Evaluating and Optimizing the Quality of Silane-Based Self-Assembled Monolayers

by

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Abstract

Self-assembled monolayers (SAMs) form spontaneously through the adsorption of surfactant molecules onto surfaces, forming ordered molecular assemblies due to a specific affinity of the molecule's headgroup to these surfaces. Monolayers are a simple means of modifying the properties of surfaces, which can be important to many fields. It is, however, still a challenge to achieve high quality SAMs using alkylsilane-based molecules. In this thesis, high quality monolayers of alkylsilanes are sought through the use of mono-reactive perfluoroalkylsilanes. Monolayers created by the deposition of monoreactive perfluoroalkylsilanes from toluene solutions were investigated to correlate the quality of these SAMs to changes in their processing conditions. Surface sensitive spectroscopic techniques were used to monitor and guide further improvements in the quality of these monolayers. Changes to the process conditions included altering the solution temperature, silane concentration, and reaction times. Initial work is also presented on the use of microwave processing to significantly decrease the time required to form monolayers from mono-reactive perfluoroalkylsilanes. As a demonstration of the potential utility of these SAMs, we analyzed the ability of the silane-modified surfaces to resist the non-specific adsorption of proteins. In this example, the non-specific adsorption of bovine serum albumin (BSA) was evaluated on surfaces coated with perfluoroalkylsilane monolayers.

Keywords: self-assembled monolayer; defects; mono-reactive; perfluoroalkylsilanes; microwave processing; non-specific protein adsorption

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List of Acronyms

AFM	Atomic Force Microscopy
BSA	Bovine Serum Albumin
FAS	1H,1H,2H,2H-perfluorodecyldimethylchlorosilane
FTIR	Fourier Transform Infrared
IMFP	Inelastic Mean Free Path
KE	Kinetic Energy
MEMs	Micro-electromechanical System
MSDSs	Material Safety Data Sheets
OTS	Octadecyltrichlorosilane
PBS	Phosphate Buffered Saline
SAMs	Self-assembled Monolayers
STM	Scanning Tunneling Microscopy
XPS	X-ray Photoelectron Spectroscopy
UHV	Ultra-high Vacuum

List of Symbols

θ	water contact angle
Φ_0	incident light angle, ellipsometry
Φ	work function of spectrometer, XPS
λ	IMFP, XPS

1. An Introduction to Self-Assembled Monolayers

1.1. Self-Assembled Monolayers (SAMs)

In 1946, Zisman discovered self-assembled monolayers (SAMs) when he put a clean platinum film into a solution containing a surfactant.[1] The surfactants in solution spontaneously adsorbed onto the surfaces of the metal forming a single-molecule-thick film. He discovered the self-limiting nature of this molecular film by a series of sequential tests. After removing the surfactant-coated metal from the dilute solution, the researchers removed this organic film from the Pt by thermal oxidation. Repeating this procedure over and over, the authors were able to count the number of surfactant based films that could be produced before exhausting the supply of the surfactants dissolved in solution. By dividing the number of retractions by the total number of initial surfactant molecules, the authors estimated the approximate cross-sectional area of per molecule absorbed onto the clean Pt surfaces. The result of this calculation demonstrated that the film contained a monolayer of surfactant.[1] From this analysis, they predicted this monolayer to be a single-molecule-thick film of closely packed and highly ordered surfactant molecules.

Over the past 30 years, SAMs have gained a particularly increasing attention for their use in the development of applications, materials, and processes related to the fields of biotechnology and nanotechnology. Monolayers have been pursued for stabilizing the growth and solubility of nanoparticles.[2] These coatings have also found applications in resisting chemical attack in lithographic process,[3] repelling the non-specific adsorption of proteins,[4] and interacting in a specific manner with targeted biomolecules as part of a biosensor.[5] Monolayers of different compositions and on different surfaces have been reported, such as n-alkanoic acids chemisorbed via proton transfer to a lattice oxygen atom on aluminum oxide.[6, 7] N-alkanoic acids chemisorbed as a monolayer onto copper, forming metal carboxylate salts.[8] One commonly studied monolayers are those formed by covalent bonds between organothiols or disulfides and noble or transition metal surfaces.[9, 10] Another one is organosilanes bound to glasses and oxides through covalent interactions.[8] Monolayer grown on silica can form through silyl ether bonds,[11] and monolayers on hydrogen terminated silicon can form by radical-free initiated cross-linking with alkenes and alkynes .[12]

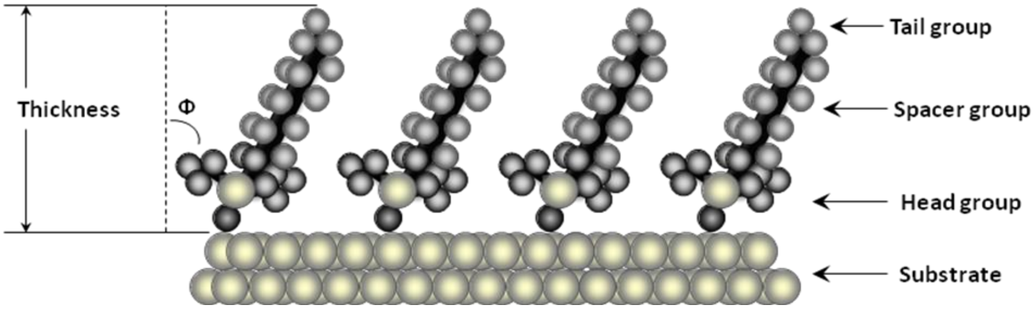


Figure 1.1. *Schematic illustration depicting the structure of self-assembled monolayers, defining both thickness and tilt angle Φ of the molecules within this molecular film. For consistency the molecules used in this schematic are the same molecules, 1H,1H,2H,2H-perfluorodecyldimethylchlorosilanes ($C_{12}H_{10}ClF_{17}Si$), used in the research pursued in this thesis.*

The molecules of SAMs are composed of a head group, a spacer or linker chain, and the tail group (Figure 1.1). The head group has a specific affinity for the atoms on the surfaces of the substrate. These groups can bind either through covalent or non-covalent interactions with atoms on the surfaces of the substrate. For example, alkylthiols bind covalently with atoms on the surfaces of noble metals (e.g., Ag, Au, Pt, or Cu) through sulfur-metal interactions.[13] Alkylsilane molecules can form covalent links with oxides through condensation reactions with surface bound hydroxyl groups.[8] The assembly of these monolayers are not only driven by the interactions of the head group with the exposed surfaces, but also through intermolecular interactions within the monolayers. These interactions influence the tilt angle Φ of molecules within the SAMs. For example, the average tilt angle of alkylthiols on gold (111) surfaces is approximately 30-35°. However, it was determined that alkylthiols are oriented almost perpendicular to the plane of the surface when bound to the silver (111) surfaces.[14] A high degree of variability is also observed in the packing density of molecules within the SAMs. This density is determined by a combination of interactions between the assembled molecules and the surfaces, as well as the intermolecular interactions in the monolayers.

The thickness of monolayer and density of molecules within this film are largely defined by the spacer group, which can include alkylchains $(CH_2)_n$, fluorinated carbon chains $(CF_2)_n$, and polyoxyethylene chains $(CH_2CH_2O)_n$. For example, the length of an octadecylsilane (OTS) molecule is 2.35 nm.[15] This value is a maximum anticipated thickness for OTS monolayers. If the film thickness measurement is greater than 2.35 nm, the surfaces are most likely coated with a multilayer of OTS. These linker chains interact with each other through van der Waals bonds and form compact monolayer arrays with optimized contact between chains. These interactions assist in formation of the monolayers. An increased chain length strengthens the intermolecular interactions, which correlates with molecules that pack into ordered monolayers with a high density and surface coverage.[15] The longer spacer groups pack into higher quality monolayers, which provide substantial barriers to electron transfer and ion penetration.[18] One application of these well-packed monolayers is to resist chemical attack in lithographic processes.[3,16] In the fabrication of microelectromechanical systems (or MEMS), monolayers are used to reduce the friction between moving parts, such as gears, adjustable lenses, and other actuators.[17] Applications of monolayer-modified surfaces are largely determined by the quality of the SAMs and the new properties of these modified surfaces. These properties are, to a large degree, controlled by the terminal functional group (or tail group) on the assembled molecules (Figure 1.1).

The terminal functional group determines the hydrophobic and hydrophilic nature of the monolayers. This terminal group can easily change the solvent wetting properties of a substrate. Controlled wetting of interfaces is important to applications that include solar cell panels and other optical components. Many applications desire the outermost surfaces to be superhydrophobic, rendering these surfaces self-cleaning. [18] The hydrophilic and hydrophobic properties of the monolayer are important for rendering the surfaces resistant to non-specific adhesion of biomolecules, such as proteins.[19] The absence of these monolayers would normally lead to denaturation of proteins onto the otherwise high energy surfaces of the underlying substrate. The terminal functional group of the SAMs can also be further chemically modified to fine-tune the properties of the monolayers. Reactions involving the terminal groups (e.g. -COOH) of SAMs have been explored to link biomolecules to the surfaces, such as through carbodiimide coupling reactions forming an amide bond.[20] Monolayers have also been modified by binding molecules of interest through antibody-antigen or protein-specific interactions, which are widely used for biosensors and biochips.[20] These capabilities are also useful in the build-up of anchoring layers in complex layered structures for man-made tissue engineering.[21] The monolayer serves as a molecular building block upon which surfaces can be rendered to possess different chemical functionalities and, thus, different properties.

Self-assembled monolayers are a good model to investigate interfacial phenomena due to molecular interactions between the monolayer and its surroundings. Monolayers have many potential uses in fundamental interface science, as well as the modification of surfaces for engineered and biological applications mentioned above.[14] Most applications of SAMs demand high quality films. Quality of these films depends on the organization, tilt and density of molecules within the monolayers.[22] In reality, monolayers are not perfect, and include a number of defects. It is essential to understand these defects. Only then can the processes for the formation of a high quality monolayer be truly optimized.

1.2. The Significance of Defects in SAMs

The schematic representation of a monolayer (Figure 1.1) represents an ideal structure of SAMs and atomically smooth surfaces. In reality, the surfaces of substrates are non-flat, which creates defects and domain boundaries within the monolayers. These defects may disrupt the perfect packing of a monolayer.[23, 24] Methods for preparing substrate greatly affect the surface quality. For example, the quality of evaporated gold on a mica sheet depends on the temperature of the substrate while depositing the gold film. As characterized by scanning tunneling microscopy (STM) the roughness of gold surfaces prepared at 300 °C is 0.25 ± 0.07 nm, which is 22 times lower than for gold films prepared at room temperature.[23] Silicon substrates are widely used in the field of nanotechnology. Processing of silicon includes growth of single crystal ingots that are then cut, etched, and polished to form wafer rounds. This process introduces contaminants that include metal impurities and organic chemicals that may influence the cleanliness of silicon surfaces.[25] Another contributor to the purity of the monolayer is the solution, which can contain some contaminants that adsorb onto the surfaces as defects in the SAMs. For example, the quality of dodecyl thiocyanate ($C_{12}H_{25}SCN$) based monolayers assembled onto Au coated mica substrates depends largely on the purity of thiocyanate.[26] Defects in SAMs are not only caused by external factors, such as methods for preparing the substrates, cleanliness of the surfaces and purity of the solvents and precursor materials. These molecular-scale defects can also be attributed to intrinsic factors.

Intrinsic defects are attributed to the dynamics and complex phase behaviours of monolayers.[13] Monolayers form by a thermodynamically driven assembly of adsorbates onto the surfaces. Various processes taking place at this interface include the coexistence of the adsorption and desorption of species on these surfaces,[27] competition between solvent and molecular reagents for interactions with the surfaces ,[26] and the interactions between adsorbates that stabilize or destabilize the adsorbed layers.[28] The molecules assemble automatically into a monolayer, but they may not align perfectly with the same orientation. The ability of SAMs to uniformly modify the surface is determined by both the composition of the assembled molecules and the arrangement of these molecules within the monolayers. We define the quality of these films by the surface density, orientation, and tilt angle of molecules within the monolayers.[22,29]

There are many different types of defects that can exist within SAMs (Figure 1.2). These defects include ‘pinhole defects’ within the monolayer of missing molecules, physically adsorbed impurities (metal atoms, salts, organic molecules, and organometallic complexes), non-uniform reactive sites, and other irregularities in the surfaces of the substrate (e.g., step edges and non-planar regions). The pinhole defects can be proportional to the size of the assembled molecules (or larger) , which expose the underlying surfaces to the surrounding solution.[30] Detecting these pinhole defects within SAMs has been approached by a number of different methods. One example is to chemically amplify the defects, such as through chemical etching [31] or electroless deposition of silver onto exposed regions of a silicon substrate within silane-based SAMs.[32] Other chemical amplification techniques include polymerisation of tyramine onto defect sites within SAMs of hexadecanethiol on gold.[33] A second approach to identifying defects is through direct observation such as with a scanning probe microscopy technique [e.g., scanning tunnelling microscopy (STM)[22] or atomic force microscopy (AFM)].[34] Electron microscopy has also been used to image defects in hexadecanethiolate-based SAMs on gold.[31] In the alkysilane-based monolayers, the diameter of a pinhole defect can range from the diameter of a single molecule to hundreds of nanometers.[34] In the case that a multi-layered molecular film is formed, instead of a monolayer, the long carbon chains of the alkysilane can physically mask the pinhole defects.[35] These branched, multi-layered structures are, however, not sufficient to mask the surfaces from chemical attack.

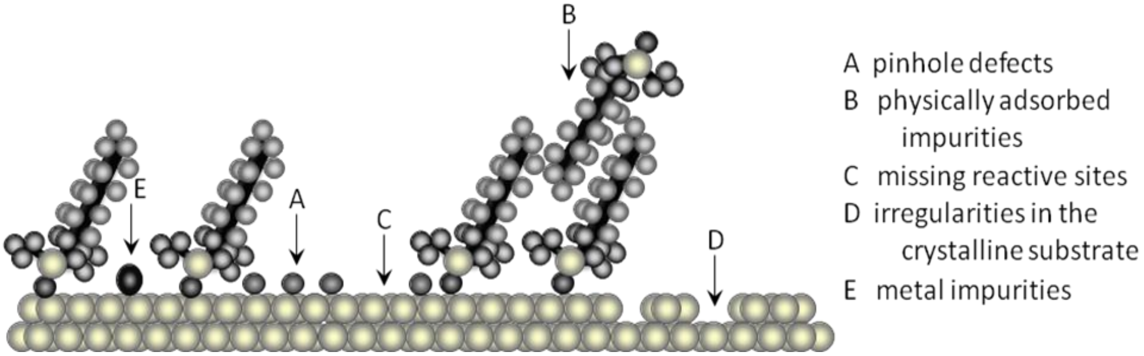


Figure 1.2. *Schematic illustration of different types of structural defects within SAMs.*

The presence of defects within the SAMs can lead to progressive or catastrophic failure of this molecular film in its ability to maintain the altered properties of surfaces.[22,30,36] Degradation of the monolayers may result from corrosion and etching of the underlying substrate in the presence of chemical etchants and oxidants.[37] In other applications, the density of the SAMs play a critical role in the function of a device, such as SAMs acting as an electron transfer barrier or biospecific layer in biosensors. The presence of defects could be a source of erratic signals that decrease the sensitivity of the biosensors and also reduce the biospecificity in patterned arrays of SAMs.[33] The fabrication of pinhole-free SAMs is an important challenge to address for all applications of SAMs. Equivalently, we also need techniques that are sufficient to observe and characterize defects in SAMs, and methods that are appropriate for assessing the quality of these monolayers as a function of changes in the reaction conditions.

1.3. Methods of Characterizing SAMs

The coverage of SAMs on the surfaces of a substrate is very small; such that appropriate techniques need to be chosen in order to analytically determine the uniformity of these films. A variety of techniques are also used to build a complete picture of the quality of monolayers. Simple techniques to assess the quality of monolayers include measuring their hydrophobicity and film thickness, and to determine the uniformity of these properties across the surfaces. These properties can be assessed by measuring their water contact angle,[38,39] and using spectroscopic ellipsometry to determine the changes in dielectric layer at the interface.[40,41] Another surface sensitive technique that we utilize is x-ray photoelectron spectroscopy (XPS).[42,43] This technique is used to determine the density of surface coverage and the relative tilt of the molecules within SAMs. Topography of the SAMs is also determined, using atomic force microscopy (AFM) techniques.[32,33] Although scanning tunnelling microscopy (STM) has higher spatial resolution,[44,45] this technique requires the use of a conductive substrate, and the primary materials of interest in these studies are silicon oxide coated substrates. Some of the techniques used in these studies are geared to macro-scale measurements (e.g. water contact angles) and others micro-scale measurements (e.g. XPS) in the information they provide regarding the quality of the SAMs. Multiple techniques are used in parallel to create a general picture of the quality of SAMs. The following sections describe each technique used in these measurements, as well as the principles and limitations of these techniques.

