solution the chips were blown dry with compressed N_2.

After the cleaning operation the wafer pieces were immersed 10 min in the chemical solution and again dried. Despite extensive literature research no data was found for the CMC of the used chemicals in THF and IPA. According to literature[53] the concentration of 0.5 mM and the immersion time were chosen. Mass calculations were done using the general concentration equation (Equation

[53] *Patent Application Publication*, Liquid Chemical for Forming Protecting Film, US 201200174945A1, Jul. 12, **2012**

[54] Reinhardt, K. A.; Reidy, R. F. Handbook of Cleaning for Semiconductor Manufacturing, Scrivener Publishing LLC, New Jersey, **2011**

8), the rearranged amount of substance n [mol] equation (Equation 9) and the molecular weights of Table 30.

$$c = \frac{n}{V} \rightarrow n = c \cdot V$$

Equation 8

$$n = \frac{m}{M} \rightarrow m = n \cdot M$$

Equation 9

A part of the chips were subjected to a rinsed process. Immediately after coating the chips were dipped fast in fresh, clean solvent and not till then dried. The rinsed process was carried out to remove any remaining non adsorbed material and to figure out if there is a difference on the ordering of the coating layer.

Next, removing of the coating was carried out in three steps. First the chips were immersed in 5% NH_3, than in isopropyl alcohol and 10% HF each one minute. Between all solutions it was blown dry with nitrogen. The chips were measured after every step.

Contact angle measurements were done to examine the wettability and therefore the hydrophilic and hydrophobic properties of the surfaces, ellipsometry to examine layer thicknesses. Measurements were done after all treatments. All the contact angles were obtained with a KRÜSS DAS 100 Drop Shape Analyzer and the DSH Registered Version software. As liquids with known surface tension double deionized water and diiodomethane (Reagent Plus®, 99% (GC); Sigma Aldrich; CAS: 75-11-6) were used. Drops with the volume of 3 µL were put on the surfaces. The angles both water and CH_2I_2 were measured after 2 seconds via sessile drop analysis and the calculation model of Ström (at 25 °C). All reported values were an average of five measurement points.

Ellispometric analyses were performed on a Philips PZ 2000 ellipsometer and PQ Diamond as standard software. Within the range of 20 mm five points were measured with a HeNe-laser generating light with wavelength of 632.8 nm from different parts of the substrate. Again all reported values are the averaged ones. Layer thicknesses for all the experiments on tungsten and SiO_2 surfaces were determined via ellipsometric measurements. The modeling was not correct for the thin organic layers on the different metal surfaces. The laser beam went through the organic material and was reflected by the W respectively SiO_2. Due to the oxide-nitride material mix of the used titanium nitride surfaces it was not possible to get ellipsometric data because a plausible recipe could not be achieved.

4.2 Coating and wet chemical removal experiments

4.2.1 Tungsten coated silicon wafer

4.2.1.1 Octadecylphosphonic acid

Solution: 0.0099 g ODPA solved in 60 mL THF.

Table 31: Water contact angle (CA) of ODPA (solved in THF) modified tungsten surface.

Water	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	14.8 ± 4.14	93.9 ± 2.32	76.8 ± 5.77	79.7 ± 6.97	87.9 ± 4.17
Pretreatment 1 and rinsed process	17.0 ± 3.28	88.6 ± 4.92	79.9 ± 3.16	77.6 ± 6.06	89.4 ± 1.81
Pretreatment 2	10.2 ± 1.70	98.5 ± 0.44	84.9 ± 2.74	88.6 ± 1.28	94.5 ± 1.64
Pretreatment 2 and rinsed process	12.3 ± 0.95	88.6 ± 3.50	79.6 ± 2.81	79.9 ± 4.27	92.1 ± 2.43

Table 32: Diiodomethane contact angle (CA) of ODPA (solved in THF) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	27.9 ± 2.98	72.1 ± 2.27	54.1 ± 2.95	54.7 ± 4.71	63.0 ± 5.03
Pretreatment 1 and rinsed process	34.8 ± 3.39	59.6 ± 2.82	54.2 ± 3.29	51.3 ± 3.40	60.6 ± 4.62
Pretreatment 2	26.5 ± 5.47	71.7 ± 0.84	61.1 ± 1.18	62.9 ± 1.06	67.6 ± 1.38
Pretreatment 2 and rinsed process	31.8 ± 2.35	59.4 ± 3.59	59.9 ± 1.43	55.7 ± 3.05	63.2 ± 1.68

Table 33: Surface energy (σ) of ODPA (solved in THF) modified tungsten surface (calculated via data of Table 31 and Table 32).

	σ after pretr. [mN/m]	σ after ODPA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	76.82 ± 1.35	24.61 ± 0.49	38.53 ± 0.96	37.05 ± 1.37	30.45 ± 1.19
Pretreatment 1 and rinsed process	74.95 ± 1.38	31.74 ± 0.75	37.20 ± 0.89	39.34 ± 1.07	31.02 ± 1.05
Pretreatment 2	78.07 ± 2.03	23.60 ± 0.16	32.30 ± 0.36	30.26 ± 0.26	26.41 ± 0.31
Pretreatment 2 and rinsed process	76.72 ± 0.87	31.85 ± 0.87	34.95 ± 0.45	36.55 ± 0.88	29.06 ± 0.41

Table 34: Ellipsometric data of ODPA (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after ODPA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	47.75 ± 0.31	50.75 ± 0.08	50.27 ± 0.73	50.05 ± 0.45	49.18 ± 0.57
Pretreatment 1 and rinsed process	46.79 ± 0.33	49.88 ± 0.54	49.22 ± 0.86	48.81 ± 0.79	47.59 ± 1.60
Pretreatment 2	47.83 ± 0.26	50.77 ± 0.13	50.47 ± 0.21	50.41 ± 0.16	50.34 ± 0.38
Pretreatment 2 and rinsed process	47.01 ± 0.20	50.42 ± 0.42	50.45 ± 0.36	49.51 ± 0.80	48.82 ± 0.91

Solution: 0.0106 g ODPA solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 35: Water contact angle (CA) of ODPA (solved in IPA) modified tungsten surface.

Water	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	12.2 ± 4.61	94.6 ± 3.55	77.7 ± 6.35	70.1 ± 12.39	86.7 ± 2.72
Pretreatment 1 and rinsed process	15.0 ± 1.99	87.6 ± 2.94	62.3 ± 12.25	63.7 ± 13.04	65.5 ± 12.73

Table 36: Diiodomethane contact angle (CA) of ODPA (solved in IPA) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	26.4 ± 3.31	62.0 ± 3.84	48.7 ± 1.37	49.6 ± 2.84	58.5 ± 2.66
Pretreatment 1 and rinsed process	25.0 ± 3.50	59.1 ± 5.04	40.7 ± 5.47	45.2 ± 3.15	49.4 ± 5.86

Table 37: Surface energy (σ) of ODPA (solved in IPA) modified tungsten surface (calculated via data of Table 35 and Table 36).

	σ after pretr. [mN/m]	σ after ODPA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	77.68 ± 1.51	29.04 ± 0.85	40.39 ± 0.63	43.49 ± 1.45	32.85 ± 0.66
Pretreatment 1 and rinsed process	77.27 ± 1.34	32.29 ± 1.19	50.60 ± 2.23	48.35 ± 1.70	45.94 ± 2.28

Table 38: Ellipsometric data of ODPA (solved in IPA) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after ODPA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	50.01 ± 0.39	50.61 ± 0.44	50.22 ± 0.40	50.10 ± 0.54	49.72 ± 0.86
Pretreatment 1 and rinsed process	49.21 ± 0.54	50.89 ± 0.56	49.55 ± 0.64	49.70 ± 0.62	48.77 ± 1.35

Solution: 0.0100 g ODPA solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 39: Water contact angle (CA) of ODPA (solved in IPA) modified tungsten surface.

Water	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2	13.1 ± 2.37	94.4 ± 1.29	79.3 ± 4.27	84.8 ± 3.87	84.6 ± 8.75
Pretreatment 2 and rinsed process	14.9 ± 2.75	82.9 ± 2.79	65.6 ± 5.04	68.2 ± 7.93	77.4 ± 5.36

Table 40: Diiodomethane contact angle (CA) of ODPA (solved in IPA) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2	32.3 ± 2.17	64.3 ± 0.94	59.3 ± 1.83	55.6 ± 2.44	57.4 ± 4.18
Pretreatment 2 and rinsed process	34.5 ± 3.22	58.6 ± 2.11	51.0 ± 2.75	47.5 ± 2.07	48.0 ± 1.90

Table 41: Surface energy (σ) of ODPA (solved in IPA) modified tungsten surface (calculated via data of Table 39 and Table 40).

	σ after pretr. [mN/m]	σ after ODPA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2	76.44 ± 0.92	27.98 ± 0.22	35.33 ± 0.61	34.74 ± 0.67	34.02 ± 1.24
Pretreatment 2 and rinsed process	75.56 ± 1.29	34.13 ± 0.57	45.29 ± 1.00	45.17 ± 1.01	40.77 ± 0.69

Table 42: Ellipsometric data of ODPA (solved in IPA) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after ODPA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2	47.98 ± 0.35	50.23 ± 0.26	49.08 ± 0.50	49.54 ± 0.47	48.66 ± 0.75
Pretreatment 2 and rinsed process	47.54 ± 0.07	49.71 ± 0.39	48.12 ± 0.59	48.35 ± 0.37	46.95 ± 0.69

4.2.1.2 Tetradecylphosphonic acid

Solution: 0.0081 g TDPA solved in 60 mL THF.

Table 43: Water contact angle (CA) of TDPA (solved in THF) modified tungsten surface.

Water	CA after pretr. [°]	CA after TDPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	9.3 ± 1.61	94.3 ± 0.30	48.8 ± 3.30	54.7 ± 2.38	49.1 ± 15.68
Pretreatment 1 and rinsed process	15.0 ± 1.57	89.6 ± 3.02	51.4 ± 3.36	56.5 ± 5.32	46.0 ± 5.18
Pretreatment 2	11.6 ± 1.24	97.9 ± 1.67	50.9 ± 5.78	59.9 ± 3.81	66.6 ± 4.88
Pretreatment 2 and rinsed process	12.5 ± 3.01	87.7 ± 5.41	39.2 ± 5.39	51.9 ± 2.48	47.4 ± 10.01

Table 44: Diiodomethane contact angle (CA) of TDPA (solved in THF) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after TDPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	25.1 ± 1.01	64.6 ± 2.57	44.5 ± 2.45	44.1 ± 2.74	40.4 ± 8.70
Pretreatment 1 and rinsed process	31.2 ± 2.55	58.4 ± 3.87	44.1 ± 1.23	40.3 ± 0.92	38.2 ± 3.91
Pretreatment 2	31.0 ± 2.03	66.5 ± 4.87	45.3 ± 1.20	42.4 ± 2.94	50.2 ± 5.71
Pretreatment 2 and rinsed process	27.9 ± 4.06	60.5 ± 4.99	42.1 ± 1.13	33.4 ± 1.14	42.5 ± 5.54

Table 45: Surface energy (σ) of TDPA (solved in THF) modified tungsten surface (calculated via data of Table 43 and Table 44).

	σ after pretr. [mN/m]	σ after TDPA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	78.45 ± 0.49	27.87 ± 0.54	57.18 ± 0.94	53.83 ± 0.92	58.19 ± 3.68
Pretreatment 1 and rinsed process	76.16 ± 0.98	31.99 ± 0.91	55.75 ± 0.61	53.91 ± 0.67	60.57 ± 1.53
Pretreatment 2	77.02 ± 0.65	26.14 ± 0.98	55.72 ± 0.84	51.34 ± 1.03	45.04 ± 1.73
Pretreatment 2 and rinsed process	77.38 ± 1.61	31.60 ± 1.23	63.41 ± 0.87	58.52 ± 0.51	58.58 ± 2.37

Table 46: Ellipsometric data of TDPA (solved in IPA) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after TDPA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	50.73 ± 0.49	51.35 ± 0.11	49.58 ± 0.86	50.41 ± 0.11	48.83 ± 0.46
Pretreatment 1 and rinsed process	49.87 ± 0.89	50.64 ± 0.46	49.49 ± 0.76	49.76 ± 0.54	46.32 ± 0.51
Pretreatment 2	48.51 ± 1.11	50.48 ± 0.58	49.44 ± 1.20	49.12 ± 0.27	46.77 ± 0.88
Pretreatment 2 and rinsed process	50.66 ± 0.71	50.56 ± 0.99	48.81 ± 0.82	49.17 ± 0.38	46.33 ± 0.94

Solution: 0.0081 g TDPA solved in 60 mL IPA.

Table 47: Water contact angle (CA) of TDPA (solved in IPA) modified tungsten surface.

Water	CA after pretr. [°]	CA after TDPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	15.7 ± 3.27	87.5 ± 3.60	38.9 ± 3.99	39.4 ± 5.90	54.0 ± 6.04
Pretreatment 1 and rinsed process	12.1 ± 3.49	83.5 ± 3.32	45.3 ± 5.75	54.4 ± 4.14	70.7 ± 6.13

Table 48: Diiodomethane contact angle (CA) of TDPA (solved in IPA) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after TDPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	27.3 ± 2.12	59.7 ± 3.87	33.3 ± 2.44	39.8 ± 0.52	43.6 ± 3.89
Pretreatment 1 and rinsed process	27.3 ± 3.02	52.0 ± 3.67	39.8 ± 2.69	39.7 ± 2.25	36.3 ± 4.77

Table 49: Surface energy (σ) of TDPA (solved in THF) modified tungsten surface (calculated via data of Table 47 and Table 48).

	σ after pretr. [mN/m]	σ after TDPA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	76.70 ± 1.00	32.07 ± 0.94	65.71 ± 1.07	63.87 ± 0.78	54.37 ± 1.50
Pretreatment 1 and rinsed process	77.58 ± 1.31	36.82 ± 0.95	60.51 ± 1.25	55.29 ± 0.92	48.01 ± 1.53

Table 50: Ellipsometric data of TDPA (solved in IPA) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after TDPA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	49.16 ± 0.73	50.10 ± 0.48	49.17 ± 0.66	49.65 ± 0.58	47.64 ± 0.56
Pretreatment 1 and rinsed process	49.05 ± 0.41	50.03 ± 0.28	49.68 ± 0.52	49.46 ± 0.28	48.55 ± 0.48

4.2.1.3 4-Dodecylbenzenesulfonic acid

Solution: 0.0103 g DDBSA solved in 60 mL THF.

Table 51: Water contact angle (CA) of DDBSA (solved in THF) modified tungsten surface.

Water	CA after pretr. [°]	CA after DDBSA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	20.6 ± 0.69	36.5 ± 1.18	39.8 ± 4.52	42.3 ± 1.99	29.5 ± 3.11
Pretreatment 1 and rinsed process	15.0 ± 0.52	42.9 ± 1.35	34.3 ± 2.39	46.2 ± 2.77	32.3 ± 2.73

Table 52: Diiodomethane contact angle (CA) of DDBSA (solved in THF) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after DDBSA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	29.5 ± 0.79	46.8 ± 6.41	35.3 ± 3.25	34.3 ± 1.39	32.1 ± 4.48
Pretreatment 1 and rinsed process	25.0 ± 0.99	49.1 ± 10.19	30.8 ± 3.67	35.5 ± 0.81	36.2 ± 1.98

Table 53: Surface energy (σ) of DDBSA (solved in THF) modified tungsten surface (calculated via data of Table 51 and Table 52).

	σ after pretr. [mN/m]	σ after DDBSA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	74.80 ± 0.32	63.80 ± 0.14	64.73 ± 1.34	63.64 ± 0.57	70.68 ± 1.68
Pretreatment 1 and rinsed process	77.26 ± 0.38	59.54 ± 0.15	68.64 ± 1.35	61.12 ± 0.47	68.46 ± 0.84

Table 54: Ellipsometric data of DDBSA (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after DDBSA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	48.15 ± 0.17	50.81 ± 0.14	47.89 ± 1.06	48.22 ± 0.68	47.91 ± 0.86
Pretreatment 1 and rinsed process	47.29 ± 0.23	50.11 ± 0.43	47.00 ± 0.24	47.94 ± 0.41	46.51 ± 0.54

Solution: 0.0097 g DDBSA solved in 60 mL IPA.

Table 55: Water contact angle (CA) of DDBSA (solved in IPA) modified tungsten surface.

Water	CA after pretr. [°]	CA after DDBSA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	13.5 ± 4.42	19.7 ± 2.36	16.3 ± 3.78	23.5 ± 3.99	21.2 ± 4.43
Pretreatment 1 and rinsed process	13.4 ± 3.22	25.8 ± 1.28	14.6 ± 3.18	26.6 ± 1.52	24.2 ± 5.12

Table 56: Diiodomethane contact angle (CA) of DDBSA (solved in IPA) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after DDBSA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	31.2 ± 1.93	53.1 ± 2.76	36.1 ± 3.53	32.1 ± 0.57	32.4 ± 0.57
Pretreatment 1 and rinsed process	26.4 ± 2.22	43.8 ± 1.83	34.7 ± 3.58	31.2 ± 1.44	33.2 ± 1.50

Table 57: Surface energy (σ) of DDBSA (solved in IPA) modified tungsten surface (calculated via data of Table 55 and Table 56).

	σ after pretr. [mN/m]	σ after DDBSA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	76.56 ± 1.08	70.54 ± 1.06	74.89 ± 1.48	73.24 ± 0.63	74.02 ± 0.70
Pretreatment 1 and rinsed process	77.44 ± 1.03	69.84 ± 0.68	75.64 ± 1.44	72.15 ± 0.59	72.71 ± 1.01

Table 58: Ellipsometric data of DDBSA (solved in IPA) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after DDBSA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	47.49 ± 0.48	48.98 ± 0.62	49.38 ± 0.86	48.55 ± 1.17	47.56 ± 0.68
Pretreatment 1 and rinsed process	48.64 ± 0.56	48.59 ± 0.41	48.09 ± 0.23	48.09 ± 0.85	48.04 ± 1.03

Solution: 0.0101 g DDBSA solved in 60 mL THF.

Table 59: Water contact angle (CA) of DDBSA (solved in THF) modified tungsten surface.

Water	CA after pretr. [°]	CA after DDBSA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2	18.9 ± 1.67	29.2 ± 2.39	20.8 ± 3.62	32.3 ± 5.65	32.0 ± 3.67
Pretreatment 2 and rinsed process	18.2 ± 2.35	37.5 ± 2.98	24.4 ± 1.96	35.3 ± 5.00	38.6 ± 3.96

Table 60: Diiodomethane contact angle (CA) of DDBSA (solved in THF) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after DDBSA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2	32.7 ± 1.97	59.5 ± 2.35	34.2 ± 1.69	37.2 ± 2.51	28.2 ± 1.55
Pretreatment 2 and rinsed process	30.1 ± 2.09	51.1 ± 3.54	35.9 ± 2.13	33.5 ± 5.52	32.4 ± 2.21

Table 61: Surface energy (σ) of DDBSA (solved in THF) modified tungsten surface (calculated via data of Table 59 and Table 60).

	σ after pretr. [mN/m]	σ after DDBSA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2	74.74 ± 0.78	65.27 ± 0.90	73.79 ± 0.89	68.21 ± 1.30	70.33 ± 0.82
Pretreatment 2 and rinsed process	75.48 ± 0.89	62.33 ± 1.28	72.09 ± 0.84	67.57 ± 2.11	66.05 ± 1.00

Table 62: Ellipsometric data of DDBSA (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after DDBSA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2	48.52 ± 0.50	51.19 ± 0.13	49.13 ± 0.36	49.14 ± 0.63	47.22 ± 0.77
Pretreatment 2 and rinsed process	47.61 ± 0.15	50.08 ± 0.12	48.28 ± 0.30	47.89 ± 0.38	47.34 ± 0.53

4.2.1.4 Tetradecylamine

Solution: 0.0064 g Tetradecylamine solved in 60 mL THF.

Table 63: Water contact angle (CA) of TDA (solved in THF) modified tungsten surface.

Water	CA after pretr. [°]	CA after TDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	13.9 ± 2.74	96.0 ± 1.32	88.0 ± 8.08	81.8 ± 3.33	75.8 ± 3.38
Pretreatment 1 and rinsed process	10.3 ± 2.22	89.0 ± 3.44	84.3 ± 6.50	76.5 ± 4.81	61.9 ± 8.47

Table 64: Diiodomethane contact angle (CA) of TDA (solved in THF) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after TDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	29.1 ± 2.27	66.4 ± 1.01	62.9 ± 1.06	54.0 ± 1.19	43.8 ± 2.20
Pretreatment 1 and rinsed process	27.3 ± 6.39	65.0 ± 0.88	59.4 ± 1.62	48.9 ± 2.27	46.6 ± 3.86

Table 65: Surface energy (σ) of TDA (solved in THF) modified tungsten surface (calculated via data of Table 63 and Table 64).

	σ after pretr. [mN/m]	σ after TDA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	76.85 ± 0.99	26.62 ± 0.22	30.47 ± 0.54	36.52 ± 0.41	43.11 ± 0.69
Pretreatment 1 and rinsed process	77.92 ± 2.38	29.21 ± 0.31	33.25 ± 0.62	40.78 ± 0.76	48.85 ± 1.57

Table 66: Ellipsometric data of TDA (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after TDA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	47.98 ± 0.25	50.04 ± 0.32	48.90 ± 0.51	48.90 ± 0.58	46.95 ± 0.50
Pretreatment 1 and rinsed process	46.80 ± 0.33	49.37 ± 0.57	47.86 ± 0.88	47.36 ± 0.37	46.01 ± 1.68

Solution: 0.0063 g Tetradecylamine solved in 60 mL IPA.

Table 67: Water contact angle (CA) of TDA (solved in IPA) modified tungsten surface.

Water	CA after pretr. [°]	CA after TDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	10.3 ± 1.62	93.2 ± 4.29	85.5 ± 6.59	80.0 ± 2.81	68.1 ± 3.57
Pretreatment 1 and rinsed process	9.5 ± 2.09	93.6 ± 1.77	86.8 ± 6.29	79.2 ± 2.29	64.5 ± 3.54

Table 68: Diiodomethane contact angle (CA) of TDA (solved in IPA) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after TDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	33.4 ± 8.39	68.3 ± 1.55	58.9 ± 2.63	54.2 ± 1.61	42.8 ± 3.21
Pretreatment 1 and rinsed process	23.9 ± 3.98	66.1 ± 1.22	60.8 ± 2.75	76.5 ± 4.81	48.1 ± 5.39

Table 69: Surface energy (σ) of TDA (solved in IPA) modified tungsten surface (calculated via data of Table 67 and Table 68).