1.3.1. Water Contact Angle (WCA) Measurements

Water contact angle measurements are determined from the angle at which a liquid-vapor interface meets a solid surface (Figure 1.3). This measurement depends on the free energy and wettability of the surfaces. The measurements commonly use water as the liquid to determine these properties of the surfaces. After placing a measured droplet of water onto the surfaces, an angle θ is measured between the interfaces (Figure 1.3) that is a function of the adhesive and cohesive forces. The adhesive forces are between the water molecules and the solid surfaces, which cause water to spread on surface. But the cohesive forces are between the water molecules, which cause the water droplet to form a ball-like shape in order to avoid contact with the solid surfaces. The balance of forces is defined by Young's equation:

$$\gamma^{sv} = \gamma^{sl} + \gamma^{lv} \cos\theta$$ **Equation 1-1** [46]

In this equation, γ^{sl} is the solid-liquid interfacial tension, γ^{sv} is the solid-vapor interfacial tension, and γ^{lv} is the liquid-vapor interfacial tension. A substrate whose surfaces are coated with hydrophobic SAMs produces a larger contact angle, indicating a lower surface free energy. For instance, the water contact angle for gold surfaces coated with octadecanethiol ($C_{18}H_{37}SH$) is 119°,[47] and for octadecyltrichlorosilane ($C_{18}H_{37}SiCl_3$) on silicon oxide surfaces is 109° [39] and on glass surfaces is 120°.[48] The magnitude and error in measuring the water contact angles relates to the quality of the SAMs,[47,48] but it mostly independent of the chain length of the molecules within the monolayers. [48]

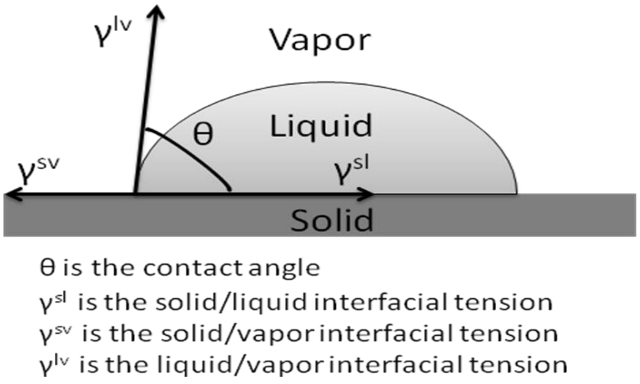


Figure 1.3. *Schematic illustration of water contact angle (θ), measuring the tension between liquid-vapor (γ^{lv}), solid-vapor (γ^{sv}), solid-liquid (γ^{sl}) interfaces.*

The Young's equation assumes perfectly flat surfaces, but in reality the roughness of the substrate, physically adsorbed species, and defects within the SAMs can lead to deviations in the predicted contact angle measurements for a specific surface modification. These irregularities are one of the reasons to measure both the advancing and receding contact angles for surfaces. Advancing contact angles are measured by continually adding water droplets in a fixed position onto the surfaces.

During this process, the physically absorbed species are pushed away by the advancing water droplet. Receding contact angle measurements are taken by removing measured amounts of water from this same water droplet. Usually advancing and receding angle do not agree. The difference between these contact angle measurements, which is referred to as contact angle hysteresis, is used to determine the heterogeneity of the monolayer modified surfaces. For example, a difference of 19° was reported between the advancing water contact angles (119°) and the receding angles (100°) for octadecanethiol-modified gold.[47] This demonstrates a relatively high degree of hysteresis for these SAMs.

The water contact angle measurements are very quick and offer a relatively simple method to check the quality of surfaces modified by SAMs. In a typical measurement, about 2 μl of water is added to the surfaces of the substrate. This water droplet covers an area of ~2 mm^2. This macroscopic measurement is a limitation of this technique. Another potential limitation is the introduction of contaminants from the water. Other techniques were pursued to determine the micron-scale irregularities in the monolayer-modified surfaces, as well as other properties of the monolayers (e.g., film thickness and uniformity).

1.3.2. Spectroscopic Ellipsometry Measurements

Ellipsometry is commonly used to measure the thickness of SAMs.[41,42] A comparison of the measured thickness with the theoretically predicted thickness of monolayers is one measure of the quality of the SAMs. Thickness of the monolayers is determined by both the density and tilt angle of assembled molecules. The principle of ellipsometry is to measure the dielectric properties of layered materials, and to correlate an optical dielectric response of these films to predicted thickness of each layer based on the measured reflections of incident polarized light. Light can be described as an electromagnetic wave. For p-polarized light, the electric fields of incident and reflected light waves oscillate within the same plane, perpendicular to the surfaces and parallel to the plane of incidence (Figure 1.4). For s-polarized light, the plane of the reflected light oscillation is perpendicular to the plane of incidence. P- and s- polarized light are orthogonal. When the two light waves are in-phase, the resulting light will be linearly. If they are 90° out-of-phase and equal in amplitude, the resultant light is circularly polarized. The incident polarized light will often become ‘elliptical’ upon reflection from the surfaces, from which is derived the term ‘ellipsometry’. The incidence angle of light upon semiconductor surfaces is typically 70 to 80° to maximize the sensitivity of measurements. In other incidence angles, p- and s-polarizations cannot be distinguished.[49]

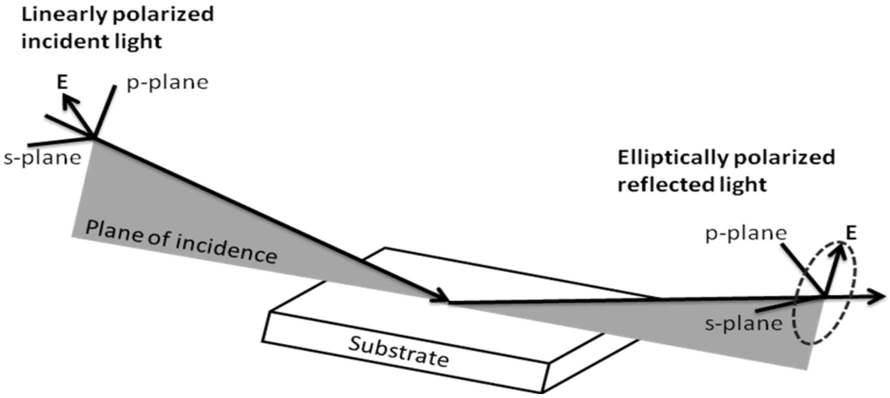


Figure 1.4. *Schematic representation of the principles of ellipsometry. Light polarized in the S direction is perpendicular to the plane of incidence, and the P polarization is in a direction parallel to the plane of incidence. After reflecting from the substrate surfaces, the linearly polarized light becomes elliptical.*

Ellipsometry measurements yield two values (Ψ and Δ). These variables represent a ratio of the amplitudes (Ψ) and the differences in phase (Δ) between the p- and s-polarized light waves. In spectroscopic ellipsometry, spectra of Ψ and Δ are measured by changing the wavelength of incident light. Typically the range of frequencies used is from ultraviolet through the visible region of the electromagnetic spectrum. The measured change in polarization is commonly written as a function of both Ψ and Δ:

$$\rho = \tan(\Psi)\, e^{i\Delta}$$ **Equation 1-2**[49]

Ellipsometry is primarily used to determine the thickness and dielectric properties of a film. The thickness measurements are, however, indirectly determined, as they are a function of the optical properties assuming a homogeneous material. The measurements for a sample are fit with an optical model to describe the sample. In this optical model (Figure 1.5) the change in polarization, ρ, is expressed by the following equation:

$$\tan(\Psi)\, e^{i\Delta} = \rho(N_0, N_1, N_2, d, \Phi_0) \qquad \textbf{Equation 1-3}\ ^{49}$$

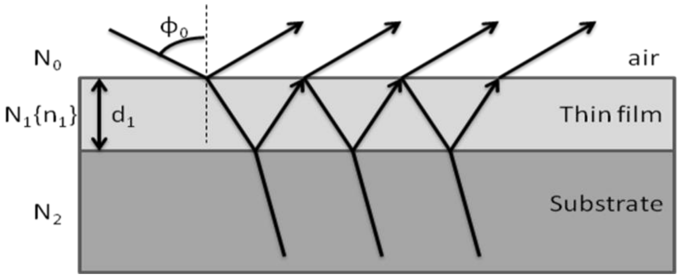


Figure 1.5. *Schematic illustration of an ellipsometric model consisting of a structure composed of air/thin film/substrate interfaces. The thickness of the film,* d_1*, is calculated from the refractive index of the air (*N_0*), thin film (*N_1*), and substrate (*N_2*), as well as the incident angle (*Φ_0*), the amplitude ratio (Ψ), and the phase difference (Δ) of the p- and s-polarized light waves.*

In Equation 1-3, N is the complex refractive index defined by N = n-ik, where n is the refractive index, i is the imaginary unit ($i^2 = -1$) and k is the extinction coefficient of a specific layer. The optical constants (n and k) of a single layer can be derived from Ψ and Δ by using mathematical inversion. Because refractive index $N_0 = 1$ for air, substrate refractive index N_2 and incident angle Φ_0 are usually known in advance, the film thickness, d, can be calculated from Equation 1-3. The iterative nature of these calculations typically relies on software assisted analysis. A model is constructed to assist the determination of the film thickness, but the choice of model requires prior knowledge of the structure of the film (e.g., number of layers and approximate thickness). My research focuses on SAMs of 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane ($C_{12}H_{10}ClF_{17}Si$) on silica surfaces. The monolayers are assembled on silicon oxide substrates. Theoretically, a three-layer model (silicon substrate + oxide + monolayer) would be the best model for this system, but it repeatedly gave inconsistent results. Therefore, a two-layer model was chosen instead. The difference in thickness of the SAMs and the bare silicon substrates is determined to be the thickness of the monolayers. This result reflects the observed trends for the formation of the monolayers. Further discussion on the design and choice of a model that is appropriate for describing silane-based SAMs will be provided in Chapter 3.

Spectroscopic ellipsometry is a non-destructive measurement, and requires less than a minute to measure a single area on a sample. These measurements have a very high precision, and also sensitivity down to ~0.01 nm variations in thicknesses. The largest drawbacks of this technique are its relatively large area of measurement and that it is an indirect characterization, relying upon the fit of a model to accurately predict a film thickness. The minimum measured spot size on a sample is ~1mm^2 through the available techniques, which provides relatively poor spatial resolution.[49] Additionally, ellipsometry does not provide information on the chemical composition of monolayers. This type of measurement requires another analytical technique, namely XPS.

1.3.3. X-ray Photoelectron Spectroscopy (XPS) Measurements

X-ray photoelectron spectroscopy (XPS) is one of the most widely used techniques for characterizing the chemical modifications of surfaces.[53] In this technique, samples are placed under high vacuum conditions and their surfaces irradiated with x-rays to generate photoelectron emission from the sample. Typical x-ray sources are Al Kα spectral line (at 1486.6eV) and Mg Kα spectral line (at 1253.6eV). The incident x-ray photons transfer energy to core-level electrons of atoms in the sample (Figure 1.6). A photoinduced electron (or photoelectron) is ejected with a specific kinetic energy (KE). The binding energy, E_B, of the emitted photoelectron is characteristic of its parent element and its chemical environment. The basic principles of XPS can be described by the Einstein equation, where $h\nu$ is the energy of the incident x-rays, and Φ is the work function of the spectrometer:

$$E_B = h\nu - KE + \Phi$$ **Equation 1-4** [50]

Ultimately, KE is measured by the x-ray photoelectron spectrometer and converted into a binding energy after accounting for the incident x-ray energy and spectrometer work function.

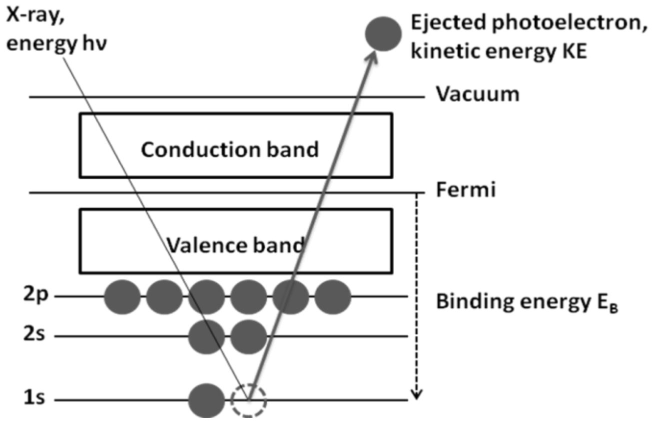


Figure 1.6. *Schematic representation of the principles behind x-ray photoelectron spectroscopy (XPS). An incident x-ray transfers energy to a core-level electron of an atom, which is ejected as a photoelectron with a specific kinetic energy.*

In XPS, only those photoelectrons emitted from the surfaces of a sample will contribute to the observed photoemission peak. Photoelectrons emitted from deeper within the sample will suffer energy loss, but may still have sufficient energy to escape from the surface. These photoelectrons contribute to the background signal in the acquired spectrum. The probability for escape of a photoelectron from a sample is expressed as its inelastic mean free path (IMFP), which depends upon the interactions of the photoelectron with the material, such as its electron density. The IMFP for a material, often referred to as λ, is the thickness through which 63% of the traversing photoelectrons will lose energy. For most materials, this thickness corresponds to 1 to 4 nm. The sampling depth into a sample by XPS is nominally 3λ, which contributes to 95% of the observed photoemission.[50]

X-ray photoelectron spectroscopy is a surface sensitive technique. It is used to analyze both electrically conductive and insulating surfaces.[49] It can also identify most of the elements (except H and He) present at the surface of a sample; it is sensitive to a depth of ~10 nm of a sample.[50] This technique can be very useful for analysis of SAMs. For instance, the absence of a chlorine signal by XPS can indicate that the reaction (i.e., hydrolysis) of octadecyltrichlorosilanes with silicon oxide surfaces and surface bound water is complete.[43] The area under each peak in an x-ray photoelectron spectrum is proportional to the amount of material present for each element. In order to quantify the amount of an element that is present, the associated spectral peaks must be corrected with a relative sensitivity factor (RSF).[50] This correction will be discussed further in later chapters with a specific example. The observed shifts of the binding energy for each element is specific to its chemical environment.[42] This information can include the oxidation state of an element, covalently bound atoms and other atoms in its vicinity (e.g., physically adsorbed or electrostatically interacting elements).

The combination of water contact angle measurements, spectroscopic ellipsometry measurements, and the XPS analysis of monolayers creates a depiction of the quality of these molecular films. An actual picture of the surface can be obtained using atomic force microscopy (AFM).

1.3.4. Atomic Force Microscopy (AFM) Measurements

Atomic force microscopy has proved to be one of the most exciting developments in the past three decades in analytical instrumentation for observing the surface structures of materials. This technique can measure the three-dimensional topography of a sample, creating an image of surfaces. It is capable of achieving high resolution images of surfaces, especially in the z (or vertical) direction with a resolution of at least 0.01 nm. The technique is limited to relatively small lateral scans with a maximum scan size of around 100 μm x 100 μm (the exact values for this area will depend on the specific tool being used).[50] For the analysis of SAMs, AFM can reveal the local structure of the modified surfaces. It has been used to monitor the formation of SAMs at a microscopic level of detail.[51,52] Pinhole defects in SAMs are mostly too small to be observed by AFM as the lateral resolution is limited by the size of the probe that is scanned over the surfaces (Figure 1.7). These defects can be amplified by the growth of a surface bound polymer, which can then be visualized by AFM techniques. The observed polymers correspond to defects in the monolayers.[33]

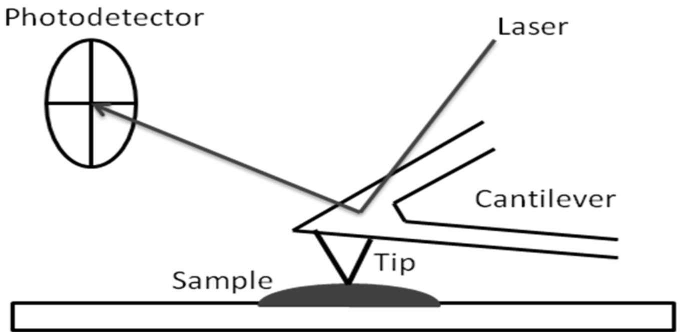


Figure 1.7. *Atomic force microscopy (AFM) provides a topographic image of the surfaces of a sample. The forces between the tip and these surfaces cause the cantilever tip to be deflected. A position-sensitive detector monitors changes in laser light reflected from the back side of the cantilever, which is correlated to changes in the topography of the surfaces.*

The basic functions of an atomic force microscope are depicted in Figure 1.7. A cantilever is positioned parallel to the surface. At the end of this cantilever is a sharp tip (radius of curvature <10 nm) that interacts with the surfaces of a sample. These interactions include electrostatic, capillary, van der Waals and mechanical contact forces.[50] Variations in the interactions between the cantilever tip and the surfaces produce changes in the deflection of the cantilever. These deflections are detected through the reflection of laser light off the back side of the cantilever. The laser signal collected on a position sensitive detector is used to create an image of the surfaces. There are two common imaging modes for AFM: contact mode and tapping mode. In contact mode imaging, the tip is in continuous physical contact with the surfaces. This contact might be harmful to the sample, and also commonly leads to a relatively quick contamination of the tip. In tapping mode imaging of surfaces, the tip is oscillated above the surface, bringing the tip in and out of contact (or at least in proximity of contacting the surfaces). A shift in the resonant frequency or amplitude of the cantilever's motion is detected in the laser deflection and correlated to changes in topography. Tapping mode minimizes damage to a sample's surfaces. This type of imaging mode is especially important for soft samples, such as biological samples and other polymers.[50] Surface damage and contamination of the sample and/or tip are two of the main challenges for imaging samples by AFM.