	σ after pretr. [mN/m]	σ after TDA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	76.83 ± 3.06	26.44 ± 0.43	33.07 ± 0.81	37.14 ± 0.49	46.95 ± 1.02
Pretreatment 1 and rinsed process	78.61 ± 1.53	27.34 ± 0.29	31.82 ± 0.81	38.97 ± 0.73	46.94 ± 1.62

Table 70: Ellipsometric data of TDA (solved in IPA) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after TDA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	47.88 ± 0.30	50.23 ± 0.20	48.64 ± 0.22	48.84 ± 0.32	47.52 ± 0.32
Pretreatment 1 and rinsed process	47.67 ± 0.25	49.90 ± 0.43	48.37 ± 0.74	48.84 ± 0.35	47.84 ± 0.97

Solutions: 0.0064 g Tetradecylamine solved in 60 mL THF.

Table 71: Water contact angle (CA) of TDA (solved in THF) modified tungsten surface.

Water	CA after pretr. [°]	CA after TDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 THF	12.8 ± 2.09	92.9 ± 3.24	82.0 ± 4.08	67.5 ± 5.52	79.2 ± 2.01
Pretreatment 2 and rinsed process	18.0 ± 2.61	84.2 ± 3.45	81.3 ± 8.74	69.5 ± 5.29	70.9 ± 1.98

Table 72: Diiodomethane contact angle (CA) of TDA (solved in THF) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after TDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 THF	31.0 ± 3.96	62.1 ± 1.05	56.7 ± 1.88	50.5 ± 2.56	47.2 ± 2.13
Pretreatment 2 and rinsed process	25.5 ± 4.04	61.3 ± 2.30	51.8 ± 3.07	43.6 ± 2.26	44.0 ± 1.57

Table 73: Surface energy (σ) of TDA (solved in THF) modified tungsten surface (calculated via data of Table 71 and Table 72).

	σ after pretr. [mN/m]	σ after TDA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 THF	76.74 ± 1.50	29.39 ± 0.30	35.27 ± 0.59	44.45 ± 0.97	40.39 ± 0.59
Pretreatment 2 and rinsed process	76.36 ± 1.56	32.49 ± 0.63	37.63 ± 1.06	45.98 ± 0.86	45.15 ± 0.49

Table 74: Ellipsometric data of TDA (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after TDA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 THF	47.35 ± 0.03	49.87 ± 0.28	48.94 ± 0.47	48.88 ± 0.46	47.74 ± 0.37
Pretreatment 2 and rinsed process	47.75 ± 0.43	50.45 ± 0.86	48.86 ± 0.65	48.58 ± 0.55	47.21 ± 0.47

4.2.1.5 1-Octadecanethiol

Solution: 0.0085 g ODT solved in 60 mL THF.

Table 75: Water contact angle (CA) of ODT (solved in THF) modified tungsten surface.

Water	CA after pretr. [°]	CA after ODT [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	25.4 ± 1.93	58.7 ± 3.63	44.2 ± 6.21	42.2 ± 4.04	41.4 ± 5.17
Pretreatment 1 and rinsed process	10.6 ± 1.19	59.6 ± 5.21	37.9 ± 1.12	41.7 ± 2.27	39.8 ± 3.44

Table 76: Diiodomethane contact angle (CA) of ODT (solved in THF) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after ODT [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	35.4 ± 5.24	45.7 ± 1.02	41.9 ± 4.04	35.6 ± 1.31	30.6 ± 0.63
Pretreatment 1 and rinsed process	25.9 ± 4.35	44.7 ± 0.82	38.0 ± 2.42	36.1 ± 2.68	29.7 ± 4.03

Table 77: Surface energy (σ) of ODT (solved in THF) modified tungsten surface (calculated via data of Table 75 and Table 76).

	σ after pretr. [mN/m]	σ after ODT [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	71.80 ± 1.88	50.98 ± 0.54	60.64 ± 1.67	63.32 ± 0.75	64.98 ± 0.69
Pretreatment 1 and rinsed process	78.10 ± 1.61	50.79 ± 0.62	65.16 ± 0.84	63.49 ± 0.98	66.04 ± 1.50

Table 78: Ellipsometric data of ODT (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after ODT [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	48.78 ± 0.16	51.05 ± 0.81	51.30 ± 1.47	48.37 ± 0.82	46.09 ± 0.44
Pretreatment 1 and rinsed process	47.72 ± 0.41	50.43 ± 0.69	48.41 ± 0.97	47.83 ± 0.57	46.13 ± 0.72

Solution: 0.0087 g ODT solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 79: Water contact angle (CA) of ODT (solved in IPA) modified tungsten surface.

Water	CA after pretr. [°]	CA after ODT [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	17.9 ± 1.75	45.4 ± 1.29	31.7 ± 4.94	39.0 ± 3.72	46.3 ± 6.85
Pretreatment 1 and rinsed process	14.1 ± 2.16	44.2 ± 1.11	38.3 ± 3.98	41.1 ± 1.85	32.0 ± 4.47

Table 80: Diiodomethane contact angle (CA) of ODT (solved in IPA) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after ODT [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	24.9 ± 1.10	39.8 ± 1.10	36.8 ± 2.34	35.0 ± 1.65	39.0 ± 4.63
Pretreatment 1 and rinsed process	26.2 ± 1.21	40.4 ± 3.06	37.9 ± 2.03	36.3 ± 1.23	30.5 ± 1.96

Table 81: Surface energy (σ) of ODT (solved in IPA) modified tungsten surface (calculated via data of Table 79 and Table 80).

	σ after pretr. [mN/m]	σ after ODT [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	76.49 ± 0.52	60.45 ± 0.42	68.59 ± 1.18	65.28 ± 0.82	60.13 ± 1.87
Pretreatment 1 and rinsed process	77.30 ± 0.60	60.98 ± 1.02	64.97 ± 0.95	63.82 ± 0.52	69.81 ± 1.02

Table 82: Ellipsometric data of ODT (solved in IPA) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after ODT [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	48.90 ± 0.31	49.49 ± 0.13	49.65 ± 1.44	49.12 ± 0.65	47.99 ± 0.51
Pretreatment 1 and rinsed process	48.86 ± 0.51	49.16 ± 0.37	48.94 ± 0.86	49.31 ± 0.52	48.16 ± 1.32

4.2.1.6 Perfluorotetradecanoic acid

Solution: 0.0216 g PFTDA solved in 60 mL THF.

Table 83: Water contact angle (CA) of PFTDA (solved in THF) modified tungsten surface.

Water	CA after pretr. [°]	CA after PFTDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	11.6 ± 1.99	40.4 ± 2.17	39.5 ± 6.15	41.4 ± 3.15	34.5 ± 6.39
Pretreatment 1 and rinsed process	11.5 ± 3.00	43.9 ± 1.37	30.7 ± 4.32	34.6 ± 4.45	35.5 ± 7.12

Table 84: Diiodomethane contact angle (CA) of PFTDA (solved in THF) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after PFTDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	27.0 ± 2.62	69.2 ± 2.97	51.1 ± 8.33	39.0 ± 2.57	35.3 ± 3.94
Pretreatment 1 and rinsed process	23.1 ± 4.13	51.1 ± 6.47	34.3 ± 3.40	38.7 ± 1.32	33.1 ± 4.00

Table 85: Surface energy (σ) of PFTDA (solved in THF) modified tungsten surface (calculated via data of Table 83 and Table 84).

	σ after pretr. [mN/m]	σ after PFTDA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	77.73 ± 1.04	57.23 ± 0.99	61.07 ± 2.92	62.96 ± 1.01	67.53 ± 1.76
Pretreatment 1 and rinsed process	78.37 ± 1.64	58.40 ±2.06	69.64 ± 1.43	66.71 ± 0.84	67.56 ± 1.84

Table 86: Ellipsometric data of PFTDA (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after PFTDA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	46.28 ± 0.47	48.72 ± 0.64	45.86 ± 0.37	46.66 ± 0.24	45.76 ± 0.65
Pretreatment 1 and rinsed process	46.93 ± 0.11	49.33 ± 0.38	46.53 ± 0.68	47.07 ± 0.49	46.13 ± 1.07

Solution: 0.0219 g PFTDA solved in 60 mL IPA.

Table 87: Water contact angle (CA) of PFTDA (solved in IPA) modified tungsten surface.

Water	CA after pretr. [°]	CA after PFTDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	10.5 ± 2.20	28.7 ± 2.68	22.6 ± 4.33	32.4 ± 3.17	31.8 ± 6.19
Pretreatment 1 and rinsed process	11.3 ± 3.39	28.3 ± 2.56	25.7 ± 6.15	33.7 ± 6.36	26.5 ± 3.00

Table 88: Diiodomethane contact angle (CA) of PFTDA (solved in IPA) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after PFTDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	28.5 ± 1.56	80.2 ± 3.19	41.3 ± 2.67	37.3 ± 0.67	42.0 ± 8.01
Pretreatment 1 and rinsed process	31.8 ± 2.07	73.4 ± 1.85	36.7 ± 8.51	33.6 ± 3.90	35.4 ± 2.82

Table 89: Surface energy (σ) of PFTDA (solved in IPA) modified tungsten surface (calculated via data of Table 87 and Table 88).

	σ after pretr. [mN/m]	σ after PFTDA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	77.67 ± 0.72	64.18 ± 1.11	71.68 ± 1.25	68.17 ± 0.54	67.43 ± 2.98
Pretreatment 1 and rinsed process	76.92 ± 1.00	64.42 ± 0.77	71.40 ± 3.22	68.34 ± 1.75	71.32 ± 1.15

Table 90: Ellipsometric data of PFTDA (solved in IPA) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after PFTDA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	49.12 ± 0.17	49.94 ± 0.83	48.33 ± 0.72	48.79 ± 0.47	48.06 ± 0.46
Pretreatment 1 and rinsed process	49.36 ± 0.33	49.64 ± 0.61	49.67 ± 0.84	49.02 ± 0.30	49.01 ± 0.51

4.2.1.7 1-Octadecylamine

Solution: 0.0084 g ODA solved in 60 mL THF.

Table 91: Water contact angle (CA) of ODA (solved in THF) modified tungsten surface.

Water	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	17.9 ± 4.61	97.1 ± 1.57	93.5 ± 0.23	91.5 ± 3.41	92.4 ± 1.42
Pretreatment 1 and rinsed process	11.1 ± 1.41	92.8 ± 1.66	89.4 ± 1.47	86.0 ± 4.58	85.6 ± 4.72

Table 92: Diiodomethane contact angle (CA) of ODA (solved in THF) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	23.7 ± 1.88	68.3 ± 1.25	68.6 ± 1.02	68.6 ± 2.46	60.8 ± 1.44
Pretreatment 1 and rinsed process	24.1 ± 1.61	64.6 ± 1.29	61.9 ± 2.95	59.0 ± 4.26	56.5 ± 4.16

Table 93: Surface energy (σ) of ODA (solved in THF) modified tungsten surface (calculated via data of Table 91 and Table 92).

	σ after pretr. [mN/m]	σ after ODA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	76.70 ± 1.07	25.47 ± 0.27	26.22 ± 0.01	28.56 ± 0.08	30.10 ± 0.33
Pretreatment 1 and rinsed process	78.29 ± 0.66	28.26 ± 0.30	30.47 ± 0.06	32.86 ± 0.02	34.08 ± 1.07

Table 94: Ellipsometric data of ODA (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after ODA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	48.66 ± 0.11	50.97 ± 0.18	50.11 ± 0.66	50.26 ± 0.46	48.26 ± 0.93
Pretreatment 1 and rinsed process	48.05 ± 0.52	49.99 ± 0.56	48.51 ± 0.28	48.67 ± 0.04	47.99 ± 0.85

Solution: 0.0083 g ODA solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 95: Water contact angle (CA) of ODA (solved in IPA) modified tungsten surface.

Water	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	17.6 ± 4.57	100.1 ± 1.66	88.5 ± 3.76	86.5 ± 1.41	90.2 ± 1.39
Pretreatment 1 and rinsed process	14.6 ± 3.64	95.0 ± 0.71	92.0 ± 2.79	86.6 ± 2.01	89.5 ± 1.36

Table 96: Diiodomethane contact angle (CA) of ODA (solved in IPA) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	25.1 ± 1.71	70.4 ± 1.34	67.3 ± 1.57	59.4 ± 2.25	62.5 ± 0.72
Pretreatment 1 and rinsed process	26.4 ± 1.21	69.0 ± 1.12	68.1 ± 1.46	59.8 ± 2.87	62.1 ± 1.24

Table 97: Surface energy (σ) of ODA (solved in THF) modified tungsten surface (calculated via data of Table 95 and Table 96).

	σ after pretr. [mN/m]	σ after ODA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	76.54 ± 1.02	23.86 ± 0.28	28.38 ± 0.46	32.48 ± 0.54	29.94 ± 0.19
Pretreatment 1 and rinsed process	77.14 ± 0.78	25.64 ± 0.23	26.88 ± 0.37	32.27 ± 0.69	30.32 ± 0.30

Table 98: Ellipsometric data of ODA (solved in IPA) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after ODA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	48.44 ± 0.59	50.77 ± 0.23	50.06 ± 0.38	49.18 ± 0.24	49.63 ± 0.47
Pretreatment 1 and rinsed process	48.70 ± 0.98	50.54 ± 0.09	50.14 ± 0.33	49.82 ± 0.18	50.02 ± 0.39

Solution: 0.0082 g ODA solved in 60 mL THF.

Table 99: Water contact angle (CA) of ODA (solved in THF) modified tungsten surface.

Water	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2	12.2 ± 1.50	93.4 ± 1.87	96.4 ± 1.66	84.9 ± 2.97	91.8 ± 2.33
Pretreatment 2 and rinsed process	18.8 ± 2.54	91.5 ± 1.59	94.8 ± 2.37	79.9 ± 8.08	87.4 ± 3.46

Table 100: Diiodomethane contact angle (CA) of ODA (solved in THF) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2	24.7 ± 3.46	67.3 ± 1.23	63.2 ± 0.73	59.7 ± 0.44	60.6 ± 1.56
Pretreatment 2 and rinsed process	31.6 ± 1.77	61.6 ± 2.40	62.0 ± 2.00	55.9 ± 3.83	54.1 ± 2.25

Table 101: Surface energy (σ) of ODA (solved in THF) modified tungsten surface (calculated via data of Table 99 and Table 100).

	σ after pretr. [mN/m]	σ after ODA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2	77.98 ± 1.31	26.83 ± 0.29	28.06 ± 0.18	32.92 ± 0.22	30.39 ± 0.38
Pretreatment 2 and rinsed process	75.00 ± 0.80	30.01 ± 0.54	28.96 ± 0.45	36.49 ± 1.22	34.62 ± 0.60

Table 102: Ellipsometric data of ODA (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after ODA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2	47.15 ± 0.10	50.67 ± 0.25	50.33 ± 0.60	49.71 ± 0.56	48.90 ± 0.22
Pretreatment 2 and rinsed process	48.33 ± 0.13	50.53 ± 0.57	49.46 ± 0.42	49.22 ± 0.56	48.90 ± 0.98

Solution: 0.0080 g ODA solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 103: Water contact angle (CA) of ODA (solved in IPA) modified tungsten surface.

Water	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2	13.9 ± 1.11	96.5 ± 2.33	94.9 ± 2.80	86.7 ± 5.25	78.4 ± 7.31
Pretreatment 2 and rinsed process	18.8 ± 2.88	91.6 ± 3.35	91.4 ± 3.30	85.4 ± 1.69	80.8 ± 8.09

Table 104: Diiodomethane contact angle (CA) of ODA (solved in IPA) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2	29.6 ± 1.15	68.5 ± 0.67	65.3 ± 2.37	57.6 ± 1.42	54.0 ± 2.87
Pretreatment 2 and rinsed process	36.8 ± 2.49	64.3 ± 0.94	63.7 ± 2.21	53.6 ± 2.66	51.4 ± 4.55

Table 105: Surface energy (σ) of ODA (solved in IPA) modified tungsten surface (calculated via data of Table 103 and Table 104).

	σ after pretr. [mN/m]	σ after ODA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2	76.75 ± 0.48	25.50 ± 0.19	27.39 ± 0.53	33.24 ± 0.50	37.90 ± 1.00
Pretreatment 2 and rinsed process	73.98 ± 1.05	28.73 ± 0.30	29.06 ± 0.54	35.44 ± 0.66	38.03 ± 1.37

Table 106: Ellipsometric data of ODA (solved in IPA) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after ODA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2	47.42 ± 0.67	50.54 ± 0.25	49.84 ± 0.30	48.68 ± 0.40	47.00 ± 0.53
Pretreatment 2 and rinsed process	47.08 ± 0.12	49.80 ± 0.34	48.44 ± 0.34	48.12 ± 0.46	47.42 ± 0.52

4.2.1.8 1-Octadecanol

Solution: 0.0087 g ODO solved in 60 mL THF.

Table 107: Water contact angle (CA) of ODO (solved in THF) modified tungsten surface.

Water	CA after pretr. [°]	CA after ODO [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	13.5 ± 3.76	32.1 ± 2.79	29.1 ± 5.57	40.0 ± 1.99	41.6 ± 5.68
Pretreatment 1 and rinsed process	11.4 ± 0.42	40.0 ± 1.65	31.5 ± 3.82	41.4 ± 3.14	51.1 ± 6.41
Pretreatment 2	12.2 ± 2.28	31.1 ± 2.02	35.7 ± 1.71	36.3 ± 5.03	32.9 ± 4.07
Pretreatment 2 and rinsed process	8.5 ± 2.21	37.6 ± 2.34	35.4 ± 4.99	36.9 ± 5.84	36.4 ± 4.35

Table 108: Diiodomethane contact angle (CA) of ODO (solved in THF) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after ODO [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	33.1 ± 3.96	69.3 ± 2.08	37.2 ± 1.41	35.7 ± 1.31	32.7 ± 2.56
Pretreatment 1 and rinsed process	27.8 ± 3.45	49.1 ± 6.24	36.5 ± 2.36	31.5 ± 2.38	39.8 ± 2.68
Pretreatment 2	27.5 ± 2.13	70.4 ± 2.60	55.2 ± 10.15	36.2 ± 0.40	36.7 ± 2.95
Pretreatment 2 and rinsed process	26.1 ± 2.49	52.0 ± 2.67	39.8 ± 2.68	33.6 ± 0.58	32.1 ± 2.43

Table 109: Surface energy (σ) of ODO (solved in THF) modified tungsten surface (calculated via data of Table 107 and Table 108).

	σ after pretr. [mN/m]	σ after ODO [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	76.18 ± 1.62	62.48 ± 0.85	69.78 ± 1.02	64.57 ± 0.55	64.39 ± 1.24
Pretreatment 1 and rinsed process	77.63 ± 1.26	61.25 ± 2.04	68.79 ± 1.07	64.78 ± 0.96	57.18 ± 1.25
Pretreatment 2	77.52 ± 0.90	62.98 ± 0.91	62.42 ± 3.29	66.42 ± 0.67	68.04 ± 1.26
Pretreatment 2 and rinsed process	78.46 ± 1.02	62.02 ± 0.97	66.04 ± 1.25	66.67 ± 0.79	67.31 ± 1.12

Table 110: Ellipsometric data of ODO (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after ODO [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	47.89 ± 0.31	50.65 ± 0.54	48.23 ± 1.69	47.75 ± 0.34	46.00 ± 0.54
Pretreatment 1 and rinsed process	47.15 ± 0.33	49.32 ± 0.42	47.14 ± 0.32	47.55 ± 0.17	46.64 ± 0.44
Pretreatment 2	47.08 ± 0.12	50.96 ± 0.29	49.49 ± 1.68	47.48 ± 0.20	46.24 ± 0.28
Pretreatment 2 and rinsed process	47.03 ± 0.29	49.71 ± 0.53	48.43 ± 0.81	47.62 ± 0.27	46.63 ± 0.28

Solution: 0.0079 g ODO solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 111: Water contact angle (CA) of ODO (solved in IPA) modified tungsten surface.

Water	CA after pretr. [°]	CA after ODO [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	20.3 ± 6.05	52.8 ± 3.86	53.2 ± 4.62	43.7 ± 2.01	30.3 ± 1.76
Pretreatment 1 and rinsed process	25.9 ± 1.64	45.3 ± 5.16	28.7 ± 3.41	38.1 ± 2.19	29.0 ± 3.00

Table 112: Diiodomethane contact angle (CA) of ODO (solved in IPA) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after ODO [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	30.6 ± 1.94	48.9 ± 4.52	48.1 ± 6.43	32.1 ± 1.98	37.0 ± 3.08
Pretreatment 1 and rinsed process	23.7 ± 1.30	37.4 ± 3.14	30.8 ± 3.68	34.1 ± 0.65	38.2 ± 1.48

Table 113: Surface energy (σ) of ODO (solved in IPA) modified tungsten surface (calculated via data of Table 111 and Table 112).

	σ after pretr. [mN/m]	σ after ODO [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	74.68 ± 1.25	53.55 ± 1.52	53.47 ± 2.10	63.35 ± 0.74	69.25 ± 1.12
Pretreatment 1 and rinsed process	73.86 ± 0.56	61.16 ± 1.32	71.29 ± 1.45	65.92 ± 0.40	69.63 ± 0.74

Table 114: Ellipsometric data of ODO (solved in IPA) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after ODO [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	48.86 ± 0.63	50.68 ± 0.40	49.21 ± 0.32	48.88 ± 0.33	48.06 ± 0.40
Pretreatment 1 and rinsed process	48.98 ± 0.56	49.35 ± 0.32	48.80 ± 0.36	49.15 ± 0.57	48.14 ± 0.66

4.2.1.9 Lauric acid

Solution: 0.0070 g LA solved in 60 mL THF.

Table 115: Water contact angle (CA) of LA (solved in THF) modified tungsten surface.

Water	CA after pretr. [°]	CA after LA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	9.8 ± 0.93	38.2 ± 2.85	35.2 ± 3.12	39.4 ± 1.77	23.5 ± 2.63
Pretreatment 1 and rinsed process	11.8 ± 2.13	43.9 ± 2.03	33.3 ± 2.02	38.6 ± 1.79	32.8 ± 2.22
Pretreatment 2	10.4 ± 2.85	37.6 ± 1.83	36.1 ± 1.82	41.2 ± 1.76	34.4 ± 5.02
Pretreatment 2 and rinsed process	10.9 ± 2.03	41.3 ± 1.14	37.9 ± 3.90	41.9 ± 1.64	31.2 ± 2.07

Table 116: Diiodomethane contact angle (CA) of LA (solved in THF) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after LA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	28.9 ± 2.99	41.9 ± 3.03	37.6 ± 1.90	28.5 ± 3.04	31.2 ± 0.95
Pretreatment 1 and rinsed process	30.4 ± 3.80	42.5 ± 4.34	34.0 ± 3.21	27.3 ± 3.93	29.2 ± 1.25
Pretreatment 2	31.0 ± 3.36	40.7 ± 3.31	33.4 ± 4.24	30.7 ± 2.47	28.3 ± 2.05
Pretreatment 2 and rinsed process	28.1 ± 1.71	45.6 ± 5.16	36.0 ± 2.70	29.8 ± 3.81	26.2 ± 2.91

Table 117: Surface energy (σ) of LA (solved in THF) modified tungsten surface (calculated via data of Table 115 and Table 116).