The atomic force microscopy techniques can measure forces of interaction and image the topography of samples that are either electrically conductive or insulating.

They do not require the use of a high-vacuum environment for sample analysis, and samples can be scanned in either ambient conditions or under fluids. These properties of AFM are attractive to a wide range of applications, including the investigations of monolayer-modified surfaces.

1.4. Overview of the Thesis

Self-assembled monolayers (SAMs) form spontaneously through the adsorption of surfactant molecules onto surfaces. These adsorbed surfactants form ordered molecular assemblies due to a specific affinity of the molecule's head group to the surfaces. These molecular assemblies are a simple means of modifying the properties of surfaces, which is important in many fields of study.[2-5] The quality of SAMs is determined by both the composition of the assembled molecules and the arrangement of these molecules within the monolayers. This arrangement of molecules includes the spatial distribution and density, as well as tilt angle, of the molecules within the monolayers. Often the molecules assemble into sub-monolayers as surface defects and side reactions can interfere with the assembly process. These defects affect, and limit, the applications of SAMs.

Silicon oxide surfaces have been widely introduced in the construction of biosensors and medical devices.[53] The surfaces of silica can be easily coated with silane-based SAMs. The formation of these SAMs is, however, very sensitive to the reaction conditions. It is challenging to achieve high quality SAMs of silane-based assemblies. In this thesis, the methods for preparing alkylsilane SAMs are reviewed in Chapter 2. In this review, the techniques will be assessed based on their sensitivity to water content, reaction temperatures, and similar parameters. In addition, criteria will be outlined for the reaction conditions that were used in the experiments outlined within this thesis.

The primary aim of this thesis is to assess the quality of silane-based SAMs through the optimization of reaction conditions, while also building upon techniques developed in the Gates group[32] for determining the quality of these monolayers with minimal contribution from adsorbed species. Previous research by the Gates group showed the presence of defects within silane-based monolayers of mono-reactive perfluoroalkylsilanes. This work demonstrated that multiple steps of silane solution deposition and solvent extraction are necessary to minimize the defects and improve the quality of SAMs. The long-term goal of this current research is to develop simple methods for creating silane-based SAMs that can be widely implemented in laboratories world-wide and potentially scaled-up for coating the surfaces of larger substrates. In Chapter 3, a systematic study is presented for assessing the quality of silane-based SAMs as a function of changing the reaction conditions. These conditions include varying the reaction temperature at 20, 40, 60, or 80 °C, as well as altering the solution concentration of reactants (i.e., perfluoroalkylsilanes) from 0.5 to 5 mM, and monitoring the reaction progress over periods of up to 5 h. Water contact angle measurements, spectroscopic ellipsometry measurements, XPS analyses and atomic force microscopy respectively, were used in combination to assess the uniformity of the surface hydrophobicity, monolayer thickness, composition and topography of the assembled monolayers. An important aspect of these analyses is the use of solvent extraction to thoroughly rinse away or remove the physically adsorbed molecules from these surfaces in order to determine the quality of the covalently bound monolayers.

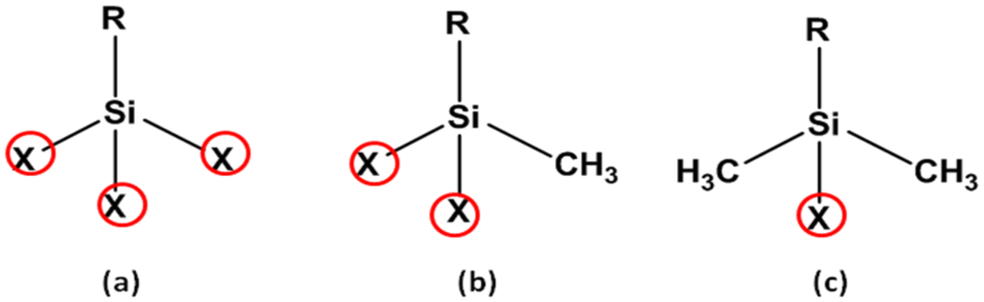
Deposition of high quality alkylsilane-based SAMs can be a time consuming process. Microwave-enhanced processing can speed up the rate of chemical reaction between the silanes and the surfaces being modified. In Chapter 4 of this thesis, research is presented that investigates the systematic use of microwave-assisted deposition of alkylsilane-based SAMs in comparison to the optimized process conditions reported in Chapter 3. One application of high quality alkylsilane-based SAMs is the creation of surfaces that resist the non-specific adsorption of proteins. The hypothesis that the non-specific adsorption of proteins is associated with defects in the monolayers is evaluated in Chapter 5. A final chapter, Chapter 6, reviews the conclusions from these studies and provides an outlook for other methods to improve the quality of alkylsilane-based SAMs, as well as insights into the potential applications of these monolayers.

2. A Review of Methods to Form Alkylsilane-Based SAMs

2.1. Composition of Alkylsilane-Based SAMs

Self-assembled monolayers of alkylsilanes on hydroxylated surfaces and thiols on gold surfaces are two widely studied monolayer systems.[14] In comparison to the thiol-based monolayers, the advantage of alkylsilane monolayers is their thermal stability. The latter are stable to 350 °C.[54] Thus alkylsilane monolayers can be used for moderate to high temperature applications. Potential applications include the use of these SAMs in micro-electromechanical systems (MEMs),[17] and biological devices (e.g., microfluidics and biosensors) that require high temperatures for sterilization.

The general formula of an alkylsilane is $L_1R_{(3-n)}SiX_{(n)}$. The leaving group attached to the silicon head group is denoted as X, which can be a halogen (chloro) or alkoxy (methoxy, ethoxy). The spacer group, L, is typically either a straight alkane chain or a perfluorinated carbon chain. The side chains, R, are also attached to the silicon head group. These side chains are typically methyl groups, chosen for their small size to decrease the lateral dimensions of the alkylsilane when it is assembled in monolayers (Figure 2.1). The commonly used spacer groups are listed in Figure 2.1. Chloro- or alkoxysilanes can be easily hydrolyzed to silanol groups when in contact with water molecules. The number of hydroxyl groups produced by this hydrolysis is equivalent to the number of leaving groups, X. The alkylsilane molecules can be tri-reactive, di-reactive or mono-reactive for molecules with 3, 2, or 1 leaving groups, respectively (Figure 2.1). The most commonly studied alkylsilane molecule is octadecyltrichlorosilane (OTS; $CH_3(CH_2)_{17}$–$SiCl_3$) for its attachment to oxidized surfaces, such as silicon oxides.[55] For this discussion, OTS is used as a model system to understand the process of silanization for alkylsilane-based SAMs on silica substrates.



$X = -Cl,\ -OCH_3,\ -OCH_2CH_3$
$R = -(CH_2)_n-CH_3,\ -(CH_2)_n-NH_2,\ -(CH_2)_n-CN,$
$-(CH_2)_n-CH{=}CH_2,\ -(CH_2)_n-COOCH_3,$
$-(CH_2)_2(CF_2)_n-CF_3$

Figure 2.1. *The drawing represents the general formulas for alkylsilanes. Based on the different leaving groups, X, the alkylsilane can be categorized as a (a) tri-reactive silane; (b) di-reactive silane or (c) mono-reactive silane.*

The accepted mechanism for silanization of surfaces includes three steps (Figure 2.2). In the first step, silane molecules physically adsorb onto the surfaces of the silica substrate, which is hydrated and covered with a film of water at least a few molecules thick. In the second step, the silicon head groups are hydrolyzed to silanol groups, which can bond to the surface silanols and to neighboring alkylsilanes by hydrogen bonding. In the third, and last step water elimination leads to the formation of a polysiloxane network composed of Si-O-Si bonds.[56] The OTS monolayers grow rapidly in the initial stage with an adsorption rate constant, Ka, of $150 M^{-1}s^{-1}$. Large islands of alkylsilanes are formed, which is followed by a slower process of filling in between these islands until achieving maximum coverage. The change in Gibbs free energy, ΔG, is -4.2 kcal/mol, which indicates a thermodynamic stability for the OTS self-assembled onto silica surfaces.[57] The reaction kinetics correlates with the number of reactive sites on the alkylsilane molecules. The tri-reactive and di-reactive alkylsilanes follow 1.5 ± 0.2 order kinetics. This reaction kinetics is due to the interaction of the alkylsilane with both single OH groups on the surfaces and OH groups on other alkylsilanes. There is about a 50% chance of each alkylsilane molecule to interact with either type of hydroxyl group. The mono-reactive alkylsilanes follow first order reaction kinetics.[58] These alkylsilanes either react with one surface OH group or one other alkylsilane molecule, but not both.

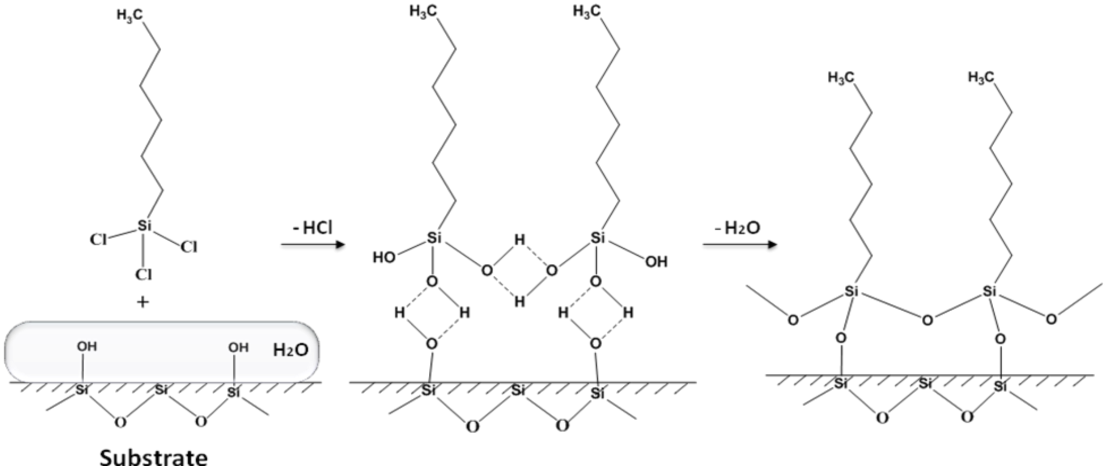


Figure 2.2 *Schematic representation of a mechanism for the reaction of alkylsilanes with surface silanol groups during monolayer formation. A thin layer of absorbed water initially covers the surfaces. The first step is physical adsorption of the alkylsilanes onto the surfaces, followed by hydrolysis of the silane head group to silanol(s), and then the condensation of a polysiloxane with surface silanol groups by forming Si-O-Si bonds.*

Packing density and tilt angle of OTS on silicon oxide surfaces are largely determined by the intermolecular interactions of the OTS molecules. The Si-O bond length of OTS attached to the silicon oxide is 1.6 Å and the O-Si-O bond is non-linear due to the tetrahedral arrangement of atoms around the Si head group. In addition, the distance between the oxygen atoms is less 3.2 Å. The steric hindrance around these surface-bound OTS molecules forces the molecules to adopt a tilt away from the surface normal. However, significant van der Waals interactions exist between the OTS spacer groups such that the carbon chain tilt angle is approaches the surface normal.[59] The influence of the number of reactive groups on the alkylsilane on their tilt within the SAMs can be seen in published studies. In one study, a spacer group of 10 carbons was held consistent for a comparison of SAMs prepared with tri-, di-, and monochloro alkylsilanes. The results of this study indicated the average tilt angles of the SAMs were $10\pm2°$, $35 \pm2°$, and $45\pm3°$, respectively.[60] The large tilt angle of mono-reactive alkylsilanes is probably associated with the steric hindrance of the methyl groups near the reactive end of the alkylsilane, and their proximity to the surfaces of the silicon oxide substrate.[60, 61] These methyl groups, as well as the cross-linked head groups of a di- and tri-reactive silane, can obscure surface hydroxyl groups, leading to the formation of submonolayers.

There are two primary techniques to form SAMs: i) deposition of alkylsilanes from a vapor phase; and ii) deposition of alkylsilanes from a liquid phase. It is particularly challenging to achieve high quality SAMs composed of alkylsilane molecules.[36, 60] The quality of the monolayers varies from laboratory to laboratory. This variance is related to multiple parameters that influence the reaction, such as temperature, surface-adsorbed water, concentration of reactants, solvents (polarity and purity), and cleanliness of substrates. These concerns will be elaborated upon in the following sections.

2.2. Vapor Phase Deposition of Alkylsilanes

Vapor phase delivery of alkylsilanes is a common method for the formation of SAMs.[21, 59, 62] In this process, a substrate is placed into an enclosed chamber and exposed to a partial pressure of volatile precursors. The precursors deposit onto and react with the surfaces of substrate to form a thin film. The pressure in the chamber can be at atmospheric, sub-atmospheric or ultra-high vacuum ($<10^{-6}$Pa) conditions. A low pressure, especially ultra-high vacuum (UHV), is preferred for vapor deposition of SAMs. The decreased pressure can reduce unwanted side reactions (e.g., intermolecular as well as with water molecules) to make high quality SAMs. This method has been used to graft chlorosilanes silica surfaces at high temperatures (e.g., 200 °C).[58] Alkylsilanes with low vapor pressures are not suitable for gas phase deposition. For example, at room temperature conditions, perfluorinated silanes (e.g., $CF_3CH_2CH_2SiCl_3$) can form SAMs, but alkylsilanes (e.g., $CH_3CH_2CH_2SiCl_3$) do not readily form SAMs. The latter require both high temperature (over 400 °C) and a partial vacuum.[62] These high temperatures could remove surface adsorbed water, and decrease surface hydroxyl group concentrations from 5-6 OH/nm^2 at room temperature to 1.4 OH/nm^2.[63] This reaction of volatile alkylsilanes with surface silanols by gas phase conditions is limited and coverage can be reduced by a factor of up to 3 in comparison to OTS delivered to the surfaces by a liquid phase reaction.[64] A volatile nitrogen-containing base can be added to promote silane deposition.[62] In comparison to liquid phase deposition at room temperature, short alkylsilane-based SAMs obtained from the vapor phase at 60-70 °C show higher water contact angles. Monofunctional alkylsilanes are preferable for gas-phase reactions because the tri-reactive or di-reactive alkylsilanes can form oligomers when in contact with water adsorbed onto on the surfaces of the substrates.[65]

Some researchers believe that “the vapor phase method appears to be the cleanest and easiest method to obtain high yield surface modification”.[66] This approach avoids potential solvent interferences and the ultra-high vacuum chamber provides a relatively clean (or at least a more easily controlled) environment. The set-up and maintenance of UHV chambers is more sophisticated and expensive than growth from liquid solutions. Typical vacuum chamber materials and vacuum pumps are easily corroded in the presence of the HCl liberated during the formation of SAMs from alkylsilanes with Cl leaving groups. In addition, the exhaust from these systems must be neutralized as the volatile species are toxic. The deposition time for vapor deposition of alkylsilanes is relatively long, generally requiring overnight reactions.[66]

2.3. Liquid Phase Deposition of Alkylsilanes

In comparison to vapor deposition of alkylsilanes, liquid phase deposition and formation of these SAMs is a much simpler and cost effective method. A clean substrate is immersed into a solution containing the alkylsilane molecules. The substrate is held in the solution for a certain period of time. During this time the monolayers will automatically assemble onto the surfaces of the substrate. The time required for the formation of SAMs varies from 3 min[56] to 24 h[67] according to literature reports. The formation of alkylsilane-based SAMs is very sensitive to the reaction conditions. During the reaction, it is very important to control the cleanliness and water content of the solution, the reaction temperature and similar parameters.[21]

2.3.1. Dependence on Water

Water is an essential ingredient in the formation of alkylsilane-based SAMs. An ultrathin film of surface-adsorbed water forms on silicon oxide substrates. This water layer is required for the hydrolysis of the head groups of the alkylsilanes. If too much water resides on the surfaces of the substrate, the alkylsilanes can polymerize with each other forming an intermolecular network.[65] This polymerization can lead to the displacement of molecules from the surfaces,[68] which may cause the alkylsilanes to pack in a disorderly manner to form mutlilayers extending from the surfaces. A low surface coverage can also be obtained when alkylsilanes form SAMs on fully dried surfaces.[2] Approximately 1 to 1.2 monolayers of surface absorbed water is optimal for the formation of dense, uniformly packed alkylsilane-based monolayers.[69]

The amount of water in solution is crucial for producing high quality alkylsilane-based SAMs. [54, 68] The OTS molecules have three reactive groups. Excess water can result in polymerization of OTS molecules with each other in solution. This polymerization could decrease the relative concentration of unreacted alkylsilane molecules in solution. Similar polymerization has also been observed in alkylsilane molecules with either two or one reactive head group(s).[65] Mono-reactive alkylsilane can, however, only form Si-O-Si bonds with either one other alkylsilane molecule or one silanol group on the reactive surfaces of the substrates.[70] If two mono-reactive alkysilane molecules become covalently linked, these molecules can no longer react with the surfaces of the substrate. The covalently linked mono-reactive alkysilane molecules can physically adsorb onto the substrate's surfaces through hydrogen bonding and block reactive sites. These adsorbed molecules can, however, be removed by heating under vacuum[70] or rinsing with hot solvents.[71] A quantity of 0.15 mg/100 mL of water in the solvent is suggested as the optimal condition for the formation of close packed (and optimal density) OTS monolayers.[48]

Humidity is another issue to be considered in the formation of alkysilane-based SAMs. At a relative humidity of 83%, the alkylsilane can convert to silanol groups completely within 48 h. This hydrolysis did not occur over an 11 day test when the relative humidity was less than 18%.[72] A liquid solution containing alkylsilanes should be stored in a dry, dark and cold environment. For obtaining reproducible and high quality alkysilane-based SAMs, some research indicates that the preparation of these films should be performed in a class 100 clean room.[73]

2.3.2. Dependence on Temperature

Temperature plays an important role in the formation of SAMs. The temperature of a liquid solution can affect both the rate of reaction and solubility of the alkylsilane molecules. Literature precedence indicates that in the formation of SAMs there is an intrinsic relationship between the molecular structure of alkylsilanes and the solution temperature.[68,74] A critical grafting temperature (T_C ~28 ± 5°C) has been reported for OTS. The self-assembly of alkylsilanes includes both physical and chemical processes. The molecules (or hydrolyzed molecules) are adsorbed onto the surfaces and organize themselves relative to each other.[75] These self-assembled molecules then react with the surfaces forming covalent bonds. At T_C, the gas, liquid-expanded (LE) and liquid–condensed (LC) phases coexist in the interface. When preparing alkylsilane-based SAMs below T_C, the monolayers contain a heterogeneous structure. Below Tc, the monolayers contain a nearly pure LC phase, in which the alkylsilane molecules are close-packed and the chains are arranged in an all-trans fashion. Above T_C, both the LE and LC phases coexist. At these elevated temperatures, the coverage of the alkyl chains is monotonically reduced with increasing temperature, which coincides with an increasing conformational disorder.[68, 75]

The value T_C is an intrinsic property of an alkylsilane molecule. It is independent of the solvents used for the formation of SAMs. A linear relationship has been established between T_C and the number of methylene groups in the spacer group of the alkylsilane. An additional 3.5°C is added to Tc for each additional $CH_{2.}$[74] As described before, the trichlorosilyl groups can hydrolyze in solution and react with similar molecules to form condensed polymer. Ideally these hydrolyzed trichlorosilyl groups would react with surface Si-OH groups to form the desired SAMs. A competition exists between these two reactions. The preference for reacting with the surfaces increases with decreasing temperatures. As the temperature decreases, the reaction kinetics decreases as well. The thermal disorder in the monolayers decreases at lower temperatures.[76] An increased chain length of the spacer group can, therefore, increase the temperature at which monolayers can be formed using that particular alkylsilane molecule.

2.3.3. Dependence on Solvent and Concentration

The importance of solution cleanliness and water content has been briefly touched upon in the previous discussions. The solvent's capacity for dissolving water will influence the formation of alkylsilane-based SAMs.[48, 77] For the formation of OTS-based SAMs on silica surfaces, a solvent with very low water content (e.g., n-pentane) cannot supply enough moisture to hydrolyze the silane molecules. This reduced hydrolysis of the alkylsilane molecules produces less alkylsilanols that are needed to react with the surfaces. In contrast, solvents with a high capacity for dissolving water (e.g., 1,4 dioxane) may lead to a rapid formation of alkyltrisilanol molecules that can subsequently polymerize with each other within the solvent.[77] Aromatic solvents (e.g., benzene and toluene) can extract optimal amounts of water from the substrate and the surrounding environment to yield optimal densities for the OTS monolayers. The latter are common solvents for dissolving alkylsilanes.[48]

The concentration of alkylsilane molecules in solution is another important parameter to consider for the formation of SAMs. If the concentration of these reactants is too high, the alkylsilane molecules could polymerize and even form spherical agglomerates.[78] Relatively high concentrations can also lead to the formation of disordered monolayers.[79] To limit this self-polymerization, it is preferred to use a lower solution concentration of alkylsilanes. There does, however, appear to be reasonable agreement that the concentration of alkylsilanes should be slightly above 10^{-5} M for deposition from a liquid phase.[80]

2.4. Summary

Formation of alkylsilane-based SAMs depends upon many different reaction conditions. The ability of the alkylsilanes to uniformly modify the surfaces of a material, such as silicon oxides, is determined by both the composition of the alkylsilane molecules and their arrangement within the monolayers. The general principles for the formation of monolayers using alkylsilane molecules were introduced using OTS as an example. The presence of more than one reactive head group in the alkylsilane molecules and composition of the spacer groups for these molecular chains determine how these molecules will interact with each other and their environment. There are many (although sometimes subtle) differences in the reaction conditions required for the formation of SAMs from specific alkylsilane molecules. The choice of temperature, alkylsilane concentration, and water content of the system each determine the extent of interaction between these molecules, as well as with the reactive surfaces of the substrate. All of these conditions can increase the complexity of forming SAMs composed of alkylsilane molecules. The reproducibility and quality of these SAMs is still a large challenge and varies from laboratory to laboratory. In the following chapter, the quality of SAMs created from mono-reactive perfluoroalkylsilanes by deposition from a toluene solution is investigated for its dependence on processing conditions.

3. Optimizing the Conditions for the Formation of Perfluoroalkylsilane Monolayers*

*This work is reproduced in part from a manuscript submitted to *Langmuir*. I acknowledge Michael C.P. Wang's contributions to XPS data analysis, Xin Zhang's contribution to creation of our ellipsometry model, Him Wai Ng's contribution to AFM imaging and Dr. Byron D. Gates' help with discussions of the results and assistance with the manuscript.

3.1. Improving the Quality of Perfluoroalkylsilane SAMs

In this chapter, we report experimental results of seeking the optimal conditions for the formation of mono-reactive perfluoroalkylsilane-based SAMs. The goal is to develop a simple approach for monolayer assembly over cm-scale substrates that can be widely implemented in other laboratories and potentially scaled-up for coating surfaces of larger substrates. A key factor is to avoid stringent requirements for environmental control during formation of the monolayer. In the molecules of a perfluoroalkylsilane-based SAMs, a part or all of the spacer group is decorated with fluorine atoms (e.g., $CF_3(CF_2)_n(CH_2)_m–SiX_3$). These fluorinated carbons have lower surface energies than hydrocarbons, which results in a reduced adhesive force and a lower friction.[81] Fluoroalkylsilane-based SAMs have been used to decrease friction in microelectromechanical systems (MEMS),[21] to make superhydrophobic surfaces,[82] and to prevent non-specific protein adsorption onto surfaces.[83] A number of prior studies report the formation of perfluoroalkylsilane-based SAMs by vapor phase,[48, 70, 84, 85] which requires a vacuum system and high temperatures. The deposition of these silanes into monolayers from a liquid solution is less expensive and simpler to set up. The latter techniques have been mainly used to form monolayers from tri-reactive fluoroalkylsilanes.[86, 84] The formation of SAMs from mono-reactive fluoroalkylsilanes by liquid-phase techniques is less common in the literature.

The molecule of particular interest for our study is $CF_3(CF_2)_7(CH_2)_2$–$SiCl(CH_3)_2$, 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane ($C_{12}H_{10}ClF_{17}Si$). This choice of molecule is in part for its perfluorinated spacer (or chain). Aside from its properties, such as protein resistance and decreased friction, the molecules assembled within this monolayer can be monitored by a number of surface-sensitive spectroscopic techniques.[68, 81, 85] Measurements from these techniques can create an assessment of the quality of molecular packing within the fluoroalkylsilane-based monolayers. These techniques include water contact angle measurements, spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The results of these studies are used in conjunction with each other to confirm impact of processing conditions on the quality of the SAMs. A key component of this analysis is the use of extensive solvent extraction of these SAMs prior to analyzing these surfaces. Techniques are also pursued in an attempt to 'repair' the defects within these SAMs, such as cleaning oxide surfaces through extensive solvent extraction followed by immersion into a fresh solution of perfluoroalkylsilane molecules. The goal for each of these studies is to achieve a high quality monolayer of mono-reactive perfluoroalkylsilane molecules.

3.2. Methods and Materials

3.2.1. Experimental Section

Preparation of Silicon Oxide Substrates. This study on monolayers of perfluoroalkylsilane-based molecules used a model substrate for assessing the quality that can be achieved for these SAMs. These substrates were single-side polished (100) silicon wafers (Silicon Quest International) with a ~1-nm thick layer of surface oxide determined by spectroscopic ellipsometry. This oxide was cleaned by immersion for 15 min into a freshly prepared piranha solution. The piranha solution was prepared from a 7:2 (v/v) mixture of concentrated sulfuric acid (Anachemia Canada, Inc.) and 30 % (v/v) hydrogen peroxide (VWR International). *CAUTION: Piranha solution is a strong oxidizing agent and reacts violently with organic compounds. This solution should be handled with extreme care.* The piranha solution is used to remove residual organic contaminants from the surfaces of the silicon oxide coated substrate, as well as to decorate the surfaces with hydroxyl groups. The silicon wafer was subsequently rinsed with 18 MΩ•cm water (from a Barnstead Nanopure DIamond Life Science water filtration system), and cut into 1 cm x 1 cm pieces under the flowing water. Each piece of cleaned silicon wafer was further rinsed with 500 mL of 18 MΩ•cm water and dried under a stream of nitrogen gas filtered with a membrane containing <0.2 μm pores.

Preparation of SAMs. The cleaned silicon substrates were coated with monolayers by immersion into a solvent containing dissolved silane molecules. The model silane compound used for these studies was 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane (product #L16582, 90%, Alfa Aesar), which was prepared as 1 mM perfluoroalkylsilane in toluene (product #9466-03, J.T. Baker CMOS grade, distributed by Anachemia Science) in a glass vessel. Variables tested in these studies included temperature of this silane-containing solution and the duration of the assembly process. For example, substrates were heated in solution to 20, 40, 60, or 80 °C for periods of time from 30 min up to 300 min. A total of eight different substrates (each 1 cm x 1 cm in size) coated with SAMs of perfluoroalkylsilanes were prepared in parallel at each temperature. Due to the small size of these substrates, it was important to reduce the number of times each substrate was handled to minimize the potential for contamination. We made a holder of glass rods (~1-mm in diameter) to support up to eight different substrates. Other crucial aspects of mitigating potential contamination sources was rigorous cleaning of the tweezers used to handle the substrates. The tweezers were cleaned by a process of sonication in 18 MΩ•cm water for 3 min, drying under a stream of filtered nitrogen gas, sonication in isopropanol for 3 min, drying with a stream of nitrogen gas, rinsing with 50 mL toluene (CMOS grade), and finally drying under a stream of nitrogen gas. In addition, each silicon piece was consistently handled from the same corner of the square substrate.

Solvent Extraction of SAMs. Monolayer-coated substrates were analyzed for the ratio between silane molecules within the monolayers that were covalently linked to the substrates to those physically adsorbed onto the SAMs. Although every substrate was rinsed in excess with fresh toluene following the formation of the monolayer, many silane molecules could remain physically adhered to the substrate.[68] These physically adsorbed molecules were removed by solvent extraction with a Soxhlet extractor. This extractor was capped with a water-cooled condenser and fitted with a 250 mL flat bottom flask containing ~150 mL of toluene. Heating toluene to >110 °C created vapors that condensed and continuously rinsed the monolayer-coated silicon substrates. Each substrate was extracted with toluene for 1 h, removing physically adsorbed silane molecules and exposing unreacted sites on the silicon substrate. The extracted substrates were dried under a stream of filtered nitrogen gas prior to further analysis. Both the oxide coating on the silicon substrates and the SAMs were analyzed by water contact angle measurements, spectroscopic ellipsometry, and X-ray photoelectron spectroscopy (XPS).

3.2.2. Characterization of SAMs

Water Contact Angle Measurements. Hydrophobicity of the substrates was determined by static water contact angle measurements performed at room temperature using a digital AST Optima contact angle system equipped with a horizontal light beam. Droplets of 18 MΩ•cm water (averaging 2.0±0.3 μL per droplet) were dispensed onto the substrates. Advancing contact angle measurements were acquired by adding another droplet onto the initial droplet. This process was repeated at least 5 times for a total of ~10 μL per analyzed area. In addition, at least three different positions—each chosen randomly—were analyzed for all of the substrates.

Spectroscopic Ellipsometry Measurements. The thicknesses of both the oxide on the silicon substrate and the assembled monolayer were determined by spectroscopic ellipsometry. Samples were analyzed using a Jobin-Yvon UVISEL NIR variable angle spectroscopic ellipsometer equipped with a 75 W Xenon lamp held at an incident angle of 70° to the substrate. To fit the data, a two layer model was constructed using DeltaPsi2 software. In this software, “C_Si_isa. Ref” is chosen to represent the silicon substrate layer. For the top layer of model, the refractive index of the silicon oxide layer was set to 1.46 and that of our silane molecule (1H,1H,2H,2H-perfluorodecyldimethylchlorosilane) was set to 1.34 in accordance with literature precedence. [40,55, 87,60] Thicknesses of these thin films were calculated using the dielectric response at 630 nm. A minimum of four different positions were measured for each substrate, and data from at least three substrates were combined for each data point.

X-ray Photoelectron Spectroscopy Measurements. Chemical composition and density of the assembled perfluoroalkylsilane molecules were investigated by XPS. These studies were conducted using a Kratos Analytical Axis ULTRA DLD system with a monochromatic aluminum source (AlKα of 1486.7 eV) operating at 150 W. At least three regions of each sample were analyzed by acquired photoelectrons over an area of 700 μm x 300 μm. Survey scans (0 to 1200 eV) were acquired using a pass energy of 160 eV and a dwell time of 100 ms. High resolution spectra (0.05 eV spectral resolution) were obtained using a pass energy of 20 eV and a dwell time of 1000 ms. The XPS peak centered at 685 eV is associated with F1s. This peak was used to determine the quantity of silane-based monolayers on the substrate. The XPS peak centered at 99 eV is associated with Si2p3/2, which was used as the internal standard to normalize the F signal between different substrates. (Note that the silicon oxide coating was maintained at a thickness of ~1.66 nm for all substrates.) Each integrated peak area, such as for F1s or Si2p3/2, was divided by the respective relative sensitivity factor for the associated element. The relative tilt of silane molecules within the monolayers were determined by analysis of the high resolution C1s peaks. The details of these analyses are discussed in further detail within the results and discussion section.

Atomic Force Microscopy Measurements. Atomic force microscopy (AFM) images were acquired in AC mode using silicon cantilevers from VistaProbes (#T300-25) and a scan speed of 0.50 MHz using an MFP3D AFM (Asylum Research). Data analysis of the topographic images was performed using Igor.

3.3. Optimizing the Conditions for Self-Assembly of Perfluoroalkylsilane-Based Monolayers

3.3.1. The Choice of Temperature Based on WCA, Ellipsometry and XPS Measurements

The primary goal for the work discussed herein is to optimize the conditions in which monochloro perfluoroalkylsilanes are assembled into monolayers on silicon oxide coated silicon substrates. Considerations for the development of these refined methods include the ease of scaling the techniques to form SAMs over large areas and the ability to avoid stringent requirements for environmental control during the growth of the monolayers. A potentially major contribution to defects in SAMs of monochloro perfluoroalkylsilanes is the surface adsorption of molecules reacted in an intermolecular manner or misoriented relative to the silane molecules that are covalently bound to the surface oxides. Our work pursues a variety of techniques for removing and/or minimizing these types of defects. One of these methods is to increase the temperature of the solution during growth of the SAMs. An increase in solution temperature should lead to an increased solubility of the perfluoroalkylsilanes in the solvent, as well as an increased mass transport of these molecules to and from the surfaces of the oxides.[36, 88]

The quality of SAMs created from monochloro perfluoroalkylsilanes was determined for samples prepared at temperatures ranging from 20 to 80 °C. This quality is measured as a function of the ability of SAMs to modify the properties of surfaces, as well as by the thickness and packing density of the monolayers. One of the simplest measures of a change in surface properties resulting from the formation of SAMs is hydrophobicity of the surfaces as determined by a change in the water contact angle. An essential component to assessing the uniformity of SAMs is to measure the surface properties without the presence of physically adsorbed molecules.[88] Although all substrates are washed in excess with fresh toluene following the formation of the monolayer, many molecules remain physically adsorbed onto the surfaces. We have previously demonstrated the importance of solvent extraction at elevated temperatures to remove these physically adsorbed molecules from the SAMs.[32] All substrates were extracted with toluene using a Soxhlet extractor prior to assessing the properties of the modified surfaces.