	σ after pretr. [mN/m]	σ after LA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	77.73 ± 1.11	64.01 ± 1.14	66.66 ± 0.85	66.54 ± 1.08	73.39 ± 0.57
Pretreatment 1 and rinsed process	77.07 ± 1.45	60.62 ± 1.45	68.45 ± 1.17	67.19 ± 1.38	69.74 ± 0.58
Pretreatment 2	77.23 ± 1.36	64.63 ± 1.16	67.19 ± 1.49	65.10 ± 0.89	69.11 ± 1.09
Pretreatment 2 and rinsed process	77.68 ± 0.75	61.35 ± 1.69	65.62 ± 1.14	64.91 ± 1.32	71.10 ± 1.10

Table 118: Ellipsometric data of LA (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after LA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	48.58 ± 0.16	50.28 ± 0.17	48.47 ± 0.24	48.39 ± 0.37	48.29 ± 2.85
Pretreatment 1 and rinsed process	48.46 ± 0.28	50.22 ± 0.14	48.09 ± 0.14	48.80 ± 0.25	47.75 ± 0.09
Pretreatment 2	48.38 ± 0.38	50.37 ± 0.25	48.11 ± 0.27	49.12 ± 0.30	47.98 ± 0.36
Pretreatment 2 and rinsed process	48.43 ± 0.49	50.32 ± 0.14	48.00 ± 0.18	48.76 ± 0.26	48.26 ± 0.38

Solution: 0.0049 g LA solved in 50 mL IPA.

Table 119: Water contact angle (CA) of LA (solved in IPA) modified tungsten surface.

Water	CA after pretr. [°]	CA after LA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	17.9 ± 2.87	43.6 ± 0.65	32.3 ± 1.61	26.0 ± 1.88	36.7 ± 2.80
Pretreatment 1 and rinsed process	22.6 ± 5.54	38.0 ± 1.20	32.8 ± 1.60	29.3 ± 2.61	39.1 ± 1.12

Table 120: Diiodomethane contact angle (CA) of LA (solved in IPA) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after LA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	36.8 ± 2.57	38.4 ± 2.15	27.4 ± 1.11	31.3 ± 3.13	31.1 ± 3.25
Pretreatment 1 and rinsed process	33.6 ± 1.15	35.7 ± 1.91	29.4 ± 2.06	31.7 ± 3.38	30.8 ± 1.80

Table 121: Surface energy (σ) of LA (solved in IPA) modified tungsten surface (calculated via data of Table 119 and Table 120).

	σ after pretr. [mN/m]	σ after LA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	74.25 ± 1.08	61.84 ± 0.71	70.33 ± 0.49	72.37 ± 1.17	67.36 ± 1.22
Pretreatment 1 and rinsed process	73.25 ± 0.98	65.63 ± 0.68	69.70 ± 0.78	70.87 ± 1.29	66.19 ± 0.64

Table 122: Ellipsometric data of LA (solved in IPA) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after LA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	48.99 ± 0.45	48.42 ± 0.56	48.28 ± 0.34	48.30 ± 0.31	47.27 ± 0.24
Pretreatment 1 and rinsed process	48.45 ± 1.03	48.47 ± 0.26	47.72 ± 0.16	47.68 ± 0.17	47.62 ± 0.90

4.2.1.10 Stearic acid

Solution: 0.0088 g STA solved in 60 mL THF.

Table 123: Water contact angle (CA) of STA (solved in THF) modified tungsten surface.

Water	CA after pretr. [°]	CA after STA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	8.8 ± 2.18	42.2 ± 2.73	46.7 ± 5.60	43.0 ± 3.49	44.8 ± 2.75
Pretreatment 1 and rinsed process	14.4 ± 1.17	42.3 ± 3.16	56.0 ± 7.24	42.2 ± 5.12	50.3 ± 2.67
Pretreatment 2	11.2 ± 2.36	38.3 ± 1.89	54.5 ± 5.85	58.1 ± 2.52	56.1 ± 5.51
Pretreatment 2 and rinsed process	8.2 ± 0.84	41.3 ± 1.03	52.5 ± 8.64	47.3 ± 0.91	46.8 ± 6.68

Table 124: Diiodomethane contact angle (CA) of STA (solved in THF) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after STA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	28.2 ± 1.58	62.2 ± 1.96	47.5 ± 3.42	34.6 ± 2.96	34.9 ± 1.93
Pretreatment 1 and rinsed process	24.3 ± 1.90	47.8 ± 4.24	48.2 ± 5.92	37.3 ± 5.01	34.0 ± 5.61
Pretreatment 2	30.4 ± 4.14	67.1 ± 2.47	52.3 ± 5.42	46.8 ± 5.68	51.7 ± 5.90
Pretreatment 2 and rinsed process	30.2 ± 3.61	53.6 ± 3.84	47.3 ± 4.19	42.7 ± 4.97	35.7 ± 4.17

Table 125: Surface energy (σ) of STA (solved in THF) modified tungsten surface (calculated via data of Table 123 and Table 124).

	σ after pretr. [mN/m]	σ after STA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	78.02 ± 0.72	57.10 ± 0.78	57.62 ± 1.41	63.17 ± 1.15	62.08 ± 0.78
Pretreatment 1 and rinsed process	77.53 ± 0.73	60.20 ± 1.48	51.79 ± 2.10	62.91 ± 1.89	59.22 ± 1.86
Pretreatment 2	77.21 ± 1.59	58.85 ± 0.84	51.48 ± 1.87	50.98 ± 1.74	50.70 ± 1.96
Pretreatment 2 and rinsed process	77.76 ± 1.33	59.47 ± 1.24	54.17 ± 1.81	58.56 ± 1.59	60.76 ± 1.72

Table 126: Ellipsometric data of STA (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after STA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	48.48 ± 0.37	51.08 ± 0.09	49.96 ± 1.60	49.76 ± 1.47	48.63 ± 0.98
Pretreatment 1 and rinsed process	49.29 ± 0.28	51.06 ± 0.20	50.16 ± 1.33	50.18 ± 1.05	49.37 ± 1.02
Pretreatment 2	48.53 ± 0.32	51.01 ± 0.06	50.59 ± 0.38	50.15 ± 0.78	50.09 ± 0.89
Pretreatment 2 and rinsed process	48.56 ± 0.26	50.66 ± 0.28	49.68 ± 0.99	49.31 ± 0.56	49.05 ± 0.52

Solution: 0.0084 g STA solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 127: Water contact angle (CA) of STA (solved in IPA) modified tungsten surface.

Water	CA after pretr. [°]	CA after STA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	18.3 ± 2.71	34.3 ± 1.45	31.8 ± 1.35	37.0 ± 3.25	40.7 ± 6.09
Pretreatment 1 and rinsed process	15.3 ± 1.79	35.2 ± 1.92	34.4 ± 2.40	30.3 ± 2.46	36.4 ± 7.04

Table 128: Diiodomethane contact angle (CA) of STA (solved in IPA) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after STA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	28.5 ± 2.88	40.3 ± 2.04	37.8 ± 0.96	32.0 ± 2.02	35.0 ± 4.93
Pretreatment 1 and rinsed process	33.4 ± 2.42	40.3 ± 1.04	40.8 ± 2.44	32.5 ± 1.86	38.1 ± 2.29

Table 129: Surface energy (σ) of STA (solved in IPA) modified tungsten surface (calculated via data of Table 127 and Table 128).

	σ after pretr. [mN/m]	σ after STA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	75.73 ± 1.17	66.53 ± 0.75	68.30 ± 0.41	66.99 ± 0.89	64.31 ± 1.96
Pretreatment 1 and rinsed process	75.70 ± 0.95	66.03 ± 0.49	66.36 ± 0.94	70.21 ± 0.79	65.93 ± 1.36

Table 130: Ellipsometric data of STA (solved in IPA) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after STA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	48.18 ± 0.43	49.75 ± 0.35	48.97 ± 0.39	48.91 ± 0.30	48.04 ± 0.42
Pretreatment 1 and rinsed process	48.85 ± 0.67	49.24 ± 0.29	48.93 ± 0.32	48.66 ± 0.48	48.23 ± 0.37

4.2.1.11 Perfluorononanoic acid

Solution: 0.0143 g PFNA solved in 60 mL IPA.

Table 131: Water contact angle (CA) of PFNA (solved in IPA) modified tungsten surface.

Water	CA after pretr. [°]	CA after PFNA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	17.5 ± 0.26	29.9 ± 7.93	24.1 ± 1.96	33.9 ± 4.45	31.6 ± 3.57
Pretreatment 1 and rinsed process	13.4 ± 6.10	34.2 ± 0.71	19.1 ± 3.49	28.7 ± 1.84	29.4 ± 12.31

Table 132: Diiodomethane contact angle (CA) of PFNA (solved in IPA) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after PFNA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	29.6 ± 3.32	87.8 ± 5.45	32.8 ± 2.55	36.2 ± 1.45	36.1 ± 1.53
Pretreatment 1 and rinsed process	28.6 ± 3.08	70.8 ± 5.53	30.9 ± 1.43	35.4 ± 2.14	30.9 ± 3.84

Table 133: Surface energy (σ) of PFNA (solved in IPA) modified tungsten surface (calculated via data of Table 131 and Table 132).

	σ after pretr. [mN/m]	σ after PFNA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	75.76 ± 1.20	64.06 ± 2.26	72.84 ± 0.98	67.65 ± 0.87	68.85 ± 0.81
Pretreatment 1 and rinsed process	77.04 ± 1.60	61.04 ± 1.70	75.04 ± 0.81	70.35 ± 0.83	70.99 ± 2.42

Table 134: Ellipsometric data of PFNA (solved in IPA) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after PFNA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	49.14 ± 0.60	50.93 ± 0.71	47.96 ± 0.64	48.71 ± 0.75	46.85 ± 0.85
Pretreatment 1 and rinsed process	47.84 ± 0.29	48.93 ± 0.42	48.09 ± 0.67	47.63 ± 0.26	47.45 ± 0.60

Solution: 0.0140 g PFNA solved in 60 mL THF.

Table 135: Water contact angle (CA) of PFNA (solved in THF) modified tungsten surface.

Water	CA after pretr. [°]	CA after PFNA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	16.5 ± 3.85	39.7 ± 2.29	27.2 ± 2.45	37.6 ± 2.07	35.6 ± 6.49
Pretreatment 1 and rinsed process	7.9 ± 2.28	44.7 ± 2.94	42.9 ± 7.19	45.2 ± 6.50	45.7 ± 6.76

Table 136: Diiodomethane contact angle (CA) of PFNA (solved in THF) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after PFNA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	31.5 ± 4.62	81.8 ± 3.30	35.6 ± 1.75	31.6 ± 1.43	36.8 ± 3.13
Pretreatment 1 and rinsed process	31.1 ± 3.10	74.1 ± 5.99	41.7 ± 4.60	34.2 ± 1.77	36.0 ± 2.39

Table 137: Surface energy (σ) of PFNA (solved in THF) modified tungsten surface (calculated via data of Table 135 and Table 136).

	σ after pretr. [mN/m]	σ after PFNA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	75.72 ± 1.84	56.99 ± 1.05	70.97 ± 0.77	66.79 ± 0.60	66.64 ± 1.53
Pretreatment 1 and rinsed process	77.65 ± 1.23	53.68 ± 1.83	61.44 ± 1.93	62.06 ± 1.08	61.31 ± 1.26

Table 138: Ellipsometric data of PFNA (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after PFNA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	48.00 ± 1.04	49.87 ± 1.00	47.71 ± 0.37	47.80 ± 0.28	46.63 ± 0.64
Pretreatment 1 and rinsed process	47.74 ± 0.09	49.36 ± 0.25	48.18 ± 0.73	48.65 ± 0.75	47.64 ± 1.83

4.2.1.12 *1H,1H,2H,3H,3H*-Perfluorononanoic-1,2-diol

Solution: 0.0112 g PFND solved in 60 mL IPA.

Table 139: Water contact angle (CA) of PFND (solved in IPA) modified tungsten surface.

Water	CA after pretr. [°]	CA after PFND [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	18.7 ± 5.03	51.8 ± 1.62	30.6 ± 3.68	30.6 ± 3.05	32.7 ± 3.16
Pretreatment 1 and rinsed process	14.3 ± 4.65	56.8 ± 8.82	30.2 ± 2.30	30.4 ± 1.75	27.8 ± 4.46

Table 140: Diiodomethane contact angle (CA) of PFND (solved in IPA) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after PFND [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	26.8 ± 1.23	57.7 ± 3.74	37.0 ± 2.87	31.2 ± 1.86	31.9 ± 0.91
Pretreatment 1 and rinsed process	27.0 ± 1.03	68.1 ± 11.67	37.0 ± 3.04	35.5 ± 1.41	32.8 ± 2.30

Table 141: Surface energy (σ) of PFND (solved in IPA) modified tungsten surface (calculated via data of Table 139 and Table 140).

	σ after pretr. [mN/m]	σ after PFND [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	75.91 ± 0.94	51.77 ± 1.15	69.12 ± 1.20	70.38 ± 0.85	69.22 ± 0.59
Pretreatment 1 and rinsed process	77.10 ± 0.85	45.93 ± 3.56	69.30 ± 1.14	69.54 ± 0.59	71.28 ± 1.14

Table 142: Ellipsometric data of PFND (solved in IPA) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after PFND [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	49.67 ± 0.99	49.83 ± 0.45	47.94 ± 0.39	49.12 ± 0.38	47.71 ± 0.61
Pretreatment 1 and rinsed process	48.82 ± 0.49	49.04 ± 0.85	47.57 ± 0.33	48.44 ± 0.37	46.94 ± 0.57

Solution: 0.0116 g PFND solved in 60 mL THF.

Table 143: Water contact angle (CA) of PFND (solved in THF) modified tungsten surface.

Water	CA after pretr. [°]	CA after PFND [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	18.3 ± 1.50	63.4 ± 1.35	33.6 ± 2.02	40.8 ± 5.62	39.6 ± 1.36
Pretreatment 1 and rinsed process	16.3 ± 0.42	68.4 ± 2.80	36.0 ± 3.52	36.9 ± 2.56	44.6 ± 3.70

Table 144: Diiodomethane contact angle (CA) of PFND (solved in THF) modified tungsten surface.

Diiodomethane	CA after pretr. [°]	CA after PFND [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	33.4 ± 1.57	77.8 ± 2.38	43.3 ± 3.11	35.8 ± 0.87	33.5 ± 3.85
Pretreatment 1 and rinsed process	31.9 ± 3.66	68.9 ± 1.71	40.4 ± 1.62	36.3 ± 1.19	38.3 ± 1.93

Table 145: Surface energy (σ) of PFND (solved in THF) modified tungsten surface (calculated via data of Table 143 and Table 144).

	σ after pretr. [mN/m]	σ after PFND [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	74.80 ± 0.64	39.42 ± 0.64	66.19 ± 1.12	64.07 ± 0.81	65.29 ± 1.32
Pretreatment 1 and rinsed process	75.68 ± 1.32	37.93 ± 0.57	65.57 ± 0.81	66.06 ± 0.59	61.30 ± 0.86

Table 146: Ellipsometric data of PFND (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after PFND [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 1	48.48 ± 0.62	49.88 ± 0.23	48.32 ± 0.58	48.14 ± 0.33	47.70 ± 1.74
Pretreatment 1 and rinsed process	48.38 ± 0.42	50.42 ± 0.21	48.46 ± 0.64	48.17 ± 0.52	47.61 ± 1.26

4.2.2 Titanium nitride coated silicon wafer

4.2.2.1 Octadecylphosphonic acid

Solution: 0.0099 g ODPA solved in 60 mL THF.

Table 147: Water contact angle (CA) of ODPA (solved in THF) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 3	36.0 ± 1.82	96.1 ± 1.88	82.3 ± 3.53	88.7 ± 2.79	89.7 ± 1.33

Table 148: Diiodomethane contact angle (CA) of ODPA (solved in THF) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 3	28.6 ± 3.26	65.8 ± 1.08	54.9 ± 0.38	57.2 ± 1.83	60.5 ± 3.18

Table 149: Surface energy (σ) of ODPA (solved in THF) modified titanium nitride surface (calculated via data of Table 147 and Table 148).

	σ after pretr. [mN/m]	σ after ODPA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 3	68.27 ± 1.17	26.87 ± 0.25	45.33 ± 0.93	32.80 ± 0.47	31.01 ± 0.72

Solution: 0.0101 g ODPA solved in 60 mL THF.

Table 150: Water contact angle (CA) of ODPA (solved in THF) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	16.8 ± 0.63	94.0 ± 2.46	91.5 ± 2.03	88.6 ± 2.90	96.0 ± 4.52
Pretreatment 1 and rinsed process	16.4 ± 1.37	96.7 ± 0.73	86.9 ± 1.38	90.8 ± 0.93	92.0 ± 2.96
Pretreatment 2	16.4 ± 1.95	96.8 ± 1.70	83.6 ± 2.47	87.6 ± 0.99	92.0 ± 3.56
Pretreatment 2 and rinsed process	24.1 ± 2.04	95.8 ± 2.90	82.5 ± 3.71	87.6 ± 1.72	94.8 ± 1.93

Table 151: Diiodomethane contact angle (CA) of ODPA (solved in THF) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	25.0 ± 6.49	63.6 ± 0.98	61.4 ± 1.33	59.8 ± 1.11	67.6 ± 2.91
Pretreatment 1 and rinsed process	22.2 ± 2.92	62.6 ± 0.92	59.5 ± 2.24	57.0 ± 1.33	64.5 ± 1.76
Pretreatment 2	26.1 ± 1.68	63.6 ± 1.75	59.8 ± 0.98	57.8 ± 1.06	63.5 ± 1.50
Pretreatment 2 and rinsed process	23.7 ± 3.44	61.2 ± 1.68	59.0 ± 2.28	57.4 ± 0.69	64.1 ± 1.95

Table 152: Surface energy (σ) ODPA (solved in THF) modified titanium nitride surface (calculated via data of Table 150 and Table 151).

	σ after pretr. [mN/m]	σ after ODPA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	76.79 ± 2.36	28.40 ± 0.26	30.07 ± 0.33	31.64 ± 0.33	26.02 ± 0.67
Pretreatment 1 and rinsed process	77.35 ± 1.10	28.28 ± 0.20	32.34 ± 0.53	32.32 ± 0.31	28.49 ± 0.44
Pretreatment 2	76.72 ± 0.72	27.78 ± 0.38	33.37 ± 0.32	32.87 ± 0.26	28.95 ± 0.41
Pretreatment 2 and rinsed process	74.56 ± 1.30	29.15 ± 0.40	34.14 ± 0.65	33.07 ± 0.20	27.97 ± 0.43

Solution: 0.0099 g ODPA solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 153: Water contact angle (CA) of ODPA (solved in IPA) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	25.4 ± 2.55	93.7 ± 1.86	83.2 ± 2.99	87.3 ± 3.02	91.1 ± 1.79

Table 154: Diiodomethane contact angle (CA) of ODPA (solved in IPA) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	33.2 ± 5.17	63.0 ± 0.88	59.4 ± 0.79	59.4 ± 1.24	61.5 ± 2.13

Table 155: Surface energy (σ) of ODPA (solved in IPA) modified titanium nitride surface (calculated via data of Table 153 and Table 154).

	σ after pretr. [mN/m]	σ after ODPA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	72.25 ± 1.90	28.76 ± 0.22	33.69 ± 0.30	32.24 ± 0.37	30.12 ± 0.49

Solution: 0.0101 g ODPA solved in 60 mL THF.

The first chip was cleaned and stored at atmosphere for one week. After the week the chip was immersed 10 min in the OPDA solution. The cleaned chip was measured before the storage. The second chip was cleaned via the immersion in 1% HF for one minute and blown dry with N_2. The coating was immediately (within 1 minute) done after the cleaning. A third chip was cleaned with 1% HF and immediately (within 10 minutes) after the cleaning measured (to receive the cleaned value).

Table 156: Contact angles (CA) of ODPA modified titanium nitride surface before and after the coating.

	CA after pretr. [°]		CA after ODPA [°]	
	H_2O	CH_2I_2	H_2O	CH_2I_2
Pretreatment 2	30.5 ± 2.97	37.3 ± 3.05	92.2 ± 0.80	58.2 ± 2.64
1% HF	13.9 ± 1.24	65.1 ± 0.23	97.0 ± 2.01	36.0 ± 1.21

Table 157: Surface energy (σ) of ODPA modified titanium nitride surface before and after the coating (calculated via data of Table 156).

	σ after pretr. [mN/m]	σ after ODPA [mN/m]
Pretreatment 2	69.07 ± 1.20	31.41 ± 0.59
1% HF	75.55 ± 0.50	26.98 ± 0.09

4.2.2.2 Tetradecylphosphonic acid

Solution: 0.0082 g TDPA solved in 60 mL THF.

Table 158: Water contact angle (CA) of TDPA (solved in THF) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after TDPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	16.5 ± 1.74	92.3 ± 3.69	66.0 ± 1.04	64.5 ± 1.34	50.4 ± 8.21
Pretreatment 1 and rinsed process	17.0 ± 3.05	93.5 ± 1.77	70.1 ± 3.58	68.7 ± 5.08	59.9 ± 16.73
Pretreatment 2	11.2 ± 1.93	96.6 ± 1.95	69.2 ± 2.86	63.0 ± 4.13	51.5 ± 5.80
Pretreatment 2 and rinsed process	17.5 ± 1.87	94.9 ± 2.34	71.1 ± 3.79	75.9 ± 2.99	82.9 ± 8.91

Table 159: Diiodomethane contact angle (CA) of TDPA (solved in THF) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after TDPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 1	29.2 ± 4.71	61.2 ± 2.25	47.2 ± 0.61	44.8 ± 1.94	49.0 ± 4.44
Pretreatment 1 and rinsed process	26.7 ± 3.09	69.4 ± 1.77	45.0 ± 2.82	44.1 ± 1.50	49.2 ± 3.97
Pretreatment 2	25.2 ± 2.66	69.1 ± 1.02	48.3 ± 3.91	46.6 ± 2.02	47.0 ± 4.01
Pretreatment 2 and rinsed process	28.1 ± 5.86	64.8 ± 2.51	50.6 ± 2.63	47.8 ± 2.74	61.5 ± 4.72

Table 160: Surface energy (σ) of TDPA (solved in THF) modified titanium nitride surface (calculated via data of Table 158 and Table 159).

	σ after pretr. [mN/m]	σ after TDPA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 1	76.12 ± 1.74	29.98 ± 0.56	46.45 ± 0.22	48.06 ± 0.59	54.99 ± 1.87
Pretreatment 1 and rinsed process	76.45 ± 1.28	25.88 ± 0.39	45.17 ± 0.90	46.17 ± 0.68	48.15 ± 2.31
Pretreatment 2	78.10 ± 1.05	25.19 ± 0.24	44.35 ± 1.14	48.24 ± 0.79	54.84 ± 1.54
Pretreatment 2 and rinsed process	76.04 ± 2.15	27.63 ± 0.55	42.57 ± 0.84	41.44 ± 0.80	32.93 ± 1.39

Solution: 0.0084 g TDPA solved in 60 mL IPA.

Table 161: Water contact angle (CA) of TDPA (solved in IPA) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after TDPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	28.0 ± 3.06	90.7 ± 2.27	67.0 ± 6.01	78.9 ± 2.81	70.1 ± 6.25

Table 162: Diiodomethane contact angle (CA) of TDPA (solved in IPA) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after TDPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	33.9 ± 1.76	61.2 ± 3.12	50.0 ± 2.67	51.5 ± 2.57	50.1 ± 3.89

Table 163: Surface energy (σ) of TDPA (solved in IPA) modified titanium nitride surface (calculated via data of Table 161 and Table 162).

	σ after pretr. [mN/m]	σ after TDPA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	70.98 ± 0.83	30.35 ± 0.71	44.87 ± 1.03	38.71 ± 0.72	43.29 ± 1.30

4.2.2.3 Tetradecylamine

Solution: 0.0067 g TDA solved in 60 mL THF.

Table 164: Water contact angle (CA) of TDA (solved in THF) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after TDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	18.6 ± 3.95	83.9 ± 2.02	68.9 ± 3.84	57.2 ± 3.34	31.3 ± 6.63

Table 165: Diiodomethane contact angle (CA) of TDA (solved in THF) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after TDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	35.9 ± 4.94	59.1 ± 2.41	53.5 ± 4.50	46.2 ± 3.18	31.9 ± 2.02

Table 166: Surface energy (σ) of TDA (solved in THF) modified titanium nitride surface (calculated via data of Table 164 and Table 165).

	σ after pretr. [mN/m]	σ after TDA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	74.22 ± 1.94	33.54 ± 0.60	42.64 ± 1.33	51.67 ± 1.08	69.85 ± 1.28

Solution: 0.0065 g TDA solved in 60 mL IPA.

Table 167: Water contact angle (CA) of TDA (solved in IPA) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after TDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	21.9 ± 1.99	78.6 ± 2.87	72.6 ± 1.30	69.2 ± 1.51	41.4 ± 6.71

Table 168: Diiodomethane contact angle (CA) of TDA (solved in IPA) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after TDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	26.0 ± 2.35	59.3 ± 1.00	55.7 ± 1.52	45.6 ± 1.38	37.5 ± 1.52

Table 169: Surface energy (σ) of TDA (solved in IPA) modified titanium nitride surface (calculated via data of Table 167 and Table 168).

	σ after pretr. [mN/m]	σ after TDA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	74.99 ± 0.93	35.66 ± 0.37	39.94 ± 0.43	45.36 ± 0.43	63.31 ± 1.08

4.2.2.4 Octadecylamine

Solution: 0.0084 g ODA solved in 60 mL THF.

Table 170: Water contact angle (CA) of ODA (solved in THF) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	20.4 ± 1.38	79.4 ± 3.57	76.6 ± 2.41	74.7 ± 2.92	59.6 ± 7.24

Table 171: Diiodomethane contact angle (CA) of ODA (solved in THF) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	28.7 ± 3.71	58.1 ± 1.26	61.1 ± 2.74	50.0 ± 3.09	45.4 ± 5.22

Table 172: Surface energy (σ) of ODA (solved in THF) modified titanium nitride surface (calculated via data of Table 170 and Table 171).

	σ after pretr. [mN/m]	σ after ODA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	75.00 ± 1.36	35.76 ± 0.45	35.88 ± 0.74	41.07 ± 0.89	50.57 ± 1.86

Solution: 0.0083 g ODA solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 173: Water contact angle (CA) of ODA (solved in IPA) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	23.5 ± 0.56	83.0 ± 2.55	77.7 ± 3.75	75.6 ± 3.22	65.6 ± 3.66

Table 174: Diiodomethane contact angle (CA) of ODA (solved in IPA) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	33.9 ± 1.91	61.3 ± 1.27	61.6 ± 2.64	48.6 ± 2.41	37.1 ± 3.56

Table 175: Surface energy (σ) of ODA (solved in IPA) modified titanium nitride surface (calculated via data of Table 173and Table 174).

	σ after pretr. [mN/m]	σ after ODA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	72.86 ± 0.68	32.98 ± 0.38	35.17 ± 0.77	41.24 ± 0.73	50.12 ± 1.15

4.2.2.5 Lauric acid

Solution: 0.0064 g LA solved in 60 mL THF.

Table 176: Water contact angle (CA) of LA (solved in THF) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after LA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	19.6 ± 0.84	76.8 ± 3.23	53.2 ± 6.28	67.7 ± 5.64	26.0 ± 1.83

Table 177: Diiodomethane contact angle (CA) of LA (solved in THF) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after LA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	28.7 ± 2.49	54.9 ± 4.59	46.9 ± 4.15	41.4 ± 2.42	37.0 ± 2.41

Table 178: Surface energy (σ) of LA (solved in THF) modified titanium nitride surface (calculated via data of Table 176 and Table 177).

	σ after pretr. [mN/m]	σ after LA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	75.26 ± 0.91	38.24 ± 1.23	53.89 ± 1.60	47.62 ± 0.94	71.19 ± 0.92

Solution: 0.0062 g LA solved in 60 mL IPA.

Table 179: Water contact angle (CA) of LA (solved in IPA) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after LA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	25.9 ± 2.07	72.5 ± 3.49	44.1 ± 4.11	55.1 ± 3.11	60.3 ± 9.94

Table 180: Diiodomethane contact angle (CA) of LA (solved in IPA) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after LA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	32.2 ± 2.01	46.5 ± 2.89	36.1 ± 2.25	40.8 ± 0.79	47.2 ± 1.64

Table 181: Surface energy (σ) of LA (solved in IPA) modified titanium nitride surface (calculated via data of Table 179 and Table 180).

	σ after pretr. [mN/m]	σ after LA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	72.26 ± 0.81	43.49 ± 0.98	62.19 ± 0.99	54.58 ± 0.46	49.59 ± 1.19

4.2.2.6 Stearic acid

Solution: 0.0087 g STA solved in 60 mL THF.

Table 182: Water contact angle (CA) of STA (solved in THF) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after STA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	20.9 ± 1.63	82.2 ± 2.98	69.6 ± 3.24	74.8 ± 2.12	39.3 ± 6.37

Table 183: Diiodomethane contact angle (CA) of STA (solved in THF) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after STA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	27.4 ± 5.67	57.9 ± 2.33	56.1 ± 2.83	51.9 ± 2.75	42.9 ± 5.25

Table 184: Surface energy (σ) of STA (solved in THF) modified titanium nitride surface (calculated via data of Table 182 and Table 183).

	σ after pretr. [mN/m]	σ after STA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	75.09 ± 2.07	34.71 ± 0.63	41.35 ± 0.87	40.34 ± 0.76	63.15 ± 2.07

Solution: 0.0085 g STA solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 185: Water contact angle (CA) of STA (solved in IPA) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after STA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	26.2 ± 0.73	75.6 ± 3.30	63.2 ± 5.13	66.6 ± 1.76	44.9 ± 8.64

Table 186: Diiodomethane contact angle (CA) of STA (solved in IPA) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after STA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	32.0 ± 2.52	51.3 ± 1.22	47.0 ± 3.40	45.3 ± 1.59	41.4 ± 2.41

Table 187: Surface energy (σ) of STA (solved in IPA) modified titanium nitride surface (calculated via data of Table 185 and Table 186).

	σ after pretr. [mN/m]	σ after STA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	72.17 ± 0.90	40.19 ± 0.45	48.02 ± 1.20	46.81 ± 0.51	60.37 ± 1.47

4.2.2.7 1-Octadecanol

Solution: 0.0084 g ODO solved in 60 mL THF.

Table 188: Water contact angle (CA) of ODO (solved in THF) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after ODO [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	18.5 ± 2.22	57.8 ± 2.25	55.0 ± 2.83	56.1 ± 4.57	32.4 ± 11.16

Table 189: Diiodomethane contact angle (CA) of ODO (solved in THF) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after ODO [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	26.8 ± 6.03	46.5 ± 0.95	40.7 ± 2.67	37.8 ± 1.11	41.1 ± 3.06

Table 190: Surface energy (σ) of ODO (solved in THF) modified titanium nitride surface (calculated via data of Table 188 and Table 189).

	σ after pretr. [mN/m]	σ after ODO [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	75.96 ± 2.23	51.27 ± 0.41	54.67 ± 0.93	54.91 ± 0.65	67.29 ± 2.07

Solution: 0.0083 g ODO solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 191: Water contact angle (CA) of ODO (solved in IPA) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after ODO [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	23.7 ± 0.89	58.6 ± 2.52	45.5 ± 4.68	55.2 ± 5.55	31.8 ± 5.05

Table 192: Diiodomethane contact angle (CA) of ODO (solved in IPA) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after ODO [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	28.3 ± 1.21	49.5 ± 1.00	36.5 ± 1.45	38.9 ± 1.22	37.2 ± 2.16

Table 193: Surface energy (σ) of ODO (solved in IPA) modified titanium nitride surface (calculated via data of Table 191 and Table 192).

	σ after pretr. [mN/m]	σ after ODO [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	73.90 ± 0.47	49.83 ± 0.45	61.29 ± 0.83	55.08 ± 0.77	68.46 ± 1.14

4.2.2.8 1-Octadecanethiol

Solution: 0.0086 g ODT solved in 60 mL THF.

Table 194: Water contact angle (CA) of ODT (solved in THF) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after ODT [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	20.1 ± 1.04	57.0 ± 2.68	55.2 ± 2.81	53.7 ± 2.33	21.1 ± 3.95

Table 195: Diiodomethane contact angle (CA) of ODT (solved in THF) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after ODT [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	30.8 ± 2.12	47.0 ± 1.75	42.6 ± 4.20	40.3 ± 1.01	37.9 ± 2.79

Table 196: Surface energy (σ) of ODT (solved in THF) modified titanium nitride surface (calculated via data of Table 194 and Table 195).

	σ after pretr. [mN/m]	σ after ODT [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	74.71 ± 0.79	51.58 ± 0.66	53.97 ± 1.37	55.55 ± 0.45	72.97 ± 1.25

Solution: 0.0088 g ODT solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 197: Water contact angle (CA) of ODT (solved in IPA) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after ODT [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	23.5 ± 1.86	49.9 ± 3.81	43.8 ± 4.33	54.3 ± 5.49	39.9 ± 1.91

Table 198: Diiodomethane contact angle (CA) of ODT (solved in IPA) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after ODT [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	28.9 ± 3.07	40.1 ± 0.84	37.7 ± 2.59	40.1 ± 1.44	41.0 ± 0.62

Table 199: Surface energy (σ) of ODT (solved in IPA) modified titanium nitride surface (calculated via data of Table 197 and Table 198).

	σ after pretr. [mN/m]	σ after ODT [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	73.84 ± 1.16	57.78 ± 0.56	61.91 ± 1.11	55.22 ± 0.83	63.27 ± 0.36

4.2.2.9 4-Dodecylbenzenesulfonic acid

Solution: 0.0097 g DDBSA solved in 60 mL THF.

Table 200: Water contact angle (CA) of DDBSA (solved in THF) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after DDBSA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	26.2 ± 1.48	51.5 ± 1.89	51.2 ± 4.93	55.1 ± 3.20	30.0 ± 3.52

Table 201: Diiodomethane contact angle (CA) of DDBSA (solved in THF) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after DDBSA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	29.3 ± 2.61	61.7 ± 0.91	40.6 ± 3.83	39.5 ± 2.24	33.4 ± 2.93

Table 202: Surface energy (σ) of DDBSA (solved in THF) modified titanium nitride surface (calculated via data of Table 200 and Table 201).

	σ after pretr. [mN/m]	σ after DDBSA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	72.67 ± 0.97	50.97 ± 0.40	56.91 ± 1.44	54.98 ± 0.84	70.16 ± 1.22

Solution: 0.0097 g DDBSA solved in 60 mL IPA.

Table 203: Water contact angle (CA) of DDBSA (solved in IPA) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after DDBSA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	19.4 ± 0.80	38.7 ± 1.81	39.6 ± 5.35	52.0 ± 4.74	21.2 ± 2.14

Table 204: Diiodomethane contact angle (CA) of DDBSA (solved in IPA) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after DDBSA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	32.8 ± 4.11	53.6 ± 3.08	37.6 ± 1.32	39.4 ± 0.97	32.0 ± 2.24

Table 205: Surface energy (σ) of DDBSA (solved in IPA) modified titanium nitride surface (calculated via data of Table 203 and Table 204).

	σ after pretr. [mN/m]	σ after DDBSA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	74.55 ± 1.48	60.99 ± 1.05	64.28 ± 0.90	56.75 ± 0.67	74.10 ± 0.91

4.2.2.10 *1H,1H,2H,3H,3H*-Perfluorononanoic-1,2-diol

Solution: 0.0115 g PFND solved in 60 mL THF.

Table 206: Water contact angle (CA) of PFND (solved in THF) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after PFND [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	29.7 ± 6.82	74.2 ± 2.05	56.0 ± 4.89	60.0 ± 4.19	29.5 ± 4.53

Table 207: Diiodomethane contact angle (CA) of PFND (solved in THF) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after PFND [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	29.0 ± 2.90	64.6 ± 4.24	39.6 ± 1.55	43.9 ± 2.63	33.7 ± 3.21

Table 208: Surface energy (σ) of PFND (solved in THF) modified titanium nitride surface (calculated via data of

	σ after pretr. [mN/m]	σ after PFND [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	71.22 ± 1.55	35.90 ± 1.09	54.39 ± 0.79	50.82 ± 0.97	70.32 ± 1.40

Solution: 0.0120 g PFND solved in 60 mL IPA.

Table 209: Water contact angle (CA) of PFND (solved in IPA) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after PFND [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	22.9 ± 2.08	67.2 ± 1.73	46.9 ± 3.39	68.9 ± 2.41	37.2 ± 2.86

Table 210: Diiodomethane contact angle (CA) of PFND (solved in IPA) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after PFND [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	32.1 ± 1.77	67.1 ± 2.79	41.2 ± 1.13	46.9 ± 2.19	30.4 ± 2.63

Table 211: Surface energy (σ) of PFND (solved in IPA) modified titanium nitride surface (calculated via data of

	σ after pretr. [mN/m]	σ after PFND [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	73.47 ± 0.75	39.22 ± 0.77	59.22 ± 0.61	45.07 ± 0.68	67.24 ± 1.04

4.2.2.11 Perfluorononanoic acid

Solution: 0.0140 g PFNA solved in 60 mL THF.

Table 212: Water contact angle (CA) of PFNA (solved in THF) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after PFNA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	32.5 ± 1.76	73.8 ± 3.17	56.4 ± 2.88	58.3 ± 3.91	40.7 ± 3.04

Table 213: Diiodomethane contact angle (CA) of PFNA (solved in THF) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after PFNA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	29.8 ± 3.53	75.3 ± 6.27	42.9 ± 0.97	41.3 ± 1.48	38.9 ± 4.32

Table 214: Surface energy (σ) of PFNA (solved in THF) modified titanium nitride surface (calculated via data of Table 212 and Table 213).

	σ after pretr. [mN/m]	σ after PFNA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	69.74 ± 1.27	32.89 ± 1.55	53.21 ± 0.48	52.60 ± 0.67	63.36 ± 1.54

Solution: 0.0137 g PFNA solved in 60 mL IPA.

Table 215: Water contact angle (CA) of PFNA (solved in IPA) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after PFNA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	21.1 ± 1.00	51.2 ± 3.50	45.5 ± 5.18	56.0 ± 4.66	31.1 ± 3.70

Table 216: Diiodomethane contact angle (CA) of PFNA (solved in IPA) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after PFNA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	31.8 ± 1.89	68.0 ± 2.32	35.9 ± 1.02	44.5 ± 1.06	32.4 ± 2.04

Table 217: Surface energy (σ) of PFNA (solved in IPA) modified titanium nitride surface (calculated via data of Table 215 and Table 216).

	σ after pretr. [mN/m]	σ after PFNA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	74.18 ± 0.71	49.88 ± 0.88	61.40 ± 0.77	52.90 ± 0.66	69.89 ± 0.97

4.2.2.12 Perfluorotetradecanoic acid

Solution: 0.0212 g PFTDA solved in 60 mL THF.

Table 218: Water contact angle (CA) of PFTDA (solved in THF) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after PFTDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	25.2 ± 1.69	63.8 ± 3.34	45.9 ± 8.78	54.8 ± 2.96	29.0 ± 2.04

Table 219: Diiodomethane contact angle (CA) of PFTDA (solved in THF) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after PFTDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	32.0 ± 2.36	69.8 ± 5.41	50.4 ± 11.54	52.4 ± 9.41	30.5 ± 2.22

Table 220: Surface energy (σ) of PFTDA (solved in THF) modified titanium nitride surface (calculated via data of Table 218 and Table 219).

	σ after pretr. [mN/m]	σ after PFTDA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	72.56 ± 0.90	40.73 ± 1.52	57.33 ± 3.95	51.25 ± 2.85	71.22 ± 0.87

Solution: 0.0213 g PFTDA solved in 60 mL IPA.

Table 221: Water contact angle (CA) of PFTDA (solved in IPA) modified titanium nitride surface.

Water	CA after pretr. [°]	CA after PFTDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	22.1 ± 1.93	63.8 ± 5.48	47.8 ± 7.93	57.4 ± 3.95	34.2 ± 4.88

Table 222: Diiodomethane contact angle (CA) of PFTDA (solved in IPA) modified titanium nitride surface.

Diiodomethane	CA after pretr. [°]	CA after PFTDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	32.7 ± 1.70	73.7 ± 5.85	51.5 ± 6.74	46.8 ± 5.51	35.3 ± 3.63

Table 223: Surface energy (σ) of PFTDA (solved in IPA) modified titanium nitride surface (calculated via data of Table 221 and Table 222).

	σ after pretr. [mN/m]	σ after PFTDA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	73.63 ± 0.71	39.89 ± 1.73	55.88 ± 2.48	51.41 ± 1.76	67.69 ± 1.52

4.2.3 Thermal silicon dioxide coated silicon wafer

4.2.3.1 1-Octadecanethiol

Solution: 0.0086 g ODT solved in 60 mL THF.

Table 224: Water contact angle (CA) of ODT (solved in THF) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after ODT [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	31.4 ± 2.20	56.9 ± 6.26	40.8 ± 5.87	47.5 ± 5.77	27.7 ± 3.20

Table 225: Diiodomethane contact angle (CA) of ODT (solved in THF) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after ODT [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	40.3 ± 1.48	53.8 ± 2.17	44.6 ± 2.17	43.2 ± 1.97	46.3 ± 1.24

Table 226: Surface energy (σ) of ODT (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 224 and Table 225).

	σ after pretr. [mN/m]	σ after ODT [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	67.95 ± 0.65	49.57 ± 1.06	61.87 ± 1.17	58.35 ± 1.05	68.47 ± 0.70

Table 227: Ellipsometric data of ODT (solved in THF) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after ODT [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	102.43 ± 0.26	104.34 ± 0.61	103.32 ± 1.08	102.73 ± 0.37	25.73 ± 1.71

Solution: 0.0088 g ODT solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 228: Water contact angle (CA) of ODT (solved in IPA) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after ODT [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	34.6 ± 0.61	46.7 ± 2.15	31.6 ± 1.91	39.7 ± 1.92	31.7 ± 5.68

Table 229: Diiodomethane contact angle (CA) of ODT (solved in IPA) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after ODT [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	40.2 ± 2.81	45.2 ± 1.53	41.8 ± 0.80	41.5 ± 1.09	46.6 ± 1.57

Table 230: Surface energy (σ) of ODT (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 228 and Table 229).

	σ after pretr. [mN/m]	σ after ODT [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	66.38 ± 0.96	58.22 ± 0.60	67.56 ± 0.43	63.22 ± 0.49	66.42 ± 1.07

Table 231: Ellipsometric data of ODT (solved in IPA) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after ODT [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	102.17 ± 0.09	102.91 ± 0.17	102.27 ± 0.07	102.20 ± 0.06	24.56 ± 1.09

4.2.3.2 4-Dodecylbenzenesulfonic acid

Solution: 0.0097 g DDBSA solved in 60 mL THF.

Table 232: Water contact angle (CA) of DDBSA (solved in THF) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after DDBSA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	27.7 ± 1.76	26.8 ± 5.91	26.3 ± 4.07	40.3 ± 1.92	22.4 ± 2.65

Table 233: Diiodomethane contact angle (CA) of DDBSA (solved in THF) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after DDBSA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	40.3 ± 1.52	62.2 ± 1.06	42.5 ± 2.03	38.8 ± 1.09	44.8 ± 2.05

Table 234: Surface energy (σ) of DDBSA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 232 and Table 233).

	σ after pretr. [mN/m]	σ after DDBSA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	69.76 ± 0.63	66.10 ± 1.05	69.89 ± 1.02	63.63 ± 0.49	71.05 ± 0.88

Table 235: Ellipsometric data of DDBSA (solved in THF) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after DDBSA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	101.78 ± 0.16	104.06 ± 0.85	102.00 ± 0.28	102.10 ± 0.33	24.93 ± 0.54

Solution: 0.0097 g DDBSA solved in 60 mL IPA.

Table 236: Water contact angle (CA) of DDBSA (solved in IPA) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after DDBSA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	35.1 ± 2.45	17.7 ± 4.63	27.9 ± 2.00	43.8 ± 3.84	19.7 ± 2.86

Table 237: Diiodomethane contact angle (CA) of DDBSA (solved in IPA) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after DDBSA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	44.4 ± 1.58	63.3 ± 0.54	43.1 ± 1.44	42.0 ± 1.18	42.7 ± 0.54

Table 238: Surface energy (σ) of DDBSA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 236 and Table 237).