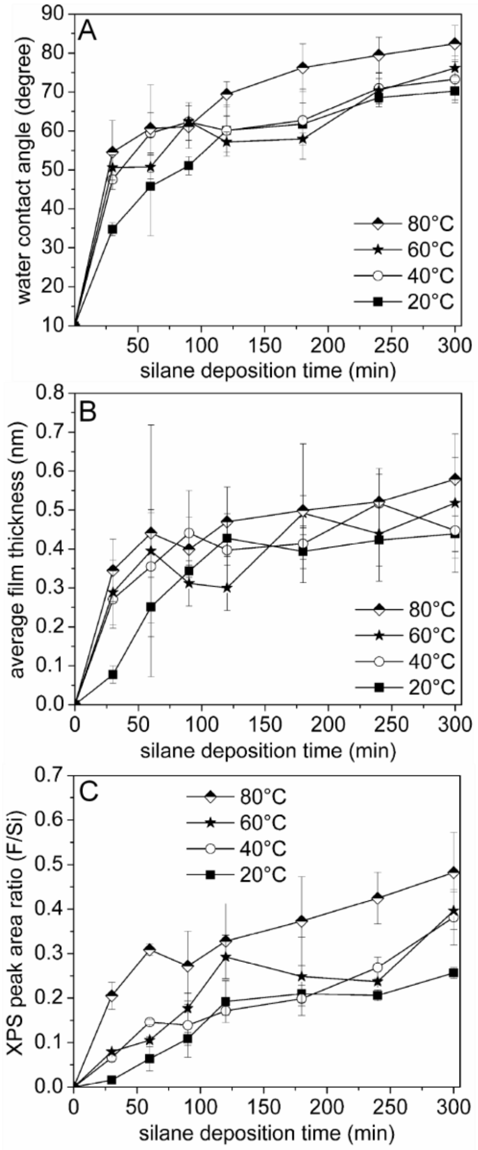


Figure 3.1. *(A) Water contact angle measurements, (B) thickness from spectroscopic ellipsometry measurements, and (C) normalized X-ray photoelectron spectroscopy (XPS) peak areas for F1s recorded at different time intervals during the formation of perfluoroalkylsilane monolayers on silicon oxide surfaces. Data is reported for the formation of SAMs at 20, 40, 60, and 80°C over a period of 5 h. All surfaces were rinsed by solvent extraction prior to analysis. The normalized peak area for XPS data is determined from the ratio of integrated peak areas for F1s to Si2p, each divided by its respective relative sensitivity factor.*

For reasons of clarity, only the trends for samples treated at 20 and 80 °C are included in Figure 3.2 to demonstrate the influence of temperature on the formation of 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane based SAMs.

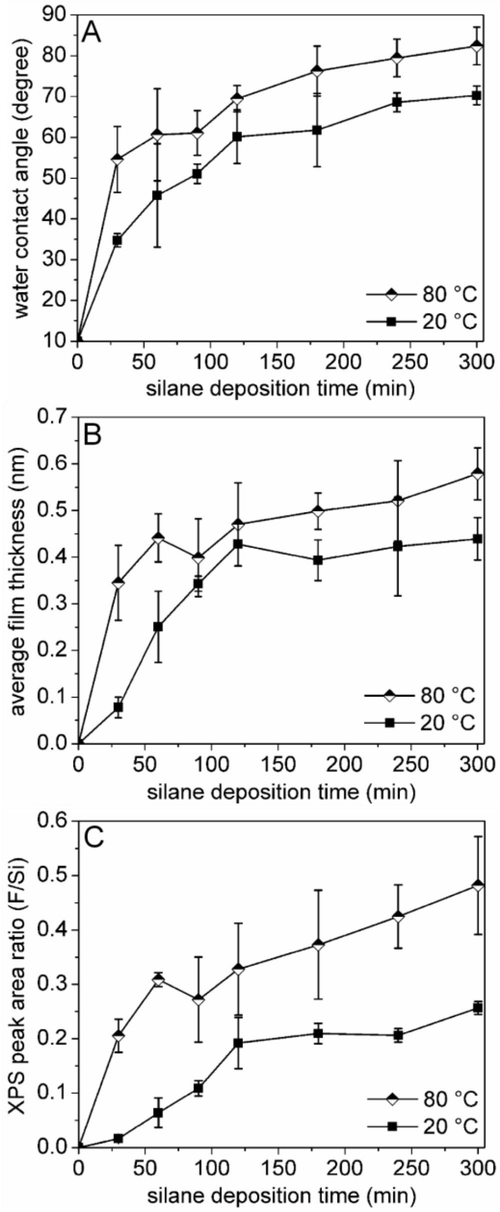


Figure 3.2. *(A) Water contact angle measurements, (B) thickness from spectroscopic ellipsometry measurements, and (C) normalized X-ray photoelectron spectroscopy (XPS) peak area for F1s recorded at different time intervals during the self-assembly of perfluoroalkylsilane monolayers on single crystalline silicon wafers at 20 and 80 °C over a period of 5 h. All data is reported for substrates that have been treated with solvent extraction. The normalized peak area for XPS data is determined from the ratio of integrated peak areas for F1s to Si2p, each divided by its respective relative sensitivity factor.*

The water contact angle was measured after specific periods of time allowed for the growth of the monolayers. Some samples were immersed into a solution of perfluoroalkylsilane for 30 min, while others were immersed continuously for periods up to 5 h (Figure 3.1). All samples were washed by toluene extraction immediately after the period of time allowed for monolayer assembly. A significant difference is observed between SAMs formed on the surfaces of polished silicon wafers at 20 and 80°C. The water contact angles for the monolayers assembled at 80 °C are larger than those formed at 20 °C for all reaction times up to 5 h (Figure 3.2 A). Each data point in the water contact angle measurements study is an average of fifteen independent advancing contact angle measurements. Measurements were taken from at least three separate regions of each sample using 2 μL droplets of water for each measurement. The associated error bars are derived from the standard deviation of these measurements. Samples treated at 20 and 80 °C followed similar trends in their water contact angles. The water contact angle increases steeply after 30 min of monolayer assembly, and continues to increase (for both 20 and 80 °C) at a reduced but steady rate. The highest obtained water contact angles for all reaction temperatures studied here are less than 90 degrees. These relatively low contact angles are attributed to the low packing density of the perfluoroalkylsilanes in the SAMs. This could be partially attributed to the relatively short periods of time given to assembly of the monolayers, in comparison to the time required for the formation of high quality SAMs of alkanethiolates on gold surfaces.[89, 90] The water contact angle measurements are simple to perform, but ultimately limited in their ability to assess the quality of the SAMs.

Spectroscopic ellipsometry has been widely used to measure the thickness of SAMs.[40, 87,60] This technique is used to evaluate the thickness of the SAMs obtained at various temperatures and times of monolayer formation. Thickness of the perfluoroalkylsilane monolayers increases with both temperature and extended time of immersion in the 1 mM silane solution (Figure 3.2 B). A two layer model of the spectroscopic ellipsometry data accounts for the underlying silicon oxide layer and the monolayer of perfluoroalkylsilane molecules. This two layer model is important in order to account for variations in the thickness of either layer both within and between samples. The thickness of the silicon oxide layer was ~1.66±0.03 nm for the polished silicon wafers after cleaning with the piranha solution as described in the experimental section. The observed trends at 80 °C closely match those at 20 °C, but the maximum achieved thickness of the monolayers at both temperatures is less than 1.0 nm after 5 h of reaction. The calculated thickness for each data point in both samples is an average of twelve independent measurements. The reported length of the perfluoroalkylsilane molecule used in these studies is 1.34 nm.[15] Thickness of the monolayer will approach, but not reach, this value. The molecules bound to the surface tilt away from the surface normal, decreasing the maximum achievable thickness of the monolayer. In addition, a sub-monolayer will have an even smaller average thickness.

Thickness of the SAMs produced in these studies are less than those reported in the literature for monolayers assembled from similar molecules.[40,84] The difference is partially attributed to the fact that data reported in Figure 3.2B, unlike most data reported in literature, are for samples that have been extracted with toluene to remove physically adsorbed species. A decrease in the average thickness of the monolayers is observed upon removal of these adsorbed molecules.[91,32] The monolayer thickness did, however, increase when the temperature of the reaction was increased from 20 to 80 °C. Higher temperatures improve the probability that the physically adsorbed molecules (silane or solvent molecules) are removed from the monolayers and the silicon oxide surfaces exposing the underlying substrate during the molecular assembly process. This improved cleaning of the surfaces opens blocked reactive sites on the oxides during the reaction. These exposed reactive sites can react with other silane molecules, improving the overall density and thickness of the monolayers at elevated reaction temperatures. The monolayers formed at the higher reaction temperature are, however, thinner than anticipated for a complete monolayer. Although relatively short periods of time were pursued for the formation of these monolayers, another contributing factor to the formation of sub-monolayers could be the presence of elemental contaminants that interacts more strongly with the reactive sites on the silicon substrates, such as metals, metal ions, or other impurities.

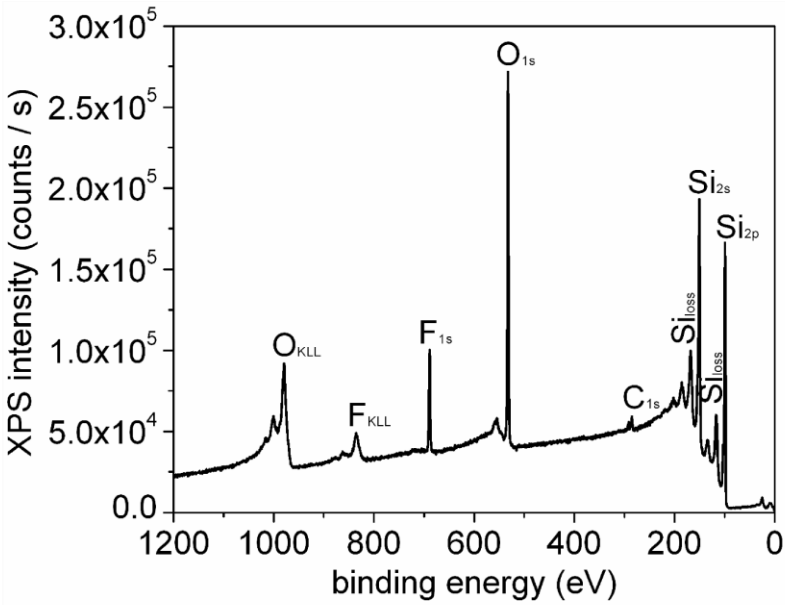


Figure 3.3. *Typical XPS survey scan for a single crystalline silicon substrate that has a thin silicon oxide surface coated with self-assembled monolayers (SAMs) of mono-reactive perfluoroalkylsilane molecules.*

We inspected the composition of the SAMs by X-ray photoelectron spectroscopy. This spectroscopic technique detected the presence of F, Si, C, and O in the samples. A typical XPS spectrum is provided in Figure 3.3. No impurities were detected by XPS. The XPS analysis did confirm that the observed trends in thickness and hydrophobicity of the SAMs do correlate to an increased density of perfluoroalkylsilane coverage on the oxidized substrates. A quantitative analysis of fluorine on the silicon oxide surfaces demonstrates an increased surface coverage of the SAMs with increasing thickness and surface hydrophobicity. In order to minimize instrument variation from run to run, this data was normalized to the silicon content of the substrate. In addition, this analysis also accounted for atomic variations in the observed XPS signals by dividing both the Si and F signal by their respective relative sensitivity factor (RSF).[92] A ratio of the resulting integrated areas for the F1s to the Si2p peaks is depicted in Figure 3.2 C. These trends closely match those observed for thickness and water contact angle measurements as a function of both time and temperature.

The XPS analysis indicates that the perfluoroalkylsilane density on the silicon substrates (or the total number of molecules per area analyzed on the substrate) increases more rapidly at 80 °C than at 20 °C. It also suggests that the monolayers assembled at a higher temperature are either denser or have more surface coverage than those assembled at lower temperatures. For example, after 5 h of reaction time at 20 °C the surface coverage of perfluoroalkylsilane molecules reaches only 49% of the surface coverage achieved for reactions at 80 °C. This conclusion is limited to the mono-reactive silane molecule that is being studied here. Some reports of alkylsilane deposition conclude that a lower temperature is preferential for higher quality SAMs.[56] Others report that higher temperatures promote a more continuous surface coverage, but also introduce disorder into the monolayers.[80] Some of these previous observations are most likely due to the fact that the molecules being studied were alkylsilanes with two or three good leaving groups. In some of these previous studies an increase in the reaction rate lead to an increased cross-linking between these molecules, and poorer quality monolayers. In the case of a mono-reactive silane, such as the one studied herein, the molecule will either react in an intermolecular manner or with reactive groups on the silicon surfaces, but will not form covalent bonds with both other molecules in solution and the oxidized substrate. Another interesting observation is that the XPS analysis (Figure 3.2 C) depicts a larger difference in properties between the monolayers grown at 20 and 80 °C than that observed for the other analysis techniques (Figures 3.2 A and 3.2 B). This difference can be attributed to the molecular arrangement within the SAMs. An alkylsilane molecule covalently linked to the oxide can partially cover neighboring regions of the substrate.[86] One example is the molecular interaction (e.g., through van der Waals forces) of neighboring silane molecules within the monolayer to block reactive sites on the surfaces.[92] This intermolecular interaction within the SAMs could lead to the observation that SAMs with significantly different packing density could have similar hydrophobic properties and calculated thicknesses. This discrepancy is observed when comparing the XPS, water contact angle, and ellipsometry data for samples prepared at 20 and 80 °C. These results further emphasize the need to use multiple techniques to properly assess the quality of SAMs.

A comparison of the trends in Figure 3.2 depicts a steady increase in thickness and packing density of the perfluoroalkylsilane molecules forming the monolayers. The associated error bars indicate a large variation for some data points, which can be attributed to the variability observed between different regions of a sample, as well as between samples. These variations could be due to differences in the density of the reactive hydroxyl groups on the substrates. The silicon substrates are treated with a piranha solution to remove organic contaminants and to form hydroxyl groups on the silicon oxide surfaces, but the uniformity of the surface oxide can vary between substrates. Molecular-scale variations can arise from non-uniformities in the polishing and handling of the silicon wafers. Attempts were made to minimize damage to the substrates from sample handling as described in the experimental section. The overall trends for the data depicted in Figure 3.2 indicate an improvement in the packing of molecules in the SAMs with increased time and temperature. This system provides a sufficient model to understand the impact on quality of the SAMs for further modifications to the procedures used to form the monolayers.

In addition to reaction time, temperature during the growth of a monolayer also plays an important role in determining the quality of the SAMs. For the perfluoroalkylsilane molecules studied here, an increase in temperature improves the quality of the monolayers. This improved quality could be attributed to an increased solubility of both silane molecules and water in the toluene at higher temperatures.[93] An increased water content could improve condensation of the perfluoroalkylsilane molecules with the oxide surfaces, or assist in the hydrolysis of dissolved perfluoroalkylsilane molecules. Water content was minimized during these reactions, but was not rigorously controlled as our aim was to develop a process that can be easily implemented in other laboratories. The other contributing factor could be the increased solubility and mass transport—both to and from the silicon oxide surfaces—of the perfluoroalkylsilane molecules in the toluene at higher temperatures. This change in mass transport could, however, be insufficient for achieving an optimal packing of the molecules into the monolayer. Aside from an increase in temperature to assist with dissolution of the adsorbed silane molecules, another method of effectively removing physically adsorbed molecules is through the assistance of solvent extraction.

3.3.2. Solvent Extraction Affects the Quality of SAMs

We have previously demonstrated that solvent extraction is important for assessing the nature of the molecules within SAMs that are covalently linked to a surface.[32] It is, however, unclear from this prior work if solvent extraction could be utilized to assist in improving the packing of the molecules into the monolayers through removal of physically adsorbed species. Substrates were immersed into solutions of 1 mM perfluoroalkylsilane in toluene at both 20 and 80 °C. After regular intervals of time, each substrate was removed from this solution and rinsed with toluene in a Soxhlet extractor to remove adsorbed silane molecules from the surfaces of the silicon oxides. These thoroughly rinsed substrates were immersed into a fresh solution of perfluoroalkylsilane at either 20 or 80 °C for further growth of the monolayers. Monolayers grown in this step-wise fashion were analyzed by water contact angle measurements, spectroscopic ellipsometry, and XPS both before and after solvent extraction (Figure 3.5). For better understanding the notation in Figure 3.5, this schematic drawing demonstrates the procedure for multiple silane depositions and solvent extractions.