	σ after pretr. [mN/m]	σ after DDBSA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	65.14 ± 0.69	69.91 ± 0.80	69.05 ± 0.62	60.82 ± 0.69	72.50 ± 0.51

Table 239: Ellipsometric data of DDBSA (solved in IPA) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after DDBSA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	101.50 ± 0.14	102.36 ± 0.25	101.58 ± 0.25	101.59 ± 0.07	23.28 ± 3.52

4.2.3.3 *1H,1H,2H,3H,3H*-Perfluorononanoic-1,2-diol

Solution: 0.0115 g PFND solved in 60 mL THF.

Table 240: Water contact angle (CA) of PFND (solved in THF) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after PFND [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	20.8 ± 2.33	48.1 ± 1.63	29.1 ± 1.77	40.0 ± 2.37	24.8 ± 2.05

Table 241: Diiodomethane contact angle (CA) of PFND (solved in THF) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after PFND [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	39.2 ± 0.89	67.1 ± 2.54	39.5 ± 2.35	39.8 ± 1.48	43.9 ± 0.67

Table 242: Surface energy (σ) of PFND (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 240 and Table 241).

	σ after pretr. [mN/m]	σ after PFND [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	72.81 ± 0.52	52.25 ± 0.80	69.27 ± 0.88	63.55 ± 0.64	70.27 ± 0.43

Table 243: Ellipsometric data of PFND (solved in THF) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after PFND [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	100.95 ± 0.14	101.94 ± 0.08	101.18 ± 0.16	101.14 ± 0.16	33.56 ± 7.14

Solution: 0.0120 g PFND solved in 60 mL IPA.

Table 244: Water contact angle (CA) of PFND (solved in IPA) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after PFND [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	30.9 ± 2.22	37.0 ± 2.81	24.8 ± 4.29	36.9 ± 1.89	34.5 ± 3.02

Table 245: Diiodomethane contact angle (CA) of PFND (solved in IPA) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after PFND [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	39.2 ± 0.48	68.1 ± 4.51	44.7 ± 1.59	42.3 ± 0.93	45.1 ± 0.82

Table 246: Surface energy (σ) of PFND (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 244 and Table 245).

	σ after pretr. [mN/m]	σ after PFND [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	68.47 ± 0.38	59.53 ± 1.49	70.09 ± 0.94	64.66 ± 0.45	65.31 ± 0.56

Table 247: Ellipsometric data of PFND (solved in IPA) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after PFND [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	98.91 ± 0.16	99.25 ± 0.31	99.00 ± 0.19	99.04 ± 0.22	19.19 ± 3.56

4.2.3.4 Perfluorononanoic acid

Solution: 0.0140 g PFNA solved in 60 mL THF.

Table 248: Water contact angle (CA) of PFNA (solved in THF) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after PFNA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	35.6 ± 0.69	41.6 ± 2.09	33.1 ± 2.59	34.6 ± 3.10	21.6 ± 1.66

Table 249: Diiodomethane contact angle (CA) of PFNA (solved in THF) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after PFNA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	41.5 ± 2.25	70.3 ± 2.21	41.6 ± 1.75	41.6 ± 0.27	45.4 ± 1.15

Table 250: Surface energy (σ) of PFNA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 248 and Table 249).

	σ after pretr. [mN/m]	σ after PFNA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	65.52 ± 0.77	56.28 ± 0.77	66.82 ± 0.76	66.03 ± 0.43	71.26 ± 0.52

Table 251: Ellipsometric data of PFNA (solved in THF) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after PFNA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	100.53 ± 0.45	101.37 ± 0.70	100.64 ± 0.36	100.65 ± 0.18	21.90 ± 0.63

Solution: 0.0137 g PFNA solved in 60 mL IPA.

Table 252: Water contact angle (CA) of PFNA (solved in IPA) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after PFNA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	31.8 ± 0.69	22.4 ± 2.08	22.1 ± 2.72	38.4 ± 0.47	22.8 ± 3.65

Table 253: Diiodomethane contact angle (CA) of PFNA (solved in IPA) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after PFNA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	40.8 ± 1.37	81.2 ± 1.04	42.5 ± 1.04	42.2 ± 1.54	44.1 ± 1.34

Table 254: Surface energy (σ) of PFNA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 252 and Table 253).

	σ after pretr. [mN/m]	σ after PFNA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	67.66 ± 0.49	67.62 ± 0.53	71.66 ± 0.61	63.82 ± 0.52	71.04 ± 0.80

Table 255: Ellipsometric data of PFNA (solved in IPA) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after PFNA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	100.69 ± 0.15	101.09 ± 0.30	100.76 ± 0.18	100.85 ± 0.22	18.87 ± 1.23

4.2.3.5 Perfluorotetradecanoic acid

Solution: 0.0212 g PFTDA solved in 60 mL THF.

Table 256: Water contact angle (CA) of PFTDA (solved in THF) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after PFTDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	32.7 ± 0.87	37.4 ± 2.01	21.0 ± 2.74	30.2 ± 2.18	35.9 ± 5.62

Table 257: Diiodomethane contact angle (CA) of PFTDA (solved in THF) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after PFTDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	37.2 ± 0.74	70.8 ± 6.69	43.1 ± 2.51	41.7 ± 0.71	46.1 ± 4.40

Table 258: Surface energy (σ) of PFTDA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 256 and Table 257).

	σ after pretr. [mN/m]	σ after PFTDA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	68.05 ± 0.30	59.05 ± 2.07	71.93 ± 1.03	68.28 ± 0.44	64.30 ± 1.79

Table 259: Ellipsometric data of PFTDA (solved in THF) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after PFTDA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	99.25 ± 0.18	99.97 ± 0.08	99.66 ± 0.30	99.71 ± 0.25	20.50 ± 1.61

Solution: 0.0213 g PFTDA solved in 60 mL IPA.

Table 260: Water contact angle (CA) of PFTDA (solved in IPA) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after PFTDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	29.5 ± 2.81	23.8 ± 5.39	23.4 ± 2.85	34.4 ± 2.72	19.8 ± 2.56

Table 261: Diiodomethane contact angle (CA) of PFTDA (solved in IPA) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after PFTDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	38.8 ± 1.78	71.5 ± 4.59	44.1 ± 2.08	42.1 ± 1.41	42.5 ± 0.85

Table 262: Surface energy (σ) of PFTDA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 260 and Table 261).

	σ after pretr. [mN/m]	σ after PFTDA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	69.22 ± 0.80	66.80 ± 1.83	70.80 ± 0.91	66.04 ± 0.67	72.50 ± 0.54

Table 263: Ellipsometric data of PFTDA (solved in IPA) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after PFTDA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	99.88 ± 0.12	100.51 ± 0.33	100.18 ± 0.31	99.99 ± 0.11	23.92 ± 1.57

4.2.3.6 Tetradecylphosphonic acid

Solution: 0.0084 g TDPA solved in 60 mL IPA.

Table 264: Water-contact-angle (CA) of TDPA (solved in IPA) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after TDPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	33.8 ± 2.62	43.6 ± 1.70	35.2 ± 1.76	38.7 ± 1.53	25.8 ± 1.11

Table 265: Diiodomethane contact angle (CA) of TDPA (solved in IPA) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after TDPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	41.6 ± 2.59	52.2 ± 3.10	42.9 ± 1.04	43.1 ± 1.51	48.1 ± 0.62

Table 266: Surface energy (σ) of TDPA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 264 and Table 265).

	σ after pretr. [mN/m]	σ after TDPA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	66.47 ± 1.01	58.31 ± 1.03	65.41 ± 0.47	63.48 ± 0.57	68.98 ± 0.30

Table 267: Ellipsometric data of TDPA (solved in IPA) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after TDPA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	98.29 ± 0.15	99.12 ± 0.77	98.81 ± 0.32	98.68 ± 0.28	8.10 ± 0.77

Solution: 0.0086 g TDPA solved in 60 mL THF.

Table 268: Water contact angle (CA) of TDPA (solved in THF) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after TDPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	31.3 ± 1.66	38.7 ± 2.57	38.0 ± 3.27	46.2 ± 6.98	39.5 ± 8.77

Table 269: Diiodomethane contact angle (CA) of TDPA (solved in THF) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after TDPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	39.1 ± 1.56	46.9 ± 1.47	42.7 ± 0.49	47.6 ± 5.68	44.9 ± 2.84

Table 270: Surface energy (σ) of TDPA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 268 and Table 269).

	σ after pretr. [mN/m]	σ after TDPA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	68.31 ± 0.62	62.53 ± 0.66	63.94 ± 0.49	57.93 ± 2.15	62.58 ± 1.67

Table 271: Ellipsometric data of TDPA (solved in THF) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after TDPA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	100.56 ± 0.19	101.60 ± 0.21	101.22 ± 0.34	101.59 ± 0.93	9.40 ± 9.87

4.2.3.7 Octadecylphosphonic acid

Solution: 0.0099 g ODPA solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 272: Water contact angle (CA) of ODPA (solved in IPA) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	36.2 ± 2.52	44.9 ± 1.83	36.9 ± 4.18	39.1 ± 0.61	28.0 ± 2.18

Table 273: Diiodomethane contact angle (CA) of ODPA (solved in IPA) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	37.6 ± 1.01	49.3 ± 2.38	47.3 ± 1.45	44.2 ± 1.19	48.3 ± 1.41

Table 274: Surface energy (σ) of ODPA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 272 and Table 273).

	σ after pretr. [mN/m]	σ after ODPA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	66.16 ± 0.28	58.24 ± 0.82	63.46 ± 0.84	62.96 ± 0.41	67.92 ± 0.63

Table 275: Ellipsometric data of ODPA (solved in IPA) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after ODPA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	98.67 ± 0.57	98.78 ± 0.32	98.07 ± 0.32	98.14 ± 0.45	13.52 ± 7.02

Solution: 0.0103 g ODPA solved in 60 mL THF.

Table 276: Water contact angle (CA) of ODPA (solved in THF) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	26.6 ± 3.10	50.6 ± 13.24	52.6 ± 6.04	54.9 ± 7.91	37.6 ± 3.52

Table 277: Diiodomethane contact angle (CA) of ODPA (solved in THF) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after ODPA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	38.6 ± 1.37	51.3 ± 4.78	45.6 ± 4.21	51.2 ± 2.68	48.2 ± 2.06

Table 278: Surface energy (σ) of ODPA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 276 and Table 277).

	σ after pretr. [mN/m]	σ after ODPA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	70.60 ± 0.73	54.21 ± 2.43	54.62 ± 1.60	51.53 ± 1.35	62.89 ± 0.92

Table 279: Ellipsometric data of ODPA (solved in THF) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after ODPA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	100.22 ± 0.49	101.59 ± 0.84	101.44 ± 0.89	101.37 ± 0.78	19.34 ± 5.67

4.2.3.8 Tetradecylamine

Solution: 0.0065 g TDA solved in 60 mL IPA.

Table 280: Water contact angle (CA) of TDA (solved in IPA) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after TDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	32.8 ± 0.96	69.9 ± 2.65	40.5 ± 3.04	41.0 ± 2.03	33.4 ± 2.23

Table 281: Diiodomethane contact angle (CA) of TDA (solved in IPA) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after TDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	40.2 ± 1.27	52.7 ± 2.77	43.1 ± 1.82	41.0 ± 1.97	49.6 ± 0.26

Table 282: Surface energy (σ) of TDA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 280 and Table 281).

	σ after pretr. [mN/m]	σ after TDA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	67.29 ± 0.28	42.41 ± 0.83	62.43 ± 0.79	62.68 ± 0.74	64.89 ± 0.34

Table 283: Ellipsometric data of TDA (solved in IPA) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after TDA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	101.47 ± 0.10	101.97 ± 0.22	101.60 ± 0.15	101.66 ± 0.13	30.08 ± 3.71

Solution: 0.0063 g TDA solved in 60 mL THF.

Table 284: Water contact angle (CA) of TDA (solved in THF) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after TDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	30.6 ± 1.52	67.9 ± 2.04	54.2 ± 6.42	49.1 ± 4.25	31.7 ± 5.03

Table 285: Diiodomethane contact angle (CA) of TDA (solved in THF) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after TDA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	44.1 ± 1.24	52.8 ± 2.50	43.4 ± 1.35	42.5 ± 2.17	44.1 ± 1.03

Table 286: Surface energy (σ) of TDA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 284 and Table 285).

	σ after pretr. [mN/m]	σ after TDA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	67.54 ± 0.51	43.40 ± 0.74	54.30 ± 0.90	57.60 ± 0.95	66.99 ± 0.86

Table 287: Ellipsometric data of TDA (solved in THF) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after TDA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	97.38 ± 0.11	98.65 ± 0.57	97.83 ± 0.34	97.81 ± 0.44	8.82 ± 2.39

4.2.3.9 Octadecylamine

Solution: 0.0083 g ODA solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 288: Water contact angle (CA) of ODA (solved in IPA) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	29.0 ± 1.01	69.8 ± 5.44	64.6 ± 5.44	49.4 ± 3.82	28.8 ± 1.66

Table 289: Diiodomethane contact angle (CA) of ODA (solved in IPA) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	38.8 ± 1.23	59.1 ± 1.93	52.2 ± 4.23	41.6 ± 2.08	48.6 ± 0.51

Table 290: Surface energy (σ) of ODA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 288 and Table 289).

	σ after pretr. [mN/m]	σ after ODA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	69.44 ± 0.47	40.17 ± 0.80	45.46 ± 1.40	57.65 ± 0.88	67.48 ± 0.33

Table 291: Ellipsometric data of ODA (solved in IPA) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after ODA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	100.56 ± 0.17	101.35 ± 0.31	101.00 ± 0.25	100.90 ± 0.21	26.59 ± 4.02

Solution: 0.0083 g ODA solved in 60 mL THF.

Table 292: Water contact angle (CA) of ODA (solved in THF) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	35.4 ± 2.44	72.9 ± 3.52	52.5 ± 4.69	49.5 ± 3.71	35.0 ± 3.77

Table 293: Diiodomethane contact angle (CA) of ODA (solved in THF) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after ODA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	42.1 ± 0.86	54.7 ± 3.12	49.2 ± 4.44	42.2 ± 2.11	46.3 ± 0.21

Table 294: Surface energy (σ) of ODA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 292 and Table 293).

	σ after pretr. [mN/m]	σ after ODA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	65.53 ± 0.49	40.12 ± 0.93	53.62 ± 1.55	57.41 ± 0.88	64.73 ± 0.51

Table 295: Ellipsometric data of ODA (solved in THF) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after ODA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	97.90 ± 0.15	99.19 ± 0.47	98.44 ± 0.29	98.45 ± 0.43	8.65 ± 3.15

4.2.3.10 Lauric acid

Solution: 0.0062 g LA solved in 60 mL IPA.

Table 296: Water contact angle (CA) of LA (solved in IPA) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after LA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	37.6 ± 3.68	40.4 ± 2.70	36.2 ± 2.69	39.1 ± 1.70	28.0 ± 4.20

Table 297: Diiodomethane contact angle (CA) of LA (solved in IPA) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after LA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	38.5 ± 1.85	46.4 ± 1.07	41.3 ± 1.31	42.1 ± 1.15	45.2 ± 0.99

Table 298: Surface energy (σ) of LA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 296 and Table 297).

	σ after pretr. [mN/m]	σ after LA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	65.20 ± 0.88	61.68 ± 0.56	65.29 ± 0.63	63.50 ± 0.48	68.54 ± 0.76

Table 299: Ellipsometric data of LA (solved in IPA) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after LA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	98.96 ± 0.30	99.16 ± 0.23	98.92 ± 0.21	98.90 ± 0.14	17.40 ± 2.09

Solution: 0.0065 g LA solved in 60 mL THF.

Table 300: Water contact angle (CA) of LA (solved in THF) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after LA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	35.0 ± 1.19	50.9 ± 7.54	35.0 ± 2.87	40.5 ± 2.43	35.7 ± 4.05

Table 301: Diiodomethane contact angle (CA) of LA (solved in THF) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after LA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	39.9 ± 1.90	48.3 ± 0.61	41.4 ± 0.80	40.4 ± 1.92	46.3 ± 0.96

Table 302: Surface energy (σ) of LA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 300 and Table 301).

	σ after pretr. [mN/m]	σ after LA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	66.22 ± 0.68	54.89 ± 0.89	65.87 ± 0.53	63.09 ± 0.76	64.39 ± 0.71

Table 303: Ellipsometric data of LA (solved in THF) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after LA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	102.16 ± 0.24	103.69 ± 0.53	102.31 ± 0.32	102.81 ± 0.58	15.09 ± 1.67

4.2.3.11 Stearic acid

Solution: 0.0085 g STA solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 304: Water contact angle (CA) of STA (solved in IPA) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after STA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	33.1 ± 1.04	39.6 ± 2.56	36.9 ± 1.99	43.1 ± 1.59	36.3 ± 5.72

Table 305: Diiodomethaen contact angle (CA) of STA (solved in IPA) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after STA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	36.2 ± 1.55	54.6 ± 3.59	42.2 ± 1.42	41.1 ± 0.96	48.0 ± 1.70

Table 306: Surface energy (σ) of STA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 304 and Table 305).

	σ after pretr. [mN/m]	σ after STA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	68.08 ± 0.57	60.24 ± 1.24	64.66 ± 0.59	61.46 ± 0.41	63.62 ± 1.08

Table 307: Ellipsometric data of STA (solved in IPA) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after STA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	97.92 ± 0.17	98.83 ± 0.46	98.01 ± 0.09	98.03 ± 0.08	13.26 ± 2.52

Solution: 0.0088 g STA solved in 60 mL THF.

Table 308: Water contact angle (CA) of STA (solved in THF) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after STA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	32.7 ± 1.64	59.5 ± 10.48	37.8 ± 7.38	37.8 ± 5.14	27.5 ± 4.72

Table 309: Diiodomethane contact angle (CA) of STA (solved in THF) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after STA [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	41.6 ± 1.65	49.1 ± 3.39	43.4 ± 1.53	43.6 ± 3.49	47.0 ± 1.23

Table 310: Surface energy (σ) of STA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 308 and Table 309).

	σ after pretr. [mN/m]	σ after STA [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	67.02 ± 0.64	49.44 ± 1.66	63.88 ± 1.21	63.82 ± 1.47	68.40 ± 0.89

Table 311: Ellipsometric data of STA (solved in THF) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after STA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	99.33 ± 0.52	100.07 ± 0.67	99.47 ± 0.51	99.36 ± 0.25	12.86 ± 6.21

4.2.3.12 1-Octadecanol

Solution: 0.0083 g ODO solved in 60 mL IPA. Complete solution occurred after 1 min in the ultrasonic bath.

Table 312: Water contact angle (CA) of ODO (solved in IPA) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after ODO [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	32.5 ± 1.31	46.4 ± 3.35	31.2 ± 1.25	40.0 ± 3.45	27.2 ± 2.97

Table 313: Diiodomethane contact angle (CA) of ODO (solved in IPA) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after ODO [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	37.3 ± 1.04	49.7 ± 0.86	40.3 ± 1.74	41.1 ± 1.42	47.1 ± 1.43

Table 314: Surface energy (σ) of ODO (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 312 and Table 313).

	σ after pretr. [mN/m]	σ after ODO [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	68.11 ± 0.43	57.28 ± 0.55	68.10 ± 0.64	63.20 ± 0.73	68.54 ± 0.43

Table 315: Ellipsometric data of ODO (solved in IPA) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after ODO [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	99.78 ± 0.17	100.44 ± 0.13	99.88 ± 0.11	99.96 ± 0.30	22.85 ± 2.05

Solution: 0.0082 g ODO solved in 60 mL THF.

Table 316: Water contact angle (CA) of ODO (solved in THF) modified thermal silicon dioxide surface.

Water	CA after pretr. [°]	CA after ODO [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	36.3 ± 1.08	43.7 ± 0.97	40.3 ± 4.13	40.4 ± 3.07	34.0 ± 1.94

Table 317: Diiodomethane contact angle (CA) of ODO (solved in THF) modified thermal silicon dioxide surface.

Diiodomethane	CA after pretr. [°]	CA after ODO [°]	CA after NH_3 [°]	CA after IPA [°]	CA after HF [°]
Pretreatment 2 and rinsed process	42.7 ± 1.20	43.9 ± 2.63	44.1 ± 1.32	41.4 ± 1.39	45.3 ± 0.24

Table 318: Surface energy (σ) of ODO (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 316 and Table 317).

	σ after pretr. [mN/m]	σ after ODO [mN/m]	σ after NH_3 [mN/m]	σ after IPA [mN/m]	σ after HF [mN/m]
Pretreatment 2 and rinsed process	64.88 ± 0.45	60.40 ± 0.87	62.29 ± 0.77	62.92 ± 0.68	65.51 ± 0.29

Table 319: Ellipsometric data of ODO (solved in THF) modified thermal silicon dioxide surface.

	Thickness after pretr. [nm]	Thickness after OOA [nm]	Thickness after NH_3 [nm]	Thickness after IPA [nm]	Thickness after HF [nm]
Pretreatment 2 and rinsed process	101.36 ± 0.17	102.48 ± 0.44	101.82 ± 0.57	101.78 ± 0.18	13.41 ± 1.32

4.3 Coating and removal experiments in the tube furnace

Further removing tests were carried out in a tube furnace. The wafer materials were cut into pieces with the size of 1x4 cm. Coating procedure was the same as described above. But instead of immersing the chips in different removing liquids the coated chips were put in the tube furnace of the fabricate GERO F40 – 300 (GERO REST40 – 300 power transformer) with a heatable zone of 18 cm and a tube diameter of 4 cm. Measurements were done at 450 °C under oxygen flow. The ellipsomteric data are one point measurements because of the smaller size of the chips. After the oven the chips were cooled under oxygen flow. 1-Octadecylamine and octadecylpohsphonic acid were chosen for these experiments because they were the most promising chemicals. The experiments were done only on tungsten surfaces.

4.3.1 Tungsten coated silicon wafer

4.3.1.1 Octacylamine

0.0068 g ODA solved in 50 ml THF. The coated surface was measured and then put in the oven for 2 min. No optical change was noticeable after the oven.

Table 320: Water and diiodomethane contact angle (CA) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 2 min in the tube furnace.

	CA after pretr. [°]		CA after ODA [°]		CA after furnace [°]	
	H_2O	CH_2I_2	H_2O	CH_2I_2	H_2O	CH_2I_2
Blank Pretreatment 2	14.4 ± 1.27	30.2 ± 1.87	-	-	32.9 ± 1.84	32.3 ± 2.64
Pretreatment 2 and rinsed process	18.8 ± 5.50	36.7 ± 0.84	80.2 ± 2.95	53.1 ± 1.58	70.3 ± 2.29	38.8 ± 1.81

Table 321: Surface energy (σ) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 2 min in the tube furnace (calculated via data of Table 320).

	σ after pretr. [mN/m]	σ after ODA [mN/m]	σ after NH_3 [mN/m]
Blank Pretreatment 2	76.52 ± 0.73	-	69.02 ± 0.98
Pretreatment 2 and rinsed process	74.00 ± 0.91	37.53 ± 0.48	47.36 ± 0.58

Table 322: Ellipsometric data of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 2 min in the tube furnace.

	Thickness after pretr. [nm]	Thickness after ODA [nm]	Thickness after furnace [nm]
Blank Pretreatment 2	44.67	-	48.84
Pretreatment 2 and rinsed process	45.16	50.05	46.31

0.0067 g ODA solved in 50 ml THF. After the CA and ellipsometric measurements of the coated surface the chip was 6 min in the oven. No change was noticeable.

Table 323: Water and diiodomethane contact angle (CA) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 6 min in the tube furnace.

	CA after pretr. [°]		CA after ODA [°]		CA after furnace [°]	
	H_2O	CH_2I_2	H_2O	CH_2I_2	H_2O	CH_2I_2
Blank Pretreatment 2	27.7 ± 4.25	34.2 ± 5.21	-	-	12.1 ± 1.83	30.7 ± 1.86
Pretreatment 2 and rinsed process	23.8 ± 3.12	37.9 ± 4.30	73.3 ± 1.97	48.7 ± 0.64	30.1 ± 3.69	30.0 ± 1.86

Table 324: Surface energy (σ) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 6 min in the tube furnace (calculated via data of Table 323).

	σ after pretr. [mN/m]	σ after ODA [mN/m]	σ after NH_3 [mN/m]
Blank Pretreatment 2	71.05 ± 2.00	-	76.95 ± 2.04
Pretreatment 2 and rinsed process	71.92 ± 1.64	42.18 ± 0.26	70.83 ± 0.92

Table 325: Ellipsometric data of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 6 min in the tube furnace.

	Thickness after pretr. [nm]	Thickness after ODA [nm]	Thickness after furnace [nm]
Blank Pretreatment 2	48.67	-	50.11
Pretreatment 2 and rinsed process	42.56	48.02	49.66

0.0081 g ODA solved in 60 ml THF. After the CA and ellipsometric measurements of the coated surface the chip was 10 min in the heated oven. The color of the uncoated chip (blank) turned from silver to golden yellow. At the coated one no optical change was noticeable.

Table 326: Water and diiodomethane contact angle (CA) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 10 min in the tube furnace.

	CA after pretr. [°]		CA after ODA [°]		CA after furnace [°]	
	H_2O	CH_2I_2	H_2O	CH_2I_2	H_2O	CH_2I_2
Blank Pretreatment 2	17.8 ± 2.63	29.6 ± 3.09	-	-	17.1 ± 2.35	43.6 ± 3.11
Pretreatment 2 and rinsed process	22.0 ± 1.30	38.6 ± 3.09	69.5 ± 1.61	48.3 ± 2.49	34.2 ± 3.72	52.0 ± 2.24

Table 327: Surface energy (σ) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 10 min in the tube furnace (calculated via data ofTable 326).

	σ after pretr. [mN/m]	σ after ODA [mN/m]	σ after NH_3 [mN/m]
Blank Pretreatment 2	75.69 ± 1.24	-	73.15 ± 1.20
Pretreatment 2 and rinsed process	72.47 ± 1.12	44.22 ± 0.72	63.98 ± 1.00

Table 328: Ellipsometric data of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 10 min in the tube furnace.

	Thickness after pretr. [nm]	Thickness after ODA [nm]	Thickness after furnace [nm]
Blank Pretreatment 2	49.75	-	44.73
Pretreatment 2 and rinsed process	47.07	49.27	50.09

0.0082 g ODA solved in 60 ml THF. After the CA and ellipsometric measurements of the coated surface the chip was put in the oven. The oven was heated up with the chips in the oven (10 min). After 10 min at 450° the chip was taken out of the furnace. A change of color was noticed. The uncoated blank was golden yellow, the coated chip was not silver anymore, but blue purple. After the oven the surface was too hydrophilic to get usable data (n. m. = not measurable).

Table 329: Water and diiodomethane contact angle (CA) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 30 min in the tube furnace.

	CA after pretr. [°]		CA after ODA [°]		CA after furnace [°]	
	H_2O	CH_2I_2	H_2O	CH_2I_2	H_2O	CH_2I_2
Blank Pretreatment 2	22.4 ± 3.19	40.7 ± 1.90	-	-	n. m.	28.6 ± 6.33
Pretreatment 2 and rinsed process	24.0 ± 1.41	29.8 ± 3.35	62.5 ± 3.65	56.7 ± 2.11	n. m.	29.8 ± 2.49

Table 330: Surface energy (σ) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 30 min in the tube furnace (calculated via data of Table 323).

	σ after pretr. [mN/m]	σ after ODA [mN/m]	σ after NH_3 [mN/m]
Blank Pretreatment 2	71.91 ± 0.90	-	n. m.
Pretreatment 2 and rinsed process	73.50 ± 1.23	45.25 ± 0.78	n. m.

Table 331: Ellipsometric data of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 10 min in the tube furnace.

	Thickness after pretr. [nm]	Thickness after ODA [nm]	Thickness after furnace [nm]
Blank Pretreatment 2	44.77	-	47.43
Pretreatment 2 and rinsed process	44.67	46.92	40.52

4.3.1.2 Octadecylphosphonic acid

0.0086 g ODPA solved in 50 ml THF. After the CA and ellipsometric measurements of the coated surfaces the chip was 10 min in the oven (at 450°). No optical change was noticeable after the oven.

Table 332: Water and diiodomethane contact angle (CA) of ODPA (solved in THF) modified tungsten surface after the pretreatment, the coating and 10 min in the tube furnace.

	CA after pretr. [°]		CA after ODPA [°]		CA after furnace [°]	
	H_2O	CH_2I_2	H_2O	CH_2I_2	H_2O	CH_2I_2
Blank Pretreatment 2	19.4 ± 0.55	26.2 ± 1.12	-	-	17.0 ± 3.17	28.9 ± 0.74
Pretreatment 2 and rinsed process	19.6 ± 1.24	27.0 ± 1.41	72.8 ± 2.70	48.4 ± 3.30	16.8 ± 1.84	31.2 ± 2.36

Table 333: urface energy (σ) of ODPA (solved in THF) modified tungsten surface after the pretreatment, the coating and 10 min in the tube furnace (calculated via data of Table 332).

	σ after pretr. [mN/m]	σ after ODPA [mN/m]	σ after furnace [mN/m]
Blank Pretreatment 2	75.79 ± 0.42	-	76.04 ± 0.59
Pretreatment 2 and rinsed process	75.59 ± 0.57	41.89 ± 0.93	75.68 ± 0.93

Table 334: Ellipsometric data of ODPA (solved in THF) modified tungsten surface after the pretreatment, the coating and 10 min in the tube furnace.

	Thickness after pretr. [nm]	Thickness after ODPA [nm]	Thickness after furnace [nm]
Blank Pretreatment 2	41.58	-	49.88
Pretreatment 2 and rinsed process	43.83	49.61	50.54

4.4 Coating experiments and AFM measurements

AFM measurements were performed on a Digital Instruments Inc. Dimension 5000 (D5000; Serie Nr. 260) AFM machine. The used evaluation software was Digital Instruments NanoScope® (III) (Version 5.31R1). A standard silicon tip (POINTPROBE-PLUS® Silicon-SPM-Sensor; Type: PPP-NCHR-10; S/N 72097F6L928) was used. The data for tungsten were achieved via tipping mode and three measurements from different parts of the chip. The scan size of all the measurements was 5x5 µm and the data scale 25 nm. The measurements were done at Lam Research® in Villach.

4.4.1 Tungsten coated silicon wafer

4.4.1.1 Octadecylamine

Solution: 0.0066 g ODA solved in 50 mL THF. The chips were blown dry with compressed air.

Table 335: Water and diiodomethane contact angles (CA) of ODA (solved in THF) modified tungsten surface before and after the coating.

	CA after pretr. [°]		CA after ODA [°]	
	H2O	CH2I2	H2O	CH2I2
Pretreatment 1	15.1 ± 2.22	37.3 ± 1.81	92.8 ± 2.66	63.6 ± 4.02
Pretreatment 1 and rinsed process	30.3 ± 0.87	30.4 ± 2.25	93.9 ± 2.43	64.9 ± 4.34

Table 336: Surface energy (σ) of ODA (solved in THF) modified tungsten surface (calculated via data of Table 335) before and after the coating (calculated via data of Table 335).

	σ after pretr. [mN/m]	σ after ODA [mN/m]
Pretreatment 1	74.98 ± 0.79	28.70 ± 0.88
Pretreatment 1 and rinsed process	70.64 ± 0.80	27.81 ± 0.93

Table 337: Ellipsometric data of ODA (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after ODA [nm]
Pretreatment 1	49.31 ± 0.62	50.82 ± 0.25
Pretreatment 1 and rinsed process	49.39 ± 0.59	50.86 ± 0.35

4.4.1.2 Octadecanethiol

Solution: 0.0071 g ODT solved in 50 mL THF. Chips were blown dry with compressed air.

Table 338: Water and diiodomethane contact angles (CA) of ODT (solved in THF) modified tungsten surface before and after the coating.

	CA after pretr. [°]		CA after ODT [°]	
	H2O	CH2I2	H2O	CH2I2
Pretreatment 1	28.5 ± 1.33	27.4 ± 0.40	79.1 ± 2.10	46.9 ± 1.47
Pretreatment 1 and rinsed process	31.2 ± 1.60	25.8 ± 1.22	74.2 ± 2.60	47.6 ± 0.99

Table 339: Surface energy (σ) of ODT (solved in THF) modified tungsten surface (calculated via data of Table 338) before and after the coating (calculated via data of Table 338).

	σ after pretr. [mN/m]	σ after ODT [mN/m]
Pretreatment 1	72.09 ± 0.26	40.57 ± 0.43
Pretreatment 1 and rinsed process	71.14 ± 0.52	42.26 ± 0.37

Table 340: Ellipsometric data of ODT (solved in THF) modified tungsten surface.

	Thickness after pretr. [nm]	Thickness after ODT [nm]
Pretreatment 1	48.02 ± 0.41	50.04 ± 0.69
Pretreatment 1 and rinsed process	48.51 ± 0.40	50.11 ± 0.39

4.5 Coating experiments and Raman measurements

Tungsten chips were coated with ODPA (0.0102 g ODPA solved in IPA). To characterize the coated surface Raman measurements were made on Perkin Elmer Raman Station 400 F Raman Spectrometer with a Perkin Elmer precisely laser. No data could be obtained out of these measurements probably because of the low amount of chemicals on the substrate.

4.6 Coating experiments and X-ray reflectivity measurements

Chips size 2x2 cm. Chips were cleaned via pretr. 1 and submerged fort 10 min (solution of 0.0135 TDPA solved in 100 ml THF).

Resel/TU Graz performed the X-ray reflectivity measurements.

5. Summary and future prospects

In this thesis chemicals to achieve a temporary hydrophobic layer on tungsten, titanium nitride and silicon dioxide coated silicon wafer are presented. Furthermore, methods to remove the coating of the different surfaces again are described. The coating experiments were successful with all the SAM materials on tungsten and titanium nitride surfaces. Water CA of 90° or above and low surface energies could be achieved on both surface materials with tetradecylamine and 1-octadecylamine for the tungsten and the tetradecylphosphonic acid and octadecylphosphonic acid on titanium nitride. For the thermal silicon dioxide surface none of the used chemicals led to a water CA of 90°. The highest water CA of 68° occurred on the tetradecylamine coated surface.

Furthermore, the influence of the solvent was shown. In general, the experiments in THF led to higher CA than the experiments carried out in IPA. This observation is traced back to weaker interactions between the SAM precursor with an aprotic (THF) solvent than a protic one (IPA). Other solvents like toluol, dimethylfurane, dichloromethane, ethylacetate and nonafluorobutlymethylether were tried and excluded.

It is assumed that no homogenous monolayer building occurred because of fluctuating values which is trace back to aggregation of the SAM materials on the surfaces. This observation correlates with AFM measurements and literature.[21, 46] Probably, the incomplete monolayer formation results because of the inadequate immersion time of 10 min in the chemical solution.

According to the CA data the binding of the polar head group to the substrate surface and formation of (incomplete) monolayers is supposed because the water CA is increasing after the coating. The angle increases because of absent interaction of water with the terminal methyl groups of the nonpolar chains. The exact binding situation (chemisorption, covalent binding…) has to be checked via further measurements like IR or XPS analysis. With the available method of Raman spectroscopy no meaningful spectra could be obtained.

The wet chemical removal of the SAMs was partial successful. However, the thermal removal in the tube furnace was totally successful even with brief heating times at least for the ODPA coated surface. Deviations of the removal are traced back to the inhomogeneous coating.

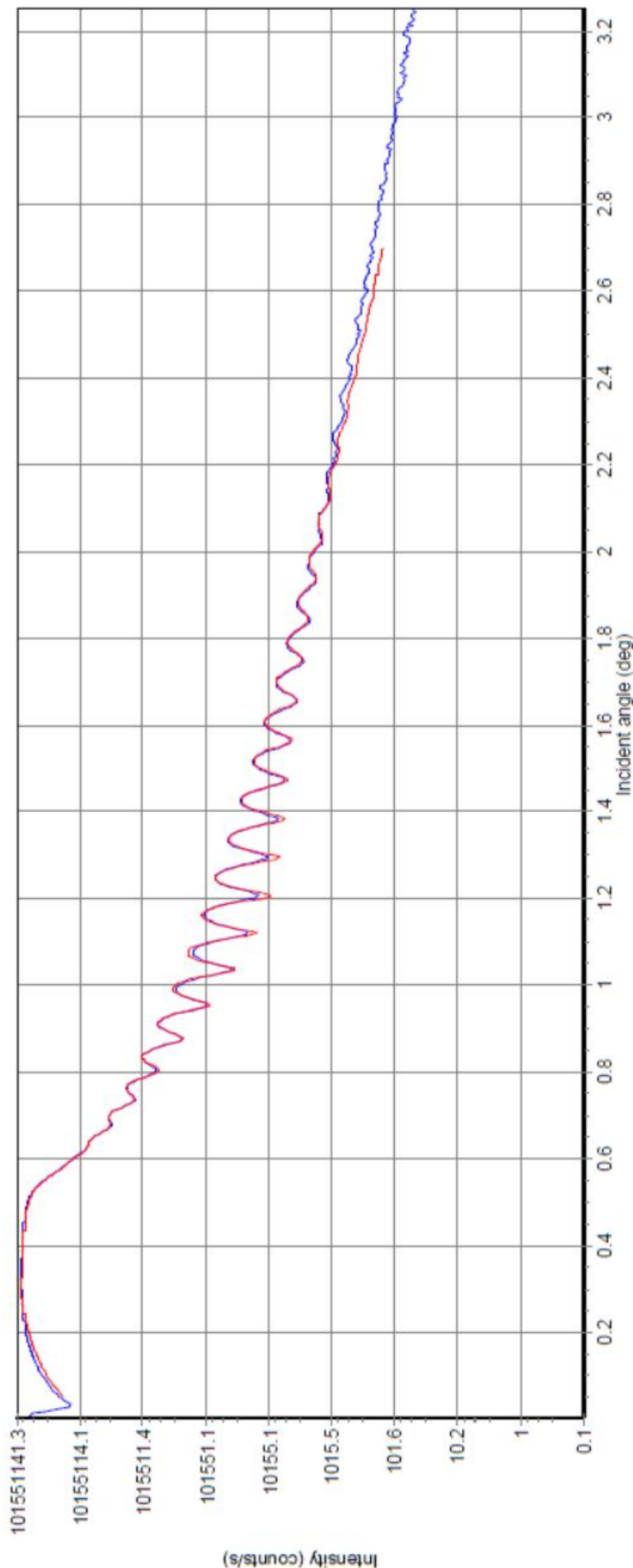
Layer thicknesses for all the experiments on tungsten and silicon dioxide surfaces were determined via ellipsometric measurements although, the modeling was not correct for the thin organic layers on the different metal surfaces. For titanium nitride no recipe was available, not at least because the material was no pure but a mixture of nitride and oxide. The evaluation of X-ray reflectivity

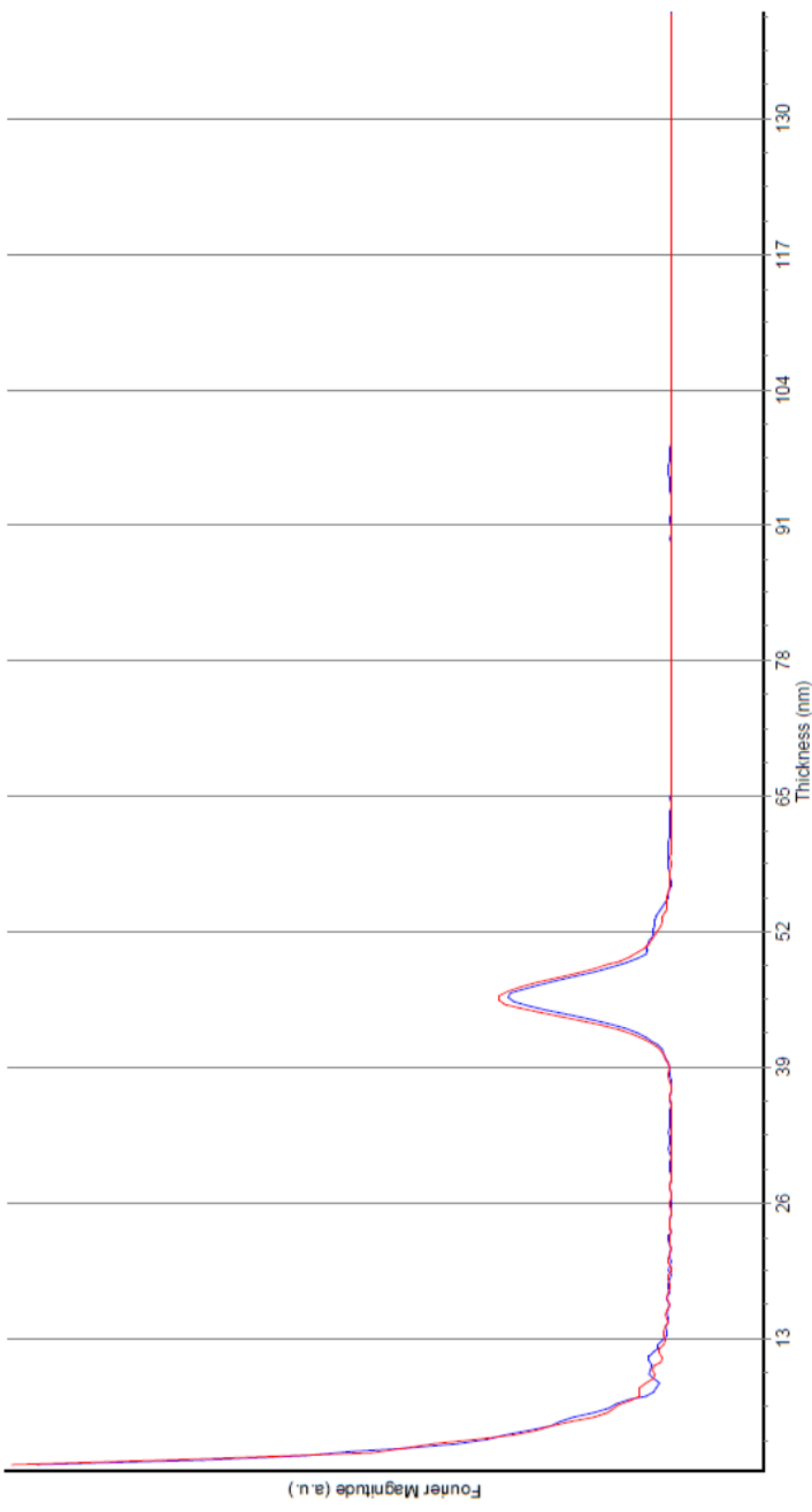
measurements as a means to determine layer thickness more accurately proved successful and therefore, constitutes a valuable analytical method for further studies.

From an industrial point of view the scale-up would be interesting for the future. Primarily, it will be interesting to test the applicability of the method to continuous flow methods used in industry. Although challenges remain to the overcome, the laboratory studies proved successful and sow a promising potential for in-line process application.