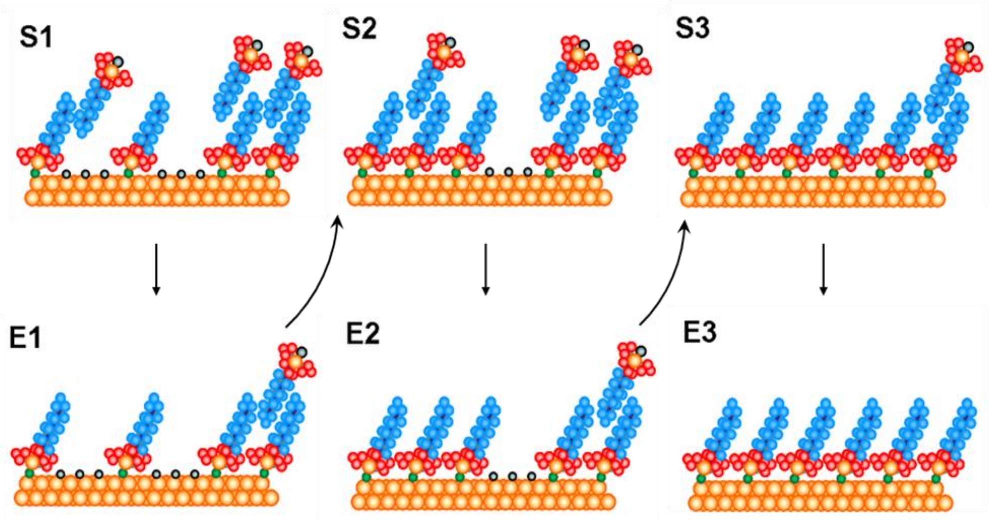


Figure 3.4. *Schematic illustration depicting the procedure for multiple silane depositions and solvent extractions. 'S' denotes silane deposition and 'E' solvent extraction. A sample associated with silane deposition without solvent extraction is referred to as S1. This sample that is subsequently treated by solvent extraction is referred to as E1. If the E1 sample is subsequently immersed into a silane solution for further deposition of silane molecules, the sample is denoted as S2. Each step of silane deposition used a freshly prepared solution of mono-reactive silanes in toluene.*

Notations are assigned to each sample according to what processing has been performed on that sample. For example, those samples associated with silane deposition (and no solvent extraction) for 30 min are referred to as S1. Samples that were subsequently treated by solvent extraction are referred to as E1. Increasing integers after the ‘S’ and ‘E’ notation indicate progressive processing steps in this series of monolayer assembly and solvent extraction. One limitation of these measurements is that the water contact angle measurements could cause irreversible damage to the substrates.[94] To avoid this potential biasing of the results, separate samples were prepared for each set of measurements needed to create the plots in Figure 3.5. The sample S1 is a different sample from E1, and is a different sample from S2, and so forth. For example, the sample prepared for S2 has been processed by an initial deposition of silane molecules for 30 min, solvent extraction with toluene for 1 h, and a second step of silane deposition for another 60 min. In this manner, we prepared a series of samples with silane deposited over periods of time up to 5 h, but with the addition of solvent extraction steps at key periods throughout this process.

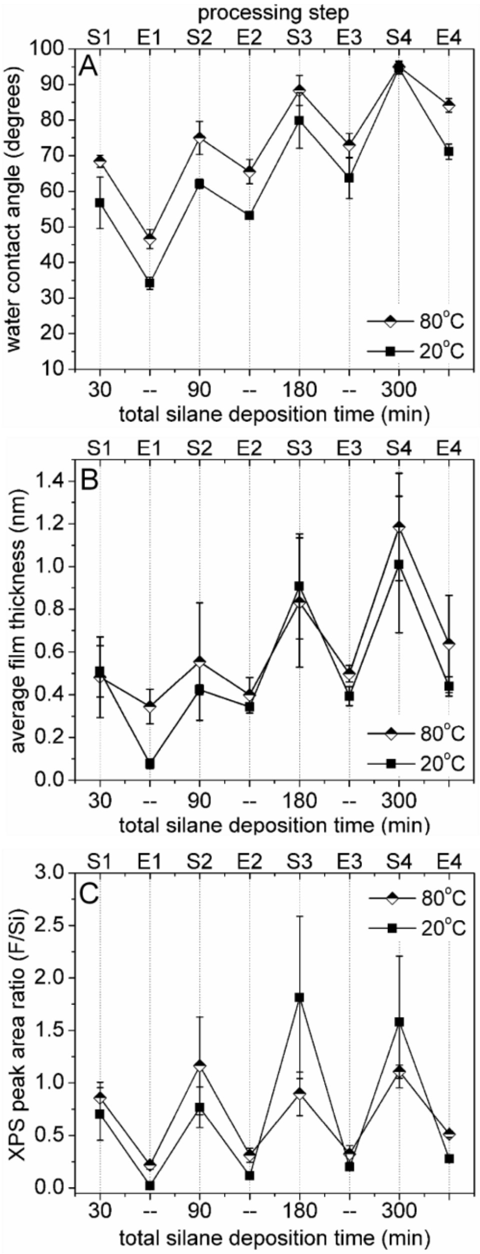


Figure 3.5. *Quality of perfluoroalkylsilane based SAMs as assessed by (A) hydrophobicity of the monolayer, (B) thickness of the monolayer, and (C) surface coverage of the assembled molecules relative to the underlying Si substrate. Results are reported for their dependence on temperature (plotted for 20 and 80 °C) and processing conditions (i.e., either for as-deposited silane molecules, Sn, or solvent extraction of these monolayer coated substrates, En, where n are integers associated with successive processing steps) over a period of up to 5 h. Error bars for each data point indicate one standard deviation for results averaged over at least nine distinct regions from a total of three different substrates.*

The differences observed in the results for the step-wise growth of SAMs (Figure 3.5) highlight the importance of washing the samples by extracting with toluene. All samples analyzed directly after silane deposition, and before solvent extraction, incorrectly indicated a thicker, more hydrophobic, and denser monolayer than what is in reality covalently linked to the oxide surfaces. Significant changes in the measured values are observed for all the samples after solvent extraction, indicating the removal of a large number of non-covalently bound molecules. The physically adsorbed perfluoroalkylsilane molecules (including dimerized silane molecules) are retained on these surfaces through non-covalent interactions with the silicon oxide, as well as with molecules that are covalently attached to the oxides. Further assembly of silane molecules into the monolayer after each step of solvent extraction increases the density of the monolayer, but also promotes further non-covalent interactions with adsorbing silane molecules. Hence the measurements for these samples produce a larger signal (e.g., average monolayer thickness) than the samples rinsed by extraction with toluene. The error bars associated with the ‘S’ samples are also—for the majority of the data points—larger than those for the ‘E’ samples because of the variability in thickness or density of the adsorbed silane molecules between different regions of each sample.

An increase in processing temperature, the sequential steps of solvent extraction, and further steps of silane deposition all lead to a higher quality monolayer. The data in Figure 3.5 depict a significant increase in thickness and density of the monolayer for samples processed at 80 °C in comparison to those processed at 20 °C. The differences within these trends for samples prepared by the step-wise growth procedure contain further confirmation that higher temperature is important for reducing the amount of adsorbed perfluoroalkylsilane molecules on the surfaces. The relative magnitude of change between the ‘as-deposited’ or ‘S’ samples and the ‘extracted’ or ‘E’ samples is similar for the water contact angle and thickness measurements. The trend for the ‘S’ and ‘E’ samples is, however, different for the XPS analysis of samples treated at 20 and 80 °C (Figure 3.5C). The magnitude of change in the XPS peak area between the ‘S’ and ‘E’ samples is less for the samples treated at 80 °C than it is for samples held at 20 °C. The observed difference in trends is attributed to a decreased amount of the adsorbed perfluoroalkylsilane molecules on the oxide surfaces at 80 °C. Heating the samples to 80 °C increases the efficiency of desorption and diffusion of physically adsorbed molecules from blocked reactive sites on the oxide surfaces during assembly of the monolayer. Similar to the previous studies (Figure 3.2), an increased density of the SAMs is observed for samples grown at elevated temperatures.

The trend observed for samples prepared by the non-stop growth of SAMs (Figure 3.2) is almost identical to that for the step-wise growth reported in Figure 3.5. This similarity is more apparent when overlapping the data points for these two experiments (Figure 3.6). The data closely match in their relative signal intensities for samples treated at either 20 or 80 °C. There is a slight variation between the two types of experiments as observed in the differences for some data points and their associated error bars. In fact, there is only a 4% difference at either temperature between the results achieved for the non-stop and step-wise growth of SAMs after a reaction time of 5 h. This difference is within the experimental error observed for these measurements. The step-wise growth requires many more processing steps than for a non-stop growth of SAMs without significantly improving the rate of monolayer formation. This observation is attributed to the fact that the formation of SAMs is a dynamic process that is controlled by molecular diffusion to and from the substrate surfaces. Removing the adsorbed silane molecules from unreacted sites by solvent extraction is not sufficient to promote enhanced growth of the SAMs. The forces present during the monolayer formation are sufficient to drive the assembly process. A comparison of the results for all samples treated at 20 °C suggests that these forces are also adequate to remove at least some of the physically adsorbed molecules that block reactive sites on the oxidized surfaces. The major contributions to the differences observed between the samples treated at 20 and 80 °C (e.g., nearly twice the density of silane molecules at 80 °C in comparison to 20 °C, as mentioned above) are an increased mass transport of perfluoroalkylsilane in solution and an increased rate of condensation of the silane with exposed hydroxyl groups on the surfaces. These dynamics could be related to multiple factors, including the removal of water from the surfaces in addition to dissolution of the physically adsorbed silanes, increased water concentration in the toluene, and achieving the necessary orientation for the silane molecules for reaction with the silicon oxide surfaces.

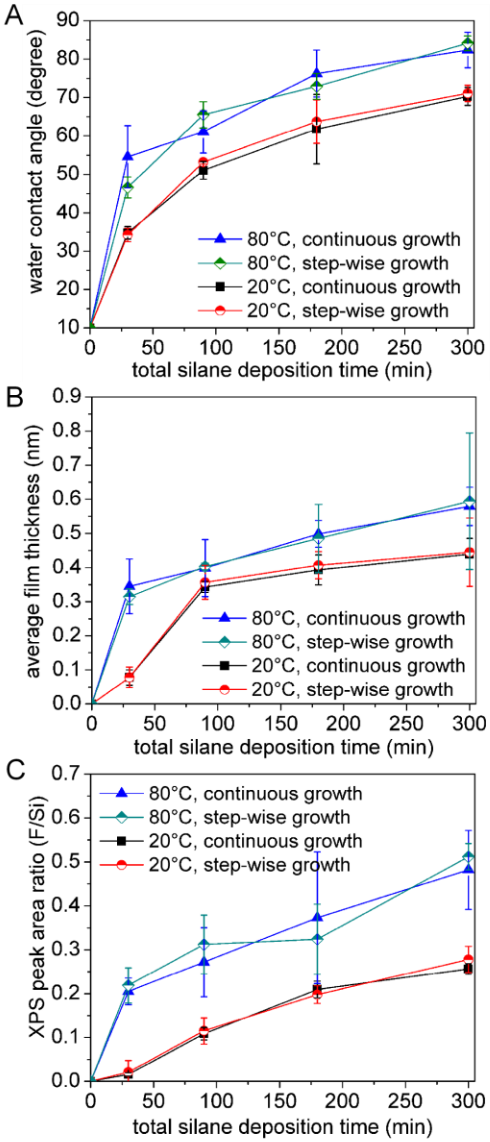


Figure 3.6. *A comparison of monolayers prepared from the self-assembly of perfluoroalkylsilane molecules onto silicon oxide surfaces at 20 and 80°C over a period of 5 h using either a process of continuous growth of the monolayers or stages of growth followed by solvent extraction and further growth of the monolayers. (A) Water contact angle measurements, (B) thickness from spectroscopic ellipsometry measurements, and (C) normalized XPS peak area for F1s recorded at different time intervals during the monolayer formation. All data is reported for samples treated with solvent extraction. Normalized peak area for the XPS data is determined from the ratio of integrated peak areas for F1s to Si2p, each divided by its respective relative sensitivity factor.*

3.3.3. The Choice of Concentration Based on WCA, Ellipsometry and XPS Measurements

Another important aspect of creating high quality SAMs of perfluoroalkylsilanes is the concentration of silane molecules in solution. The density of molecules within the SAMs will be insufficient to protect the surfaces from subsequent chemical attack if the concentration of perfluoroalkylsilane molecules in solution is too low. Alternatively, if the concentration of perfluoroalkylsilane molecules in solution is too high, intermolecular condensation of these molecules will compete with the growth of SAMs on the oxides. For the monochloro perfluoroalkylsilanes used in these studies, the most likely by-product from this reaction would be perfluoroalkylsilane dimers that could also physically adsorb onto the oxide surfaces. Concentrations of monochloro perfluoroalkylsilanes from 0.5 to 5 mM were analyzed for their ability to form high quality SAMs. These monolayers were assembled for 3 h at 80 °C in toluene and analyzed following the initial formation of the SAMs, as well as after solvent extraction for 1 h with a fresh solution of toluene.

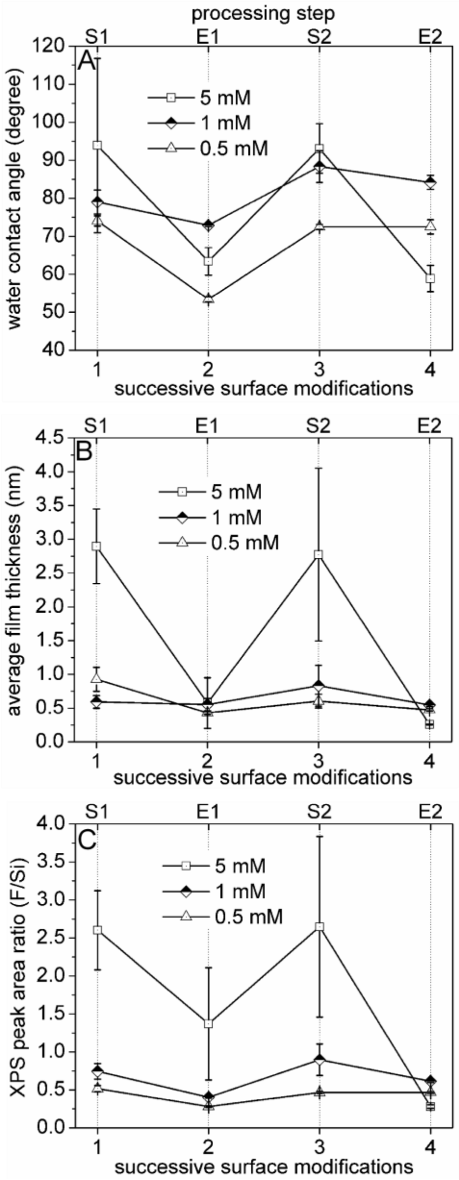


Figure 3.7 *Quality of the SAMs as a function of concentration of the mono-reactive perfluoroalkylsilane molecules in solution. These plots depict trends in (A) hydrophobicity as measured by water contact angle, (B) thickness of the monolayers as predicted by spectroscopic ellipsometry, and (C) average surface coverage of the monolayers as predicted by XPS. The quality is assessed for substrates subject to a repetitive process of surface treatment by silane deposition (Sn) for 3 h at 80 °C and subsequent solvent extraction (En) for 1 h with toluene.*

The most hydrophobic samples were those prepared from a solution of 5 mM perfluoroalkylsilane, but upon solvent extraction the hydrophobicity of these monolayers decreased significantly (Figure 3.7A). The most hydrophobic SAMs following the solvent extraction step were those prepared from 1 mM perfluoroalkylsilane. The next highest quality monolayers were those prepared from a solution of 0.5 mM perfluoroalkylsilane. A similar trend in quality of the SAMs is observed by comparing their average film thickness. Before solvent extraction, the highest concentration of perfluoroalkylsilane appears to make the thickest monolayer (Figure 3.7B). After the final step of solvent extraction, this sample had an average monolayer thickness below that observed for samples prepared from 1 and 0.5 mM perfluoroalkylsilane. The monolayers with the highest average thickness after two steps of both silane deposition (S1 and S2) and solvent extraction (E1 and E2) were those prepared at 1 mM perfluoroalkylsilane. Samples prepared from a solution of 5 mM perfluoroalkylsilane were likely inhibited in the formation of the monolayers because of a large number of physically adsorbed molecules (e.g., silanes reacted through an intermolecular manner, or misoriented silanes) blocking the reactive sites on the oxide surfaces. Those samples prepared from a concentration of 0.5 mM silane had an average thickness between that of the samples assembled from 1 and 5 mM perfluoroalkylsilane. The trends observed for the XPS analysis, plotted as a function of processing conditions and surface modification step (Figure 3.7C), further confirm the assessment that the monolayers prepared from 1 mM perfluoroalkylsilane are the highest quality. Samples prepared from 5 mM silane initially appear to be the highest quality SAMs, but the large error bars associated with these samples and their low water contact angles suggest that these E1 samples contain a large quantity of physically adsorbed molecules. The SAMs prepared from 1 mM perfluoroalkylsilane following two steps of silane deposition and growth (E2 sample) gives the highest ratio of F to Si by XPS analysis for all the samples. These results suggest that the monolayers assembled from a solution of 1 mM perfluoroalkylsilane are the densest SAMs prepared in these studies.