6. Appendix

6.1 X-ray reflectivity spectra

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Thickness (nm)
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Page #2

X'Pert Reflectivity 07-Feb-2013 14:47:54

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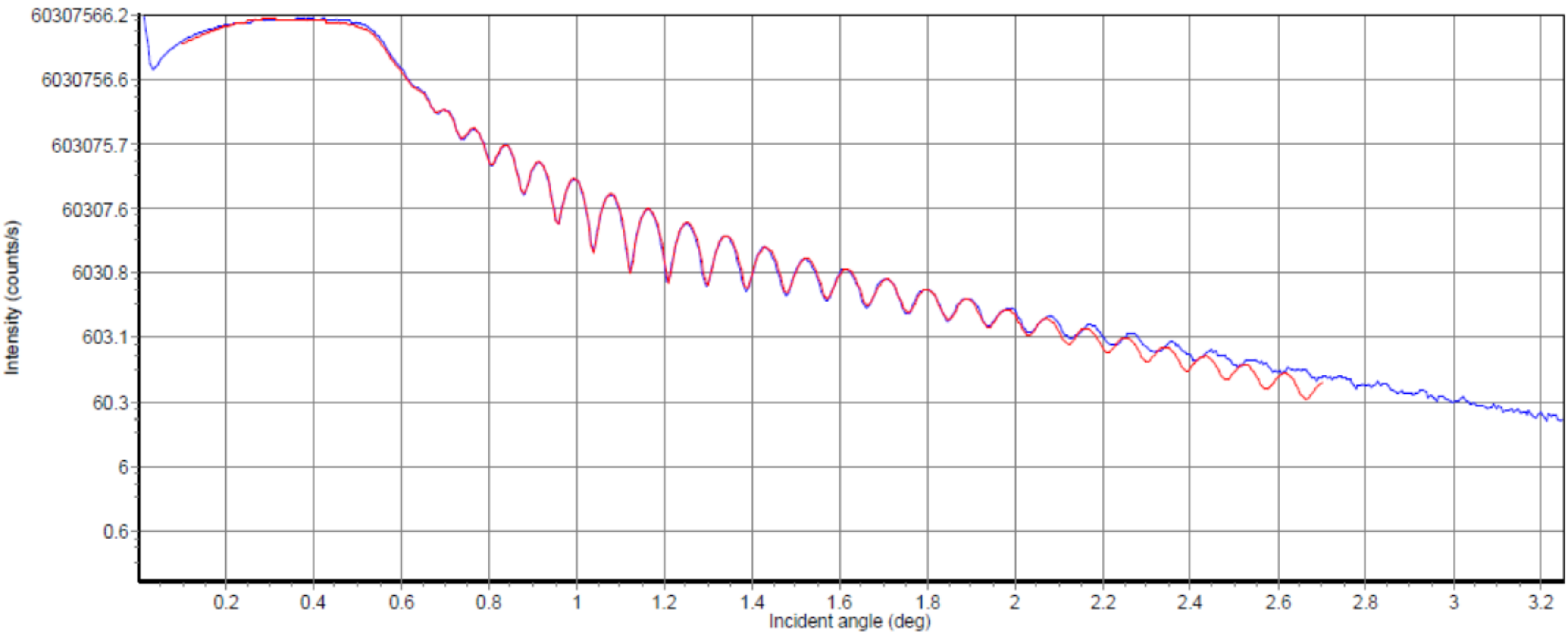
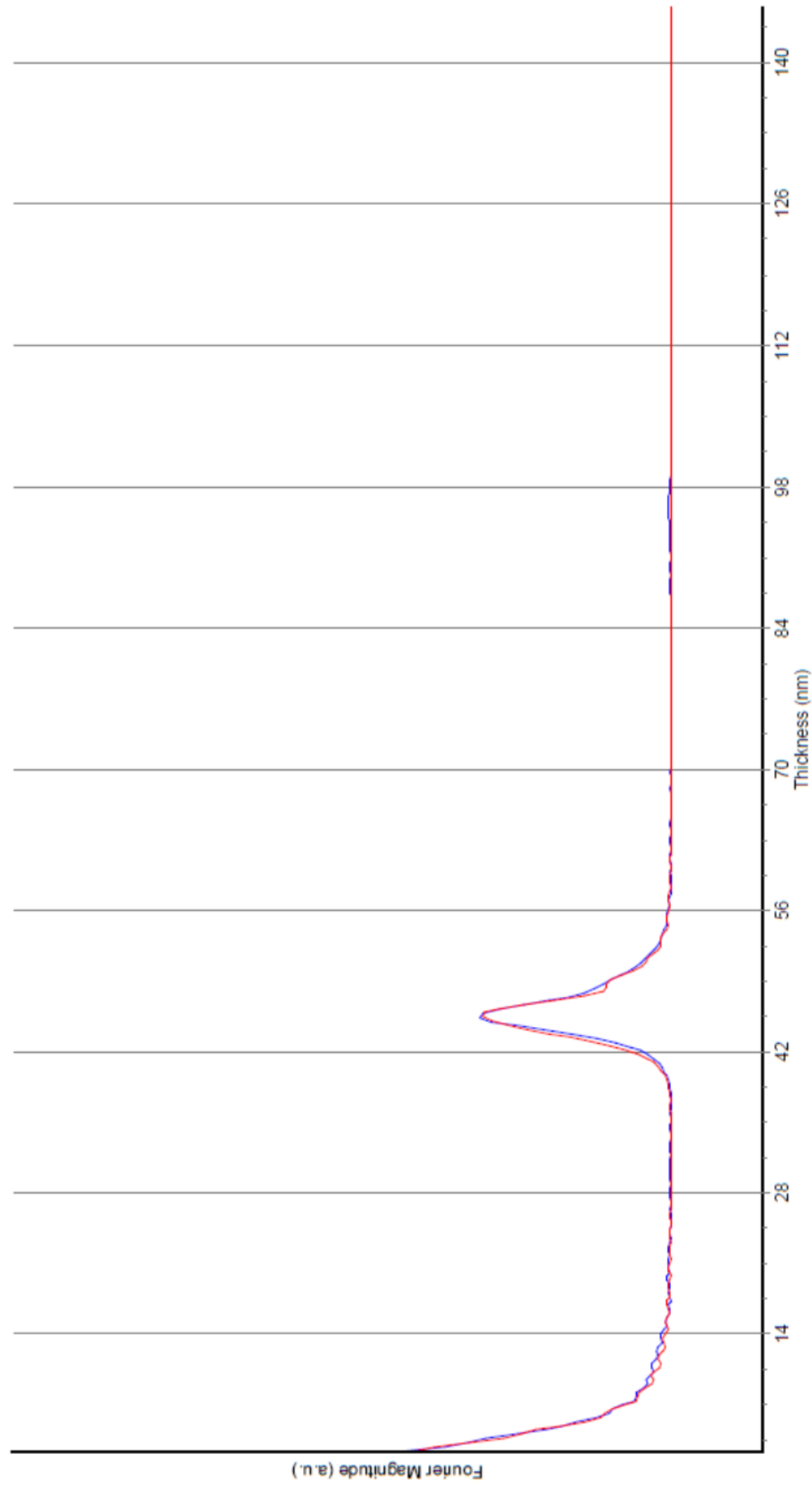
Sample file: C:\Users\MichaelZ\Desktop\Roland Fischer\sample34_35\sample34_1.sam
Used fitting mode: Segmented Fit
Used difference scheme: Abs Square Root Difference

Layer	Layer Description	Density	(Lower	Upper)	Thickness	(Lower	Upper)	Roughness	(Lower	Upper)
3, 0	DensityOnly, H2O	0.525	(0.35	0.893)	2.295	(1.911	2.387)	0.221	(-	-)
2, 0	DensityOnly, W	19.334	(19.269	19.572)	45.326	(45.212	45.468)	1.037	(1.019	1.068)
1, 0	DensityOnly, SiO2	2.21	(1.335	2.628)	100.656	(-	-)	0.494	(0.454	0.497)
Substrate	Diamond, Si	2.328	(-	3.672)	600000	(-	-)	0.5	(-	-)

Best fit value: 28.22 Best background: 10 counts/s Best divergence: 0.0089 deg Best intensity: 60307566 counts/s





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Page #2

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List of figures

Figure 1: Reaction of silicon to silicon dioxide 4
Figure 2: Wet oxidation of silicon to silicon dioxide 5
Figure 3: Scheme of a self-assembled monolayer on a solid surface. 6
Figure 4: Scheme of an angulate self-assembled monolayer on a solid surface. 6
Figure 5: Demonstration of contact angle 9
Figure 6: Comparison of more (right) and less (left) wetted contact angles 10
Figure 7: Graphical representation of the vectors 11
Figure 8: Scheme of an ellipsometer.. 12
Figure 9: Picture of the water contact angle of a tungsten surface before and after the coating with ODA (pretr. 1, without rinsed process). On the left picture the cleaned surface and on the right the coated one is shown.. 20
Figure 10: AFM picture of the tungsten surface without coating. Rms = 0.808 nm. Ra = 0.640 26
Figure 11: AFM picture of ODA (THF) coated tungsten surface (pretr.1, without rinsed process). 26
Figure 12: AFM picture of ODA (THF) coated tungsten surface (pretr. 1, with rinsed process). 27
Figure 13: AFM picture of ODT (THF) coated tungsten surface (pretr. 1, without rinsed process). 28
Figure 14: AFM picture of ODT (THF) coated tungsten surface (pretr. 1, with rinsed process). 28
Figure 15: Picture of water contact angle of an ODPA coated silicon dioxide surface (THF, pretr. 2, with rinsed process). Both images were taken from the same chip.. 34
Figure 16: Picture of the water contact angle of a TDA coated tungsten surface (THF, pretr. 2, without rinsed process). Image was taken after the NH_3 removing step.. 42
Figure 17: Picture of water contact angle of an ODA coated tungsten surface (THF, pretr. 2, without rinsed process) after the HF removing step. Both images were taken from the same chip................ 44
Figure 18: Water CA of the ODA coated surface after 30 min in the tube furnace. 60

List of tables

Table 1: Averaged contact angle (CA) and surface energy (σ) data of cleaned tungsten surface. 17
Table 2: Contact angles (CA) and surface energies (σ) on tungsten after the coating with SAM materials solved in THF and the differences to the cleaned value of Table 1. 18
Table 3: Contact angles (CA) and surface energies (σ) on tungsten after the coating with SAM materials solved in IPA and differences to the cleaned value of Table 1. 19
Table 4: Comparison of contact angles (CA) and surface energies (σ) of tungsten surfaces coated with SAM materials solved in THF or IPA. 23
Table 5: Comparison of the differences of cleaned and with SAM materials (solved in THF or IPA) coated tungsten surfaces. 24
Table 6: Averaged contact angle (CA) and surface energy (σ) data of cleaned titanium nitride surface. 29
Table 7: Contact angles (CA) and surface energies (σ) on titanium nitride after the coating with SAM materials solved in THF and differences to the cleaned values. 30
Table 8: Contact angles (CA) and surface energies (σ) on titanium nitride after the coating with ODPA solved in THF and differences to the cleaned values. Test of the importance of surface oxygen........ 32
Table 9: Contact angles (CA) and surface energies (σ) on titanium nitride after the coating with SAM materials solved in IPA and differences to the cleaned values. All values were received after pretreatment 2 and rinsed process. 32
Table 10: Averaged contact angle (CA) and surface energy (σ) data of cleaned thermal silicon dioxide surface. 33
Table 11: Contact angles (CA) and surface energies (σ) on thermal silicon dioxide surface after the coating with SAM materials solved in THF and differences to the cleaned values. All values were received after pretreatment 2 and rinsed process. 34
Table 12: Contact angles (CA) and surface energies (σ) on thermal silicon dioxide after the coating with SAM materials solved in IPA and differences to the cleaned values. All values were received after pretreatment 2 and rinsed process. 36
Table 13: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 1 without rinsed process. 38
Table 14: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 1 with rinsed process. 39
Table 15: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 without rinsed process. 40
Table 16: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 with rinsed process. 41
Table 17: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in IPA) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 1 without rinsed process. 46

Table 18: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in IPA) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 1 with the rinsed process. 47
Table 19: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in IPA) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 without rinsed process. 48
Table 20: Contact angles (CA), surface energies (σ) and differences on tungsten after the coating (done in IPA) and removing steps with 5% NH_3, IPA and 10% HF. All coated values are received after pretreatment 2 with the rinsed process. 48
Table 21: Contact angles (CA), surface energies (σ) and differences on titanium nitride after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All coated values are received after pretreatment 1 without rinsed process. 51
Table 22: Contact angles (CA), surface energies (σ) and differences on titanium nitride after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All coated values are received after pretreatment 3 without rinsed process. 51
Table 23: Contact angles (CA), surface energies (σ) and differences on titanium nitride after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 1 with the rinsed process. 51
Table 24: Contact angles (CA), surface energies (σ) and differences on titanium nitride after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 without rinsed process. 52
Table 25: Contact angles (CA), surface energies (σ) and differences on titanium nitride after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 with the rinsed process. 53
Table 26: Contact angles (CA), surface energies (σ) and differences on titanium nitride after the coating (done in IPA) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 with the rinsed process. 54
Table 27: Contact angles (CA), surface energies (σ) and differences on thermal silicon dioxide after the coating (done in THF) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 with the rinsed process. 56
Table 28: Contact angles (CA), surface energies (σ) and differences on thermal silicon dioxide after the coating (done in IPA) and removing steps with 5% NH_3, IPA and 10% HF. All the coated values are received after pretreatment 2 with the rinsed process. 57
Table 29: Contact angles (CA), surface energies (σ) and differences of coated and uncoated tungsten surfaces before and after the tube furnace experiments. All the tungsten chips were treated with pretreatment 2 and the rinsed process (after coating). The experiments were carried out under oxygen flow and 450 °C. 58
Table 30: Molecular formulas and molecular weights [g/mol] of the used SAM materials. 62
Table 31: Water contact angle (CA) of ODPA (solved in THF) modified tungsten surface. 64
Table 32: Diiodomethane contact angle (CA) of ODPA (solved in THF) modified tungsten surface. 64
Table 33: Surface energy (σ) of ODPA (solved in THF) modified tungsten surface (calculated via data of Table 31 and Table 32). 64
Table 34: Ellipsometric data of ODPA (solved in THF) modified tungsten surface. 65
Table 35: Water contact angle (CA) of ODPA (solved in IPA) modified tungsten surface. 65
Table 36: Diiodomethane contact angle (CA) of ODPA (solved in IPA) modified tungsten surface. 65

Table 37: Surface energy (σ) of ODPA (solved in IPA) modified tungsten surface (calculated via data of Table 35 and Table 36). 65
Table 38: Ellipsometric data of ODPA (solved in IPA) modified tungsten surface. 66
Table 39: Water contact angle (CA) of ODPA (solved in IPA) modified tungsten surface........ 66
Table 40: Diiodomethane contact angle (CA) of ODPA (solved in IPA) modified tungsten surface...... 66
Table 41: Surface energy (σ) of ODPA (solved in IPA) modified tungsten surface (calculated via data of Table 39 and Table 40). 66
Table 42: Ellipsometric data of ODPA (solved in IPA) modified tungsten surface. 67
Table 43: Water contact angle (CA) of TDPA (solved in THF) modified tungsten surface. 67
Table 44: Diiodomethane contact angle (CA) of TDPA (solved in THF) modified tungsten surface. 67
Table 45: Surface energy (σ) of TDPA (solved in THF) modified tungsten surface (calculated via data of Table 43 and Table 44). 68
Table 46: Ellipsometric data of TDPA (solved in IPA) modified tungsten surface. 68
Table 47: Water contact angle (CA) of TDPA (solved in IPA) modified tungsten surface. 68
Table 48: Diiodomethane contact angle (CA) of TDPA (solved in IPA) modified tungsten surface. 68
Table 49: Surface energy (σ) of TDPA (solved in THF) modified tungsten surface (calculated via data of Table 47 and Table 48). 69
Table 50: Ellipsometric data of TDPA (solved in IPA) modified tungsten surface. 69
Table 51: Water contact angle (CA) of DDBSA (solved in THF) modified tungsten surface. 69
Table 52: Diiodomethane contact angle (CA) of DDBSA (solved in THF) modified tungsten surface... 69
Table 53: Surface energy (σ) of DDBSA (solved in THF) modified tungsten surface (calculated via data of Table 51 and Table 52). 70
Table 54: Ellipsometric data of DDBSA (solved in THF) modified tungsten surface. 70
Table 55: Water contact angle (CA) of DDBSA (solved in IPA) modified tungsten surface. 70
Table 56: Diiodomethane contact angle (CA) of DDBSA (solved in IPA) modified tungsten surface.... 70
Table 57: Surface energy (σ) of DDBSA (solved in IPA) modified tungsten surface (calculated via data of Table 55 and Table 56). 71
Table 58: Ellipsometric data of DDBSA (solved in IPA) modified tungsten surface. 71
Table 59: Water contact angle (CA) of DDBSA (solved in THF) modified tungsten surface. 71
Table 60: Diiodomethane contact angle (CA) of DDBSA (solved in THF) modified tungsten surface... 71
Table 61: Surface energy (σ) of DDBSA (solved in THF) modified tungsten surface (calculated via data of Table 59 and Table 60). 72
Table 62: Ellipsometric data of DDBSA (solved in THF) modified tungsten surface. 72
Table 63: Water contact angle (CA) of TDA (solved in THF) modified tungsten surface. 72
Table 64: Diiodomethane contact angle (CA) of TDA (solved in THF) modified tungsten surface. 72
Table 65: Surface energy (σ) of TDA (solved in THF) modified tungsten surface (calculated via data of Table 63 and Table 64). 73
Table 66: Ellipsometric data of TDA (solved in THF) modified tungsten surface. 73
Table 67: Water contact angle (CA) of TDA (solved in IPA) modified tungsten surface. 73
Table 68: Diiodomethane contact angle (CA) of TDA (solved in IPA) modified tungsten surface. 73
Table 69: Surface energy (σ) of TDA (solved in IPA) modified tungsten surface (calculated via data of Table 67 and Table 68). 74
Table 70: Ellipsometric data of TDA (solved in IPA) modified tungsten surface. 74
Table 71: Water contact angle (CA) of TDA (solved in THF) modified tungsten surface. 74
Table 72: Diiodomethane contact angle (CA) of TDA (solved in THF) modified tungsten surface. 74

Table 73: Surface energy (σ) of TDA (solved in THF) modified tungsten surface (calculated via data of Table 71 and Table 72). 75
Table 74: Ellipsometric data of TDA (solved in THF) modified tungsten surface. 75
Table 75: Water contact angle (CA) of ODT (solved in THF) modified tungsten surface. 75
Table 76: Diiodomethane contact angle (CA) of ODT (solved in THF) modified tungsten surface. 75
Table 77: Surface energy (σ) of ODT (solved in THF) modified tungsten surface (calculated via data of Table 75 and Table 76). 76
Table 78: Ellipsometric data of ODT (solved in THF) modified tungsten surface. 76
Table 79: Water contact angle (CA) of ODT (solved in IPA) modified tungsten surface. 76
Table 80: Diiodomethane contact angle (CA) of ODT (solved in IPA) modified tungsten surface. 76
Table 81: Surface energy (σ) of ODT (solved in IPA) modified tungsten surface (calculated via data of Table 79 and Table 80). 77
Table 82: Ellipsometric data of ODT (solved in IPA) modified tungsten surface. 77
Table 83: Water contact angle (CA) of PFTDA (solved in THF) modified tungsten surface. 77
Table 84: Diiodomethane contact angle (CA) of PFTDA (solved in THF) modified tungsten surface. 77
Table 85: Surface energy (σ) of PFTDA (solved in THF) modified tungsten surface (calculated via data of Table 83 and Table 84). 78
Table 86: Ellipsometric data of PFTDA (solved in THF) modified tungsten surface. 78
Table 87: Water contact angle (CA) of PFTDA (solved in IPA) modified tungsten surface. 78
Table 88: Diiodomethane contact angle (CA) of PFTDA (solved in IPA) modified tungsten surface. 78
Table 89: Surface energy (σ) of PFTDA (solved in IPA) modified tungsten surface (calculated via data of Table 87 and Table 88). 79
Table 90: Ellipsometric data of PFTDA (solved in IPA) modified tungsten surface. 79
Table 91: Water contact angle (CA) of ODA (solved in THF) modified tungsten surface. 79
Table 92: Diiodomethane contact angle (CA) of ODA (solved in THF) modified tungsten surface. 79
Table 93: Surface energy (σ) of ODA (solved in THF) modified tungsten surface (calculated via data of Table 91 and Table 92). 80
Table 94: Ellipsometric data of ODA (solved in THF) modified tungsten surface. 80
Table 95: Water contact angle (CA) of ODA (solved in IPA) modified tungsten surface. 80
Table 96: Diiodomethane contact angle (CA) of ODA (solved in IPA) modified tungsten surface. 80
Table 97: Surface energy (σ) of ODA (solved in THF) modified tungsten surface (calculated via data of Table 95 and Table 96). 81
Table 98: Ellipsometric data of ODA (solved in IPA) modified tungsten surface. 81
Table 99: Water contact angle (CA) of ODA (solved in THF) modified tungsten surface. 81
Table 100: Diiodomethane contact angle (CA) of ODA (solved in THF) modified tungsten surface. 81
Table 101: Surface energy (σ) of ODA (solved in THF) modified tungsten surface (calculated via data of Table 99 and Table 100). 82
Table 102: Ellipsometric data of ODA (solved in THF) modified tungsten surface. 82
Table 103: Water contact angle (CA) of ODA (solved in IPA) modified tungsten surface. 82
Table 104: Diiodomethane contact angle (CA) of ODA (solved in IPA) modified tungsten surface. 82
Table 105: Surface energy (σ) of ODA (solved in IPA) modified tungsten surface (calculated via data of Table 103 and Table 104). 83
Table 106: Ellipsometric data of ODA (solved in IPA) modified tungsten surface. 83
Table 107: Water contact angle (CA) of ODO (solved in THF) modified tungsten surface. 83
Table 108: Diiodomethane contact angle (CA) of ODO (solved in THF) modified tungsten surface. 84

Table 109: Surface energy (σ) of ODO (solved in THF) modified tungsten surface (calculated via data of Table 107 and Table 108). 84
Table 110: Ellipsometric data of ODO (solved in THF) modified tungsten surface. 84
Table 111: Water contact angle (CA) of ODO (solved in IPA) modified tungsten surface. 85
Table 112: Diiodomethane contact angle (CA) of ODO (solved in IPA) modified tungsten surface. 85
Table 113: Surface energy (σ) of ODO (solved in IPA) modified tungsten surface (calculated via data of Table 111 and Table 112). 85
Table 114: Ellipsometric data of ODO (solved in IPA) modified tungsten surface. 85
Table 115: Water contact angle (CA) of LA (solved in THF) modified tungsten surface. 86
Table 116: Diiodomethane contact angle (CA) of LA (solved in THF) modified tungsten surface. 86
Table 117: Surface energy (σ) of LA (solved in THF) modified tungsten surface (calculated via data of Table 115 and Table 116). 86
Table 118: Ellipsometric data of LA (solved in THF) modified tungsten surface. 87
Table 119: Water contact angle (CA) of LA (solved in IPA) modified tungsten surface. 87
Table 120: Diiodomethane contact angle (CA) of LA (solved in IPA) modified tungsten surface. 87
Table 121: Surface energy (σ) of LA (solved in IPA) modified tungsten surface (calculated via data of Table 119 and Table 120). 87
Table 122: Ellipsometric data of LA (solved in IPA) modified tungsten surface. 88
Table 123: Water contact angle (CA) of STA (solved in THF) modified tungsten surface. 88
Table 124: Diiodomethane contact angle (CA) of STA (solved in THF) modified tungsten surface. 88
Table 125: Surface energy (σ) of STA (solved in THF) modified tungsten surface (calculated via data of Table 123 and Table 124). 89
Table 126: Ellipsometric data of STA (solved in THF) modified tungsten surface. 89
Table 127: Water contact angle (CA) of STA (solved in IPA) modified tungsten surface. 89
Table 128: Diiodomethane contact angle (CA) of STA (solved in IPA) modified tungsten surface. 90
Table 129: Surface energy (σ) of STA (solved in IPA) modified tungsten surface (calculated via data of Table 127 and Table 128). 90
Table 130: Ellipsometric data of STA (solved in IPA) modified tungsten surface. 90
Table 131: Water contact angle (CA) of PFNA (solved in IPA) modified tungsten surface. 90
Table 132: Diiodomethane contact angle (CA) of PFNA (solved in IPA) modified tungsten surface. 91
Table 133: Surface energy (σ) of PFNA (solved in IPA) modified tungsten surface (calculated via data of Table 131 and Table 132). 91
Table 134: Ellipsometric data of PFNA (solved in IPA) modified tungsten surface. 91
Table 135: Water contact angle (CA) of PFNA (solved in THF) modified tungsten surface. 91
Table 136: Diiodomethane contact angle (CA) of PFNA (solved in THF) modified tungsten surface. 92
Table 137: Surface energy (σ) of PFNA (solved in THF) modified tungsten surface (calculated via data of Table 135 and Table 136). 92
Table 138: Ellipsometric data of PFNA (solved in THF) modified tungsten surface. 92
Table 139: Water contact angle (CA) of PFND (solved in IPA) modified tungsten surface. 92
Table 140: Diiodomethane contact angle (CA) of PFND (solved in IPA) modified tungsten surface. 93
Table 141: Surface energy (σ) of PFND (solved in IPA) modified tungsten surface (calculated via data of Table 139 and Table 140). 93
Table 142: Ellipsometric data of PFND (solved in IPA) modified tungsten surface. 93
Table 143: Water contact angle (CA) of PFND (solved in THF) modified tungsten surface. 93
Table 144: Diiodomethane contact angle (CA) of PFND (solved in THF) modified tungsten surface. 94