3.3.4. SAMs Packing Quality Based on High Resolution C1s XPS

The properties of monolayers discussed so far provide information on their hydrophobic properties, thickness and relative monolayer density. Further analysis can provide insight into the quality of the molecular packing within these monolayers. High resolution XPS spectra contain detailed information on the chemical environments and covalent interactions of the perfluoroalkylsilanes with the silicon oxide surfaces. For example, the XPS C1s peaks contain quantitative information on the C-C, C-F, C-Si, and C-O bonding present in the samples (Figure 3.8A). The carbon binding energies associated with CF_3 (294 eV) are higher than those of C-C (284.6 eV) and C-Si (283 eV) because the fluorine pulls electron density from the C, increasing the electrons' binding energies of the associated C.[84] The observed shift in binding energies and the relative peak areas contain information about the arrangement of molecules within the monolayers.

The relative intensities of the high resolution XPS C1s peaks confirm the previous observations that a significant amount of perfluoroalkylsilane molecules are removed by solvent extraction. The C1s peaks associated with a monolayer assembled at 20 °C for 5 h (Figure 3.8A) significantly decrease upon solvent extraction (Figure 3.8 B). The XPS peaks associated with C bound to F (e.g., CF_3 and CF_2-CF_2) decreased by almost two thirds from the original peak intensity. Adsorbed molecules are also removed from the monolayers prepared at 80 °C for 5 h, but the relative decrease in peak intensity was approximately one third that of the original intensity (Figures 3.7C and D, respectively). In addition, the relative intensity of the XPS peaks for C bound to F are higher for samples prepared at 80 °C in contrast to monolayers assembled at 20 °C. These results are consistent with the previous XPS analysis of similar samples, confirming that more perfluoroalkylsilane molecules are bound to the oxide surfaces at 80 °C than when prepared at lower temperatures. Further analysis of this data reveals information on the orientation of perfluoroalkylsilane molecules within the monolayers.

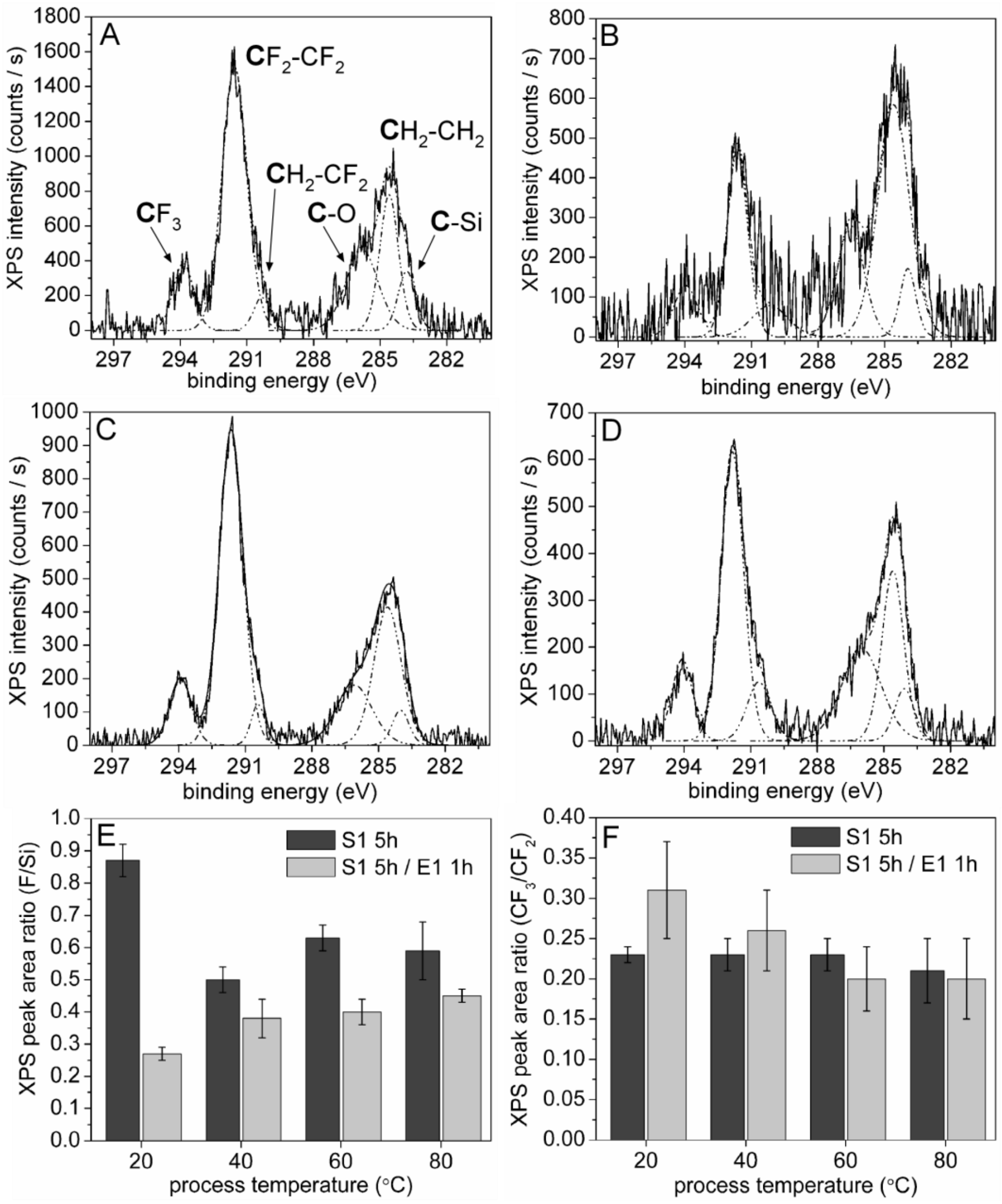


Figure 3.8. *High resolution C1s XPS results for SAMs assembled from a solution of 1 mM perfluoroalkylsilanes (A) after 3 h at 20 °C and (B) solvent extracted for 1 h, or (C) after 3 h at 80 °C and (D) solvent extracted for 1 h. (E) A plot summarizing the relative surface coverage of the perfluoroalkylsilane molecules measured by the integrated XPS peak areas for F1s and Si2p as a function of process temperature for monolayers deposited for 5 h (S1), as well as for substrates subsequently treated with solvent extraction for 1 h (E1). (F) A summary of the XPS peak area ratios of* CF_3 *to* CF_2 *for samples analyzed in (E).*

The ratio of the XPS peak areas for the C1s associated with CF_3 and CF_2-CF_2 indicate the molecular order of the perfluoroalkylsilane molecules within the SAMs. Each of these molecules has a CF_3 terminal functional group, and seven CF_2 groups within the alkyl chain. The 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane molecules within a low density monolayer are either oriented parallel to the plane of the oxide surfaces or with a large tilt angle away from the surface normal (Figure 3.9).

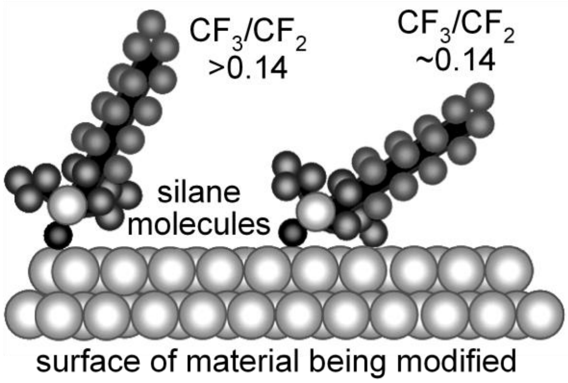


Figure 3.9. *Schematic depiction of the tilt of 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane molecules covalently attached to the oxide surfaces of a single crystalline silicon substrate. The average tilt of the molecules within a monolayer is predicted based on the C1s XPS peak area ratio of CF_3 to CF_2.*

The molecules within higher density SAMs are oriented with a smaller tilt angle away from the surface normal. X-ray photoelectron spectroscopy is sensitive to the outer most layers of a surface.[84] The closer the perfluoroalkylsilane molecules tilt towards the surface normal and away from the oxide surfaces, the higher the relative XPS intensity will be for the CF_3 terminal group relative to the signal intensity for the CF_2 groups. Perfluoroalkylsilane molecules will have a low tilt angle away from the surface normal within a dense monolayer as the molecules orient their chains relative to each other through van der Waals interactions. An XPS peak area ratio (CF_3 to CF_2) of around 0.14 (or 1/7) would suggest that the perfluoroalkylsilane molecules have a high tilt angle or are physically adsorbed onto the oxide surfaces.[30] The higher this peak area ratio, the lower the average tilt angle of the molecules within the monolayer.

Monolayers with a low molecular tilt angle (as inferred from the CF_3 to CF_2 XPS peak area ratio) might imply a high packing density of the molecules within the SAMs. These two properties of the molecules within the SAMs are related. The observed trends are, however, opposite for the average density of perfluoroalkylsilane molecules on the oxide surfaces and their relative tilt angles. The analyzed monolayers were prepared by heating a solution of 1 mM perfluoroalkylsilane for 5 h at various temperatures, followed by solvent extraction and XPS analysis. The relative density of the monolayers increases with an increase in solution temperature during growth of the SAMs (Figure 3.8E). The relative tilt angle predicted by the CF_3 to CF_2 XPS peak area ratio (Figure 3.8F) increases for higher temperatures. These results suggest that lower processing temperatures yield a more tightly packed monolayer, thus increasing the peak area ratio or the molecular tilt away from the surfaces. Monolayers prepared at 20 °C have a lower surface coverage, but the associated error bars with their peak area ratio measurements are significantly larger than those at other processing temperatures. This large error is attributed to the low signal to noise within the high resolution C1s XPS spectrum for the 20 °C samples (Figure 3.8B), and to the variability in the molecular packing within the monolayers.

The mean CF_3 to CF_2 peak area ratio is smaller for samples prepared at 80 °C, but the associated error bar is not significantly smaller (Figure 3.8F). Density of molecules within the SAMs prepared at 80 °C is higher than at the other processing temperatures, which is confirmed by ellipsometry measurements (Figures 3.2 and 3.4). The higher density of molecules within the monolayer suggests that the monolayer should have a smaller average tilt angle away from the surface normal (i.e., a higher CF_3 to CF_2 peak area ratio). The inconsistency in these results could be attributed to a high packing density of silane molecules with a relatively low surface coverage at 20 °C in contrast to samples prepared at 80 °C. This inconsistency could also be attributed to the large error in determining the CF_3 to CF_2 peak area ratio of samples prepared at lower temperatures (e.g., 20 °C) due to a low surface coverage of the monolayers and a corresponding poor signal to noise in the XPS spectra. Further analysis of the surfaces was necessary to clarify this inconsistency in surface coverage, and to verify the quality of the monolayers as a function of process temperature.

3.3.5. Topography of SAMs Based on AFM

Surface coverage of molecules within the perfluoroalkylsilane monolayers can be verified through the use of scanning probe microscopy techniques. Atomic force microscopy (AFM) has been used to assess the quality of other SAMs.[80,91,75] Silicon oxide surfaces decorated with monolayers of a monoreactive perfluoroalkylsilane prepared at higher processing temperatures are relatively more hydrophobic and contain more silane molecules. Further analysis is, however, necessary to determine the distribution or surface coverage of these molecules. Atomic force microscopy is used to image the size of the regions covered with perfluoroalkylsilanes. For the bare silicon substrate, roughness was measured over a 25 μm^2 area by AFM to be 115 pm. After piranha treatment, the roughness measured over a 25 μm^2 area increases to 337 pm. The results show piranha treatment may slightly increase the roughness of silicon substrate or remove surface contaminants exposing the underlying substrate. Roughness of the substrates is, however, much less than the height anticipated for the SAMs on these substrates. The surface roughness does not contribute significantly to the measurement of the SAMs, but this roughness could have implications on the potential mechanisms for the formation of these monolayers on the silicon oxide coated substrates.

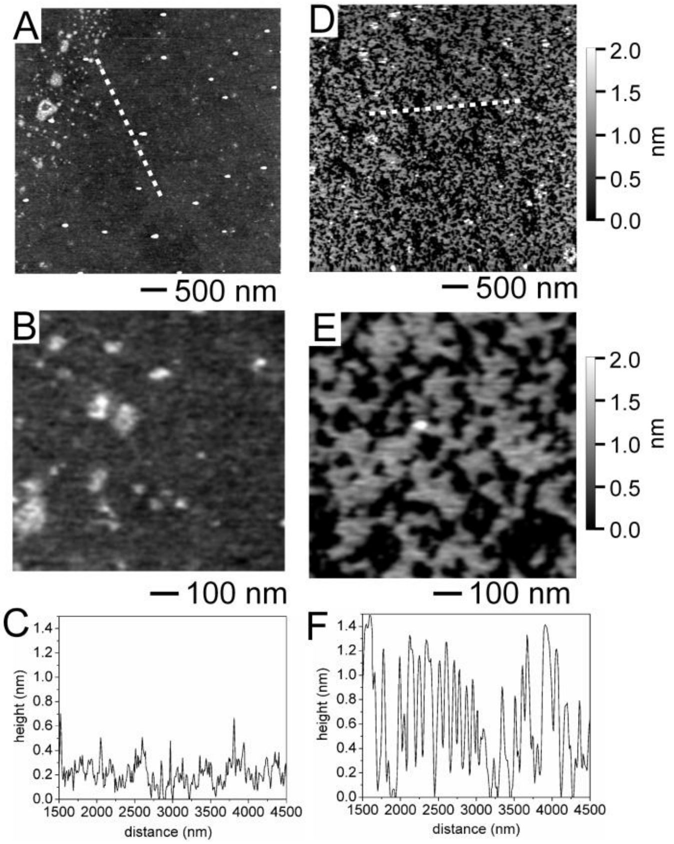


Figure 3.10. *Representative atomic force microscopy images of SAMs formed from a solution of 1 mM perfluoroalkylsilanes (A-C) after 5 h at 20 °C and solvent extracted for 1 h, and (D-F) after 5 h at 80 °C and solvent extracted for 1 h. The vertical scale, as indicated by the grey-scale rulers, is identical for all of the images (A,B,D,E). (C,F) Height traces are plotted for the regions indicated in the images (A,D) by the dotted white lines.*

The AFM data demonstrate a clear difference in topography between the monolayers prepared at 20 and 80 °C. Surfaces treated at 20 °C contain small regions of topography that might be attributed to densely packed monolayers. These monolayers have an average variation in height of ~0.25 nm (Figures 3.10A-C). Average height of the SAMs measured by AFM is, however, shorter than that measured by ellipsometry, which gave an average thickness of ~0.44 nm for these samples (Figure 3.2B). Samples prepared at 80 °C have distinct regions of topography that correspond in height to that of a close-packed monolayer of the perfluoroalkylsilanes. These samples contain both densely packed and non-close-packed monolayers with an average thickness of ~0.97 nm (Figures 3.10D-F). Ellipsometry measurements for these samples determined the average thickness for these samples to be ~0.58 nm (Figure 3.2B). The difference between the AFM and ellipsometry measurements can be attributed to both the deformation of the silane molecules by the hard AFM probe and to the scale on which these measurements are made. For example, the AFM measurements are obtained over areas up to 25 μm^2, whereas the ellipsometry measurements are taken over areas up to 1 mm^2. Density of the topographical features observed by AFM within the monolayers varies across the substrates. These measurements further confirm that the density of these monolayers is non-uniform on these silicon oxide surfaces, which agrees with the large error bars associated with other measurements reported previously(i.e., XPS analysis, ellipsometry and water contact angle measurements).

3.4. Conclusions and Outlook for Further Improvements to Perfluoroalkylsilane SAMs

The optimal silane-based monolayers covering silicon oxide surfaces would be uniformly hydrophobic and densely packed with an extensive surface coverage. Simple procedures are demonstrated for preparing and analyzing mono reactive perfluoroalkylsilane based SAMs on planar silicon oxide surfaces. Monolayers of monoreactive alkylsilane molecules demonstrated an increased surface coverage at concentrations around 1 mM and higher processing temperatures (around 80 °C) in contrast to previous reports in the literature for other alkylsilanes. A thorough understanding of the packing of these silane molecules on the silicon oxide surfaces and quality of the resulting monolayers is only obtained through the integration of data from all of the techniques demonstrated in this study. Each set of measurements, such as water contact angle, ellipsometry, XPS and AFM analyses, gives important information required to determine the quality of these SAMs. Fourier Transform Infrared (FTIR) spectroscopy was also used in an attempt to identify the chemical composition and quality of monolayers. The extracted sample of perfluoroalkylsilane SAMs was measured by Nicolet Nexus 470 FTIR. The main region of interest is the C-F stretching between 1100 and 1300 cm^{-1}, but it was not observed by FTIR spectroscopy.