Table 145: Surface energy (σ) of PFND (solved in THF) modified tungsten surface (calculated via data of Table 143 and Table 144). 94
Table 146: Ellipsometric data of PFND (solved in THF) modified tungsten surface. 94
Table 147: Water contact angle (CA) of ODPA (solved in THF) modified titanium nitride surface. 94
Table 148: Diiodomethane contact angle (CA) of ODPA (solved in THF) modified titanium nitride surface. 95
Table 149: Surface energy (σ) of ODPA (solved in THF) modified titanium nitride surface (calculated via data of Table 147 and Table 148). 95
Table 150: Water contact angle (CA) of ODPA (solved in THF) modified titanium nitride surface. 95
Table 151: Diiodomethane contact angle (CA) of ODPA (solved in THF) modified titanium nitride surface. 95
Table 152: Surface energy (σ) ODPA (solved in THF) modified titanium nitride surface (calculated via data of Table 150 and Table 151). 96
Table 153: Water contact angle (CA) of ODPA (solved in IPA) modified titanium nitride surface. 96
Table 154: Diiodomethane contact angle (CA) of ODPA (solved in IPA) modified titanium nitride surface. 96
Table 155: Surface energy (σ) of ODPA (solved in IPA) modified titanium nitride surface (calculated via data of Table 153 and Table 154). 96
Table 156: Contact angles (CA) of ODPA modified titanium nitride surface before and after the coating. 97
Table 157: Surface energy (σ) of ODPA modified titanium nitride surface before and after the coating (calculated via data of Table 156). 97
Table 158: Water contact angle (CA) of TDPA (solved in THF) modified titanium nitride surface. 97
Table 159: Diiodomethane contact angle (CA) of TDPA (solved in THF) modified titanium nitride surface. 98
Table 160: Surface energy (σ) of TDPA (solved in THF) modified titanium nitride surface (calculated via data of Table 158 and Table 159). 98
Table 161: Water contact angle (CA) of TDPA (solved in IPA) modified titanium nitride surface. 98
Table 162: Diiodomethane contact angle (CA) of TDPA (solved in IPA) modified titanium nitride surface. 98
Table 163: Surface energy (σ) of TDPA (solved in IPA) modified titanium nitride surface (calculated via data of Table 161 and Table 162). 99
Table 164: Water contact angle (CA) of TDA (solved in THF) modified titanium nitride surface. 99
Table 165: Diiodomethane contact angle (CA) of TDA (solved in THF) modified titanium nitride surface. 99
Table 166: Surface energy (σ) of TDA (solved in THF) modified titanium nitride surface (calculated via data of Table 164 and Table 165). 99
Table 167: Water contact angle (CA) of TDA (solved in IPA) modified titanium nitride surface. 99
Table 168: Diiodomethane contact angle (CA) of TDA (solved in IPA) modified titanium nitride surface. 100
Table 169: Surface energy (σ) of TDA (solved in IPA) modified titanium nitride surface (calculated via data of Table 167 and Table 168). 100
Table 170: Water contact angle (CA) of ODA (solved in THF) modified titanium nitride surface. 100
Table 171: Diiodomethane contact angle (CA) of ODA (solved in THF) modified titanium nitride surface. 100

Table 172: Surface energy (σ) of ODA (solved in THF) modified titanium nitride surface (calculated via data of Table 170 and Table 171). 100
Table 173: Water contact angle (CA) of ODA (solved in IPA) modified titanium nitride surface........ 101
Table 174: Diiodomethane contact angle (CA) of ODA (solved in IPA) modified titanium nitride surface. 101
Table 175: Surface energy (σ) of ODA (solved in IPA) modified titanium nitride surface (calculated via data of Table 173and Table 174). 101
Table 176: Water contact angle (CA) of LA (solved in THF) modified titanium nitride surface. 101
Table 177: Diiodomethane contact angle (CA) of LA (solved in THF) modified titanium nitride surface. 101
Table 178: Surface energy (σ) of LA (solved in THF) modified titanium nitride surface (calculated via data of Table 176 and Table 177). 102
Table 179: Water contact angle (CA) of LA (solved in IPA) modified titanium nitride surface. 102
Table 180: Diiodomethane contact angle (CA) of LA (solved in IPA) modified titanium nitride surface. 102
Table 181: Surface energy (σ) of LA (solved in IPA) modified titanium nitride surface (calculated via data of Table 179 and Table 180). 102
Table 182: Water contact angle (CA) of STA (solved in THF) modified titanium nitride surface. 102
Table 183: Diiodomethane contact angle (CA) of STA (solved in THF) modified titanium nitride surface. 103
Table 184: Surface energy (σ) of STA (solved in THF) modified titanium nitride surface (calculated via data of Table 182 and Table 183). 103
Table 185: Water contact angle (CA) of STA (solved in IPA) modified titanium nitride surface. 103
Table 186: Diiodomethane contact angle (CA) of STA (solved in IPA) modified titanium nitride surface. 103
Table 187: Surface energy (σ) of STA (solved in IPA) modified titanium nitride surface (calculated via data of Table 185 and Table 186). 103
Table 188: Water contact angle (CA) of ODO (solved in THF) modified titanium nitride surface. 104
Table 189: Diiodomethane contact angle (CA) of ODO (solved in THF) modified titanium nitride surface. 104
Table 190: Surface energy (σ) of ODO (solved in THF) modified titanium nitride surface (calculated via data of Table 188 and Table 189). 104
Table 191: Water contact angle (CA) of ODO (solved in IPA) modified titanium nitride surface. 104
Table 192: Diiodomethane contact angle (CA) of ODO (solved in IPA) modified titanium nitride surface. 104
Table 193: Surface energy (σ) of ODO (solved in IPA) modified titanium nitride surface (calculated via data of Table 191 and Table 192). 105
Table 194: Water contact angle (CA) of ODT (solved in THF) modified titanium nitride surface. 105
Table 195: Diiodomethane contact angle (CA) of ODT (solved in THF) modified titanium nitride surface. 105
Table 196: Surface energy (σ) of ODT (solved in THF) modified titanium nitride surface (calculated via data of Table 194 and Table 195). 105
Table 197: Water contact angle (CA) of ODT (solved in IPA) modified titanium nitride surface. 105
Table 198: Diiodomethane contact angle (CA) of ODT (solved in IPA) modified titanium nitride surface. 106

Table 199: Surface energy (σ) of ODT (solved in IPA) modified titanium nitride surface (calculated via data of Table 197 and Table 198). 106
Table 200: Water contact angle (CA) of DDBSA (solved in THF) modified titanium nitride surface. 106
Table 201: Diiodomethane contact angle (CA) of DDBSA (solved in THF) modified titanium nitride surface. 106
Table 202: Surface energy (σ) of DDBSA (solved in THF) modified titanium nitride surface (calculated via data of Table 200 and Table 201). 106
Table 203: Water contact angle (CA) of DDBSA (solved in IPA) modified titanium nitride surface. 107
Table 204: Diiodomethane contact angle (CA) of DDBSA (solved in IPA) modified titanium nitride surface. 107
Table 205: Surface energy (σ) of DDBSA (solved in IPA) modified titanium nitride surface (calculated via data of Table 203 and Table 204). 107
Table 206: Water contact angle (CA) of PFND (solved in THF) modified titanium nitride surface. 107
Table 207: Diiodomethane contact angle (CA) of PFND (solved in THF) modified titanium nitride surface. 107
Table 208: Surface energy (σ) of PFND (solved in THF) modified titanium nitride surface (calculated via data of 108
Table 209: Water contact angle (CA) of PFND (solved in IPA) modified titanium nitride surface. 108
Table 210: Diiodomethane contact angle (CA) of PFND (solved in IPA) modified titanium nitride surface. 108
Table 211: Surface energy (σ) of PFND (solved in IPA) modified titanium nitride surface (calculated via data of 108
Table 212: Water contact angle (CA) of PFNA (solved in THF) modified titanium nitride surface. 108
Table 213: Diiodomethane contact angle (CA) of PFNA (solved in THF) modified titanium nitride surface. 109
Table 214: Surface energy (σ) of PFNA (solved in THF) modified titanium nitride surface (calculated via data of Table 212 and Table 213). 109
Table 215: Water contact angle (CA) of PFNA (solved in IPA) modified titanium nitride surface. 109
Table 216: Diiodomethane contact angle (CA) of PFNA (solved in IPA) modified titanium nitride surface. 109
Table 217: Surface energy (σ) of PFNA (solved in IPA) modified titanium nitride surface (calculated via data of Table 215 and Table 216). 109
Table 218: Water contact angle (CA) of PFTDA (solved in THF) modified titanium nitride surface. 110
Table 219: Diiodomethane contact angle (CA) of PFTDA (solved in THF) modified titanium nitride surface. 110
Table 220: Surface energy (σ) of PFTDA (solved in THF) modified titanium nitride surface (calculated via data of Table 218 and Table 219). 110
Table 221: Water contact angle (CA) of PFTDA (solved in IPA) modified titanium nitride surface. 110
Table 222: Diiodomethane contact angle (CA) of PFTDA (solved in IPA) modified titanium nitride surface. 110
Table 223: Surface energy (σ) of PFTDA (solved in IPA) modified titanium nitride surface (calculated via data of Table 221 and Table 222). 111
Table 224: Water contact angle (CA) of ODT (solved in THF) modified thermal silicon dioxide surface. 111
Table 225: Diiodomethane contact angle (CA) of ODT (solved in THF) modified thermal silicon dioxide surface. 111

Table 226: Surface energy (σ) of ODT (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 224 and Table 225). 111
Table 227: Ellipsometric data of ODT (solved in THF) modified thermal silicon dioxide surface. 111
Table 228: Water contact angle (CA) of ODT (solved in IPA) modified thermal silicon dioxide surface. 112
Table 229: Diiodomethane contact angle (CA) of ODT (solved in IPA) modified thermal silicon dioxide surface. 112
Table 230: Surface energy (σ) of ODT (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 228 and Table 229). 112
Table 231: Ellipsometric data of ODT (solved in IPA) modified thermal silicon dioxide surface. 112
Table 232: Water contact angle (CA) of DDBSA (solved in THF) modified thermal silicon dioxide surface. 112
Table 233: Diiodomethane contact angle (CA) of DDBSA (solved in THF) modified thermal silicon dioxide surface. 113
Table 234: Surface energy (σ) of DDBSA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 232 and Table 233). 113
Table 235: Ellipsometric data of DDBSA (solved in THF) modified thermal silicon dioxide surface. 113
Table 236: Water contact angle (CA) of DDBSA (solved in IPA) modified thermal silicon dioxide surface. 113
Table 237: Diiodomethane contact angle (CA) of DDBSA (solved in IPA) modified thermal silicon dioxide surface. 113
Table 238: Surface energy (σ) of DDBSA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 236 and Table 237). 113
Table 239: Ellipsometric data of DDBSA (solved in IPA) modified thermal silicon dioxide surface. 114
Table 240: Water contact angle (CA) of PFND (solved in THF) modified thermal silicon dioxide surface. 114
Table 241: Diiodomethane contact angle (CA) of PFND (solved in THF) modified thermal silicon dioxide surface. 114
Table 242: Surface energy (σ) of PFND (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 240 and Table 241). 114
Table 243: Ellipsometric data of PFND (solved in THF) modified thermal silicon dioxide surface. 114
Table 244: Water contact angle (CA) of PFND (solved in IPA) modified thermal silicon dioxide surface. 115
Table 245: Diiodomethane contact angle (CA) of PFND (solved in IPA) modified thermal silicon dioxide surface. 115
Table 246: Surface energy (σ) of PFND (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 244 and Table 245). 115
Table 247: Ellipsometric data of PFND (solved in IPA) modified thermal silicon dioxide surface. 115
Table 248: Water contact angle (CA) of PFNA (solved in THF) modified thermal silicon dioxide surface. 115
Table 249: Diiodomethane contact angle (CA) of PFNA (solved in THF) modified thermal silicon dioxide surface. 116
Table 250: Surface energy (σ) of PFNA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 248 and Table 249). 116
Table 251: Ellipsometric data of PFNA (solved in THF) modified thermal silicon dioxide surface. 116

Table 252: Water contact angle (CA) of PFNA (solved in IPA) modified thermal silicon dioxide surface. 116
Table 253: Diiodomethane contact angle (CA) of PFNA (solved in IPA) modified thermal silicon dioxide surface. 116
Table 254: Surface energy (σ) of PFNA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 252 and Table 253). 116
Table 255: Ellipsometric data of PFNA (solved in IPA) modified thermal silicon dioxide surface. 117
Table 256: Water contact angle (CA) of PFTDA (solved in THF) modified thermal silicon dioxide surface. 117
Table 257: Diiodomethane contact angle (CA) of PFTDA (solved in THF) modified thermal silicon dioxide surface. 117
Table 258: Surface energy (σ) of PFTDA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 256 and Table 257). 117
Table 259: Ellipsometric data of PFTDA (solved in THF) modified thermal silicon dioxide surface. 117
Table 260: Water contact angle (CA) of PFTDA (solved in IPA) modified thermal silicon dioxide surface. 118
Table 261: Diiodomethane contact angle (CA) of PFTDA (solved in IPA) modified thermal silicon dioxide surface. 118
Table 262: Surface energy (σ) of PFTDA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 260 and Table 261). 118
Table 263: Ellipsometric data of PFTDA (solved in IPA) modified thermal silicon dioxide surface. 118
Table 264: Water-contact-angle (CA) of TDPA (solved in IPA) modified thermal silicon dioxide surface. 118
Table 265: Diiodomethane contact angle (CA) of TDPA (solved in IPA) modified thermal silicon dioxide surface. 119
Table 266: Surface energy (σ) of TDPA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 264 and Table 265). 119
Table 267: Ellipsometric data of TDPA (solved in IPA) modified thermal silicon dioxide surface. 119
Table 268: Water contact angle (CA) of TDPA (solved in THF) modified thermal silicon dioxide surface. 119
Table 269: Diiodomethane contact angle (CA) of TDPA (solved in THF) modified thermal silicon dioxide surface. 119
Table 270: Surface energy (σ) of TDPA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 268 and Table 269). 119
Table 271: Ellipsometric data of TDPA (solved in THF) modified thermal silicon dioxide surface. 120
Table 272: Water contact angle (CA) of ODPA (solved in IPA) modified thermal silicon dioxide surface. 120
Table 273: Diiodomethane contact angle (CA) of ODPA (solved in IPA) modified thermal silicon dioxide surface. 120
Table 274: Surface energy (σ) of ODPA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 272 and Table 273). 120
Table 275: Ellipsometric data of ODPA (solved in IPA) modified thermal silicon dioxide surface. 120
Table 276: Water contact angle (CA) of ODPA (solved in THF) modified thermal silicon dioxide surface. 121
Table 277: Diiodomethane contact angle (CA) of ODPA (solved in THF) modified thermal silicon dioxide surface. 121

Table 278: Surface energy (σ) of ODPA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 276 and Table 277)........ 121
Table 279: Ellipsometric data of ODPA (solved in THF) modified thermal silicon dioxide surface..... 121
Table 280: Water contact angle (CA) of TDA (solved in IPA) modified thermal silicon dioxide surface. 121
Table 281: Diiodomethane contact angle (CA) of TDA (solved in IPA) modified thermal silicon dioxide surface........ 122
Table 282: Surface energy (σ) of TDA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 280 and Table 281)........ 122
Table 283: Ellipsometric data of TDA (solved in IPA) modified thermal silicon dioxide surface......... 122
Table 284: Water contact angle (CA) of TDA (solved in THF) modified thermal silicon dioxide surface. 122
Table 285: Diiodomethane contact angle (CA) of TDA (solved in THF) modified thermal silicon dioxide surface........ 122
Table 286: Surface energy (σ) of TDA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 284 and Table 285)........ 122
Table 287: Ellipsometric data of TDA (solved in THF) modified thermal silicon dioxide surface........ 123
Table 288: Water contact angle (CA) of ODA (solved in IPA) modified thermal silicon dioxide surface. 123
Table 289: Diiodomethane contact angle (CA) of ODA (solved in IPA) modified thermal silicon dioxide surface........ 123
Table 290: Surface energy (σ) of ODA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 288 and Table 289)........ 123
Table 291: Ellipsometric data of ODA (solved in IPA) modified thermal silicon dioxide surface........ 123
Table 292: Water contact angle (CA) of ODA (solved in THF) modified thermal silicon dioxide surface. 124
Table 293: Diiodomethane contact angle (CA) of ODA (solved in THF) modified thermal silicon dioxide surface........ 124
Table 294: Surface energy (σ) of ODA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 292 and Table 293)........ 124
Table 295: Ellipsometric data of ODA (solved in THF) modified thermal silicon dioxide surface....... 124
Table 296: Water contact angle (CA) of LA (solved in IPA) modified thermal silicon dioxide surface.124
Table 297: Diiodomethane contact angle (CA) of LA (solved in IPA) modified thermal silicon dioxide surface........ 125
Table 298: Surface energy (σ) of LA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 296 and Table 297)........ 125
Table 299: Ellipsometric data of LA (solved in IPA) modified thermal silicon dioxide surface. 125
Table 300: Water contact angle (CA) of LA (solved in THF) modified thermal silicon dioxide surface. 125
Table 301: Diiodomethane contact angle (CA) of LA (solved in THF) modified thermal silicon dioxide surface........ 125
Table 302: Surface energy (σ) of LA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 300 and Table 301)........ 125
Table 303: Ellipsometric data of LA (solved in THF) modified thermal silicon dioxide surface. 126
Table 304: Water contact angle (CA) of STA (solved in IPA) modified thermal silicon dioxide surface. 126

Table 305: Diiodomethaen contact angle (CA) of STA (solved in IPA) modified thermal silicon dioxide surface. 126
Table 306: Surface energy (σ) of STA (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 304 and Table 305). 126
Table 307: Ellipsometric data of STA (solved in IPA) modified thermal silicon dioxide surface. 126
Table 308: Water contact angle (CA) of STA (solved in THF) modified thermal silicon dioxide surface. 127
Table 309: Diiodomethane contact angle (CA) of STA (solved in THF) modified thermal silicon dioxide surface. 127
Table 310: Surface energy (σ) of STA (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 308 and Table 309). 127
Table 311: Ellipsometric data of STA (solved in THF) modified thermal silicon dioxide surface. 127
Table 312: Water contact angle (CA) of ODO (solved in IPA) modified thermal silicon dioxide surface. 127
Table 313: Diiodomethane contact angle (CA) of ODO (solved in IPA) modified thermal silicon dioxide surface. 128
Table 314: Surface energy (σ) of ODO (solved in IPA) modified thermal silicon dioxide surface (calculated via data of Table 312 and Table 313). 128
Table 315: Ellipsometric data of ODO (solved in IPA) modified thermal silicon dioxide surface........ 128
Table 316: Water contact angle (CA) of ODO (solved in THF) modified thermal silicon dioxide surface. 128
Table 317: Diiodomethane contact angle (CA) of ODO (solved in THF) modified thermal silicon dioxide surface. 128
Table 318: Surface energy (σ) of ODO (solved in THF) modified thermal silicon dioxide surface (calculated via data of Table 316 and Table 317). 128
Table 319: Ellipsometric data of ODO (solved in THF) modified thermal silicon dioxide surface........ 129
Table 320: Water and diiodomethane contact angle (CA) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 2 min in the tube furnace. 129
Table 321: Surface energy (σ) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 2 min in the tube furnace (calculated via data of Table 320). 130
Table 322: Ellipsometric data of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 2 min in the tube furnace. 130
Table 323: Water and diiodomethane contact angle (CA) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 6 min in the tube furnace. 130
Table 324: Surface energy (σ) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 6 min in the tube furnace (calculated via data of Table 323). 130
Table 325: Ellipsometric data of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 6 min in the tube furnace. 131
Table 326: Water and diiodomethane contact angle (CA) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 10 min in the tube furnace. 131
Table 327: Surface energy (σ) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 10 min in the tube furnace (calculated via data ofTable 326). 131
Table 328: Ellipsometric data of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 10 min in the tube furnace. 131
Table 329: Water and diiodomethane contact angle (CA) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 30 min in the tube furnace. 132

Table 330: Surface energy (σ) of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 30 min in the tube furnace (calculated via data of Table 323). 132
Table 331: Ellipsometric data of ODA (solved in THF) modified tungsten surface after the pretreatment, the coating and 10 min in the tube furnace. 132
Table 332: Water and diiodomethane contact angle (CA) of ODPA (solved in THF) modified tungsten surface after the pretreatment, the coating and 10 min in the tube furnace. 133
Table 333: urface energy (σ) of ODPA (solved in THF) modified tungsten surface after the pretreatment, the coating and 10 min in the tube furnace (calculated via data of Table 332). 133
Table 334: Ellipsometric data of ODPA (solved in THF) modified tungsten surface after the pretreatment, the coating and 10 min in the tube furnace. 133
Table 335: Water and diiodomethane contact angles (CA) of ODA (solved in THF) modified tungsten surface before and after the coating. 134
Table 336: Surface energy (σ) of ODA (solved in THF) modified tungsten surface (calculated via data of Table 335) before and after the coating (calculated via data of Table 335)................................. 134
Table 337: Ellipsometric data of ODA (solved in THF) modified tungsten surface. 134
Table 338: Water and diiodomethane contact angles (CA) of ODT (solved in THF) modified tungsten surface before and after the coating. 134
Table 339: Surface energy (σ) of ODT (solved in THF) modified tungsten surface (calculated via data of Table 338) before and after the coating (calculated via data of Table 338). 135
Table 340: Ellipsometric data of ODT (solved in THF) modified tungsten surface............................. 135