Monolayers prepared by heating a solution of silane molecules to 80 °C for 5 h had a higher overall quality than those prepared at lower temperatures for the same or shorter reaction times. Monolayers prepared at lower temperatures, such as 20 °C, had a lower surface coverage, but the perfluoroalkylsilane molecules within these SAMs packed with a high molecular density on the oxide surfaces. The atomic force microscopy data suggest the monolayers deposited at lower temperatures were composed primarily of densely packed islands of perfluoroalkylsilane molecules, whereas the monolayers deposited at higher temperatures contained similar islands in combination with a lower density of perfluoroalkylsilanes assembled between these islands. These studies also emphasize the need for solvent extraction with toluene for appropriately assessing the quality of these monolayers and minimizing the influence of physically adsorbed molecules. Another key result of the studies presented herein is that monolayers prepared by a continuous reaction are equivalent in quality to those prepared by a sequential reaction process of monolayer assembly, solvent extraction, followed by further assembly of perfluoroalkylsilane molecules. These results highlight the importance of mass transport and concentration of perfluoroalkylsilane molecules on the quality of the assembled monolayers. In other words, optimizing the kinetics of the reaction between the perfluoroalkylsilanes and the oxide surfaces is essential for achieving high quality SAMs.

The results presented in these studies demonstrate a set of simple processes that are optimized for the reaction time, solvent temperature, and concentration of monoreactive perfluoroalkylsilane molecules to make high quality SAMs on silicon oxide surfaces. Future improvements to this work will need to address the uniformity of reactive sites on the silicon oxide surfaces (possibly through changing the choice of substrate), and the choice of solvent to further optimize silane solubility, water content, and mass transport.

4. Microwave Assisted Deposition of Perfluoroalkylsilane SAMs

4.1. Microwave Processes for Molecular Reactions

4.1.1. An Introduction to Microwave Synthesis

An increase in temperature of a solution causes molecules to move about more rapidly, which leads to a larger number of more energetic collisions. Traditionally, chemical synthesis has been achieved through conductive style heating with an external heat source. In this process, heat passes the walls of the vessel in order to reach the solvent and reactants. This is, however, a time-consuming process. Microwave radiation can couple directly with the molecules present in the reaction mixture, leading to a more rapid rise in solution temperature. Based on Arrhenius equation $k=A \exp(-Ea/RT)$, the reaction rate, k, is dependent on two factors: the frequency of collisions between molecules that have the correct geometry for a reaction to occur “A”, and fraction of those molecules that have the minimum energy required to overcome the activation energy barrier, Ea. Temperature (in Kelvin) is denoted by T, and R is the universal gas constant. Microwave processing is sought to improve the synthesis of many reactions by increasing A, and providing the reactants the necessary energy to overcome the activation energy barrier for the reaction.

Microwaves are a form of electromagnetic energy with low frequencies and are defined as those frequencies in the range from 300 to about 300,000 MHz. In both a microwave reactor and a domestic microwave, 2.450 MHz is the most widely adopted frequency. The energy of these microwaves (0.037 kcal/mole) is very low relative to the typical energy required to cleave molecular bonds (80-120 kcal/mole). Thus only molecular rotations are affected by microwaves[94] (Figure 4.1). There are two mechanisms for transferring energy from microwaves to the substance being heated: i) dipole rotation; and ii) ionic conduction. Dipole rotation is an interaction in which polar molecules try to align themselves with the rapidly changing electric field of the microwaves. In this process, energy is dissipated into the solvent in the form of heat through intermolecular friction and collisions. Ionic conduction occurs if there are free ions or ionic species present in the substance being heated. The ionic species oscillate back and forth under the influence of the microwave field. The ions collide with neighbouring molecules or atoms, creating heat.[95]

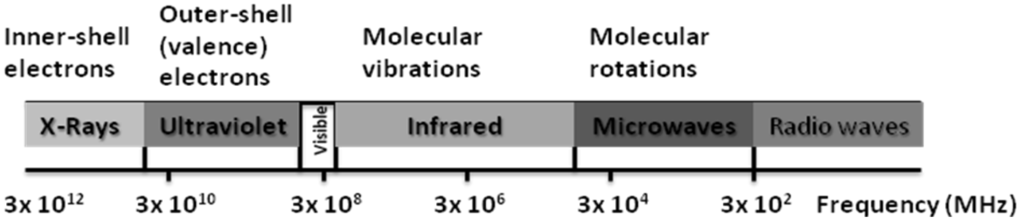


Figure 4.1. *Schematic depiction of the electromagnetic spectrum and relationship of energy affecting molecules.*

Due to its ability to dramatically speed up a chemical reaction and to make products in high yield, microwave irradiation has been applied in many different fields of chemistry. In materials chemistry, polymers have been prepared by microwave-assisted reactions.[96] A variety of nanostructures of different compositions, such as carbon nanotubes[97] copper oxide nanoparticles,[98] have been synthesized by microwave processes. In the formation of self-assembled monolayers, microwave irradiation has been used to modify the tail group of the monolayers. For example, microwaves can induce the conversion of a self-assembled amine-acid salt bilayer to a imide bilayer.[99] In general, SAMs require long periods of time to form, sometimes up to a period of a couple of days. It has, however, been reported that well-ordered SAMs of dodecanethiol can be formed on polycrystalline gold microwave irradiation for only 120 s.[100] In this chapter, mono-reactive perfluoroalkylsilane-based monolayers deposited onto silicon substrates are formed by microwave assisted reactions.

4.1.2. The Role of Solvents in Microwave Synthesis

Solvents play a very important role in molecular syntheses. One of the most important characteristics of a solvent is its polarity. During microwave processes, the solvent polarity becomes a significant factor in these reactions. Polar molecules absorb microwave radiation more efficiently than non-polar molecules. The more efficient a solvent absorbs microwave energy, the faster the temperature of the reaction mixture increases. The ability of a solvent to absorb microwave radiation can be estimated by a number of characteristics of the solvent. These properties include the dielectric constant (ε'), dipole moment (μ), dielectric loss (ε''), tangent delta (δ), and dielectric relaxation time of the solvent. All of these factors contribute to a solvent's microwave absorbing characteristics. The dielectric constant (ε'), also known as the relative permittivity, measures the polarizability of a solvent. Dielectric constant depends on both solvent temperature and the frequency used for this measurement. Dielectric loss (ε'') is the amount of microwave energy that is lost through dissipation of heat. The dielectric loss provides an assessment of the coupling efficiency of a particular solvent. The solvents can be categorized into three different groups: high (ε'' > 14.00), medium (ε'' 13.99 – 1.00), and low (ε'' < 1.00) absorbing solvents. A higher dielectric loss indicates a solvent that is more efficient at coupling with the microwave energy, which translates into the faster the temperature of the reaction mixture can increase upon microwave irradiation. Dipole moment (μ) is defined as the product of charge (Q) on a solvent molecule and the separation of charges (r). Molecules with large dipole moment typically have large dielectric constant. The tan delta (δ), or loss factor, is the heat dissipation factor of the solvent or how efficiently microwave energy is converted into thermal energy. The loss factor is calculated from the ratio of the dielectric loss to the dielectric constant (ε''/ε' = δ) [94].

Microwave irradiation can rapidly increase the temperature of a reaction. Solvent should, therefore, be chosen carefully for a microwave reaction. One should avoid using solvents that decompose to hazardous components after prolonged exposure to high temperatures, such as dichloromethane and pyridine, as well as those solvents with low flash points that might cause a fire. Nonpolar solvents (e.g., hexane, benzene, and toluene) possess very low ε'', ε', and δ values. These solvents can act as a heat sink. As the reaction mixture is exposed to microwave radiation, the nonpolar solvent, which minimally interacts with the microwaves, will help to draw away heat produced from the more polar reagents. Nonpolar solvents are, therefore, suitable to microwave reactions.[95] Toluene was used in the previous demonstrations of the formation of alkylsilane-based SAMs (Chapter 3). Toluene has a boiling point of 111°C, a dielectric constant of 2.4, a dielectric loss of 0.096, and a loss tangent of 0.040. Toluene is also a good solvent for microwave assisted deposition of SAMs.[101] This research focuses on two aspects of developing microwave-assisted reactions for the formation of alkylsilane-based SAMs. The first is an optimization of the concentration of perfluorosilane molecules in the toluene solution and the influence of reaction time on the quality of the SAMs. The other aspect that is analyzed is a comparison of different solvents on the resulting quality of the monolayers.

4.2. Methods and Materials

Preparation of Silicon Oxide Substrates. The same procedure was used as that reported in Chapter 3.

Preparation of SAMs:

1) Monolayers Prepared from Different Concentrations of Perfluorosilane in Toluene. Each cleaned substrate was put into a glass microwave tube (10mL Discover and explorer vessels, CEM Corporation). Then 5 mL of a perfluorosilane solution in toluene was added into the tube. The silane molecule used for these studies was 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane (90%, Alfa Aesar). Silane concentrations were prepared at 0.01, 0.1, 1 and 10 mM in toluene (Baker CMOS grade, distributed by Anachemia Science). The microwave reactor is located in another building. When samples are prepared, it needs to take time to transfer samples. So 30 min are counted as incubation time of the samples in the silane solution before proceeding with the microwave reactions. This period of incubation time was followed by microwave heating using a microwave reactor (Discovermate, CEM Company) operating at 300 W. Reaction times were varied from 50 to 200 s. These substrates were solvent extracted using the same procedures reported in Chapter 3, and their quality assessed by water contact angle measurements, and spectroscopic ellipsometry.

2) Monolayers Prepared from 1mM Perfluorosilane in Different Solvents. Each cleaned substrate was placed into a glass microwave reaction tube. Then 5 mL of a 1mM perfluorosilane solution in toluene was added to each tube. The reagents were identical to those reported above in addition to mesitylene (TCI America), xylenes (Anachemia Science) and 1-octadecene (90%, Aldrich). After the 30 min incubation time of the samples in the silane solution, samples were heated one-by-one in the microwave reactor at 300 W for 50 to 300 s. These substrates were solvent extracted using the same procedures reported in Chapter 3, and their quality assessed by water contact angle measurements and spectroscopic ellipsometry. Four different positions were measured for each substrate, and data from at least two substrates were combined for each data point. The error bars were calculated as the standard deviation of at least 8 measured points.

4.3. The Use of Microwaves to Form Alkylsilane-Based SAMs

Microwave processing can dramatically speed up chemical reactions. Through dipole rotation or ionic conduction, energy is transferred from microwaves to the substance being heated. In the formation of monolayers, silane molecules hydrolyze to silanol groups on the surface of substrate and bond to the surface silanols through Si-O-Si bonds. In microwave synthesis, the heating of surfaces rather than the bulk focuses the energy and heat at the reactions between the silane molecules and the surface silanol groups, which should improve the efficiency of forming alkylsilane based SAMs. Solvents play a very important role in many reactions, including microwave based reactions. In Chapter 3, toluene was demonstrated as a useful solvent in the formation of alkylsilane-based SAMs. In a microwave reaction, toluene can act as a heat sink for the reaction with a very low ε'', ε', and δ. The possibility of using microwave processes to assist in the formation of alkylsilane-based monolayers is investigated herein.

The Gates group at SFU is very interested in microwave-assisted deposition of silane-based SAMs. A previous graduate student, Hanifa Jalali, performed the initial investigation for the formation of perfluorosilane monolayers on silicon wafers using a domestic microwave.[101] Her research included an investigation into the choice of solvent and concentration of silane in the solution. The primary focus of this work was to identify the trends for silane deposition using water contact angle measurements. Based on this prior work, the investigations were expanded here to the use of a microwave reactor for the formation of these monolayers. The experiments described herein focus on solvents that have high boiling points, and comparing monolayers formed using a microwave reactor. In addition, the improvements for sample handling and other improvements in sample preparation described in this thesis were used for these new microwave studies. Conditions were monitored and the quality of these monolayers assessed using water contact angle measurements and spectroscopic ellipsometry. Another advance to this area of research was the implementation of microwave processes to extract the adsorbed silane molecules from the SAMs.

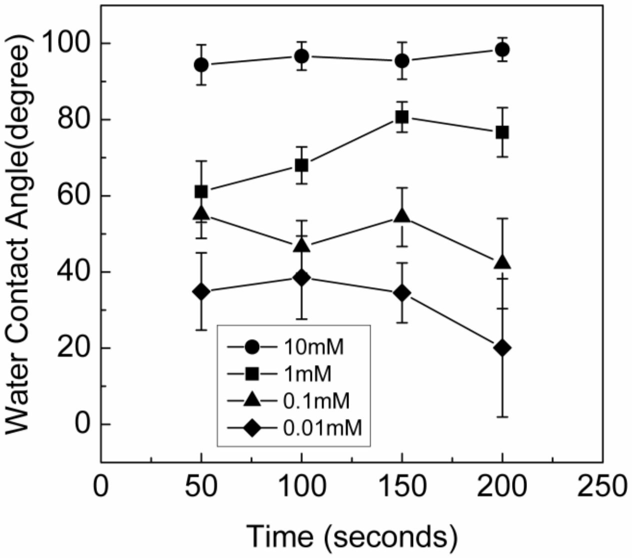


Figure 4.2. *Water contact angle measurements of perfluorosilane monolayers formed on silicon oxide surfaces from different concentrations of silane in toluene by microwave synthesis at 300 W. All data is reported for substrates that have been washed for 1 h with toluene in a Soxhlet extractor.*

Water contact angle measurements are a simple and quick approach to characterize the hydrophobicity and thus the quality of SAMs. The water angle for the perfluorosilane monolayers formed at low concentrations (e.g., 0.01 mM and 0.1 mM) of silanes decreases with increasing reaction times (Figure 4.2). The water contact angle of samples prepared in 1 mM silane for 50 s is similar to substrates immersed in silane concentrations of 0.1 mM, but increases with the longer reaction times. The water contact angle of highest concentration, 10 mM silane, is mostly consistent no matter the length of the reaction time. There is an equilibrium between adsorption and desorption of perfluorosilane molecules to and from the surfaces, respectively. The use of microwave energy could speed up both processes. It is most likely that at lower concentrations of silane, there are not enough perfluorosilane molecules in proximity to the surfaces of the substrates to completely react with these surfaces. An increased reaction time also leads to desorption of absorbed molecules, which leaves unreacted regions of the surfaces. These unreacted regions of the substrate, indicated by the lower water contact angles, are possibly due to the intermolecular reaction of silane molecules in solution, leading to an insufficient number of molecules to react with the surfaces. For higher concentrations of the perfluorosilane solution, there are enough perfluorosilane molecules remaining in solution to fill in these vacancies in the substrate after desorption processes. The higher coverage of the monolayer on the substrate gives a larger water contact angle measurement. Figure 4.2 presents water contact angles of perfluorosilane monolayers formed by microwave synthesis after 50s. We may wonder what hydrophobicity of monolayer formed in less reaction time, such as 10 s, or 20 s. Prior to microwave reaction, there is also a 30 min incubation time. What is the water contact angle of this sample without microwave? These questions need to be addressed in future investigations.

In microwave assisted synthesis, the polar molecules in the solution heat up rapidly and increase the solvent temperature above its boiling point, which is referred to as “super-heating”. Toluene, which has been used for the formation of silane-based SAMs, has a boiling point of 111°C. Other solvents are compared with the toluene for their efficiency of forming SAMs. These solvents were chosen for their higher boiling point than toluene, and also for their low ε'', ε', and δ. These solvents could improve the formation of high quality SAMs due to their increased heat capacity by microwave processes. The solvents investigated here were xylene, mesitylene and 1-octadecene (Table 4.1).

Table 4.1. *Boiling point, dielectric constant (ε'), dielectric loss (ε'') and tangent delta (δ) values of solvents measured at room temperature and 2.450MHz*[94] *(Data for mesitylene and 1-octadecene are from their Material Safety Data Sheets (MSDSs. N/A refers to data that is not available at this time.)*

Solvent	Boiling Point (°C)	Dielectric Constant (ε')	Dielectric Loss (ε'')	Tan Delta (δ)
Toluene	111	2.4	0.096	0.040
Xylene	144	2.6	0.047	0.018
Mesitylene	165	2.2	N/A	N/A
1-Octadecene	315	N/A	N/A	N/A
Water	100	80.4	9.889	0.123

Table 4.1 summarizes the boiling point, dielectric constant, dielectric loss and tan delta values of toluene, xylene, mesitylene and 1-octadecene. The first three solvents have a similar structure, which are methylbenzene, dimethylbenzene and trimethybenzene, respectively. The boiling point of mesitylene is higher than that of xylene and toluene. The dielectric loss and tan delta values are not available for mesitylene, but the estimated values are similar as those of toluene and xylene. For 1-octadecene, only the data of boiling point temperature can be found in the literature. This very high boiling point is attractive for its potential in the microwave based formation of SAMs. The deposition of alkylsilane-based SAMs in each of these solvents by microwave irradiation processes is characterized by water contact angle measurements after solvent extraction of these surfaces.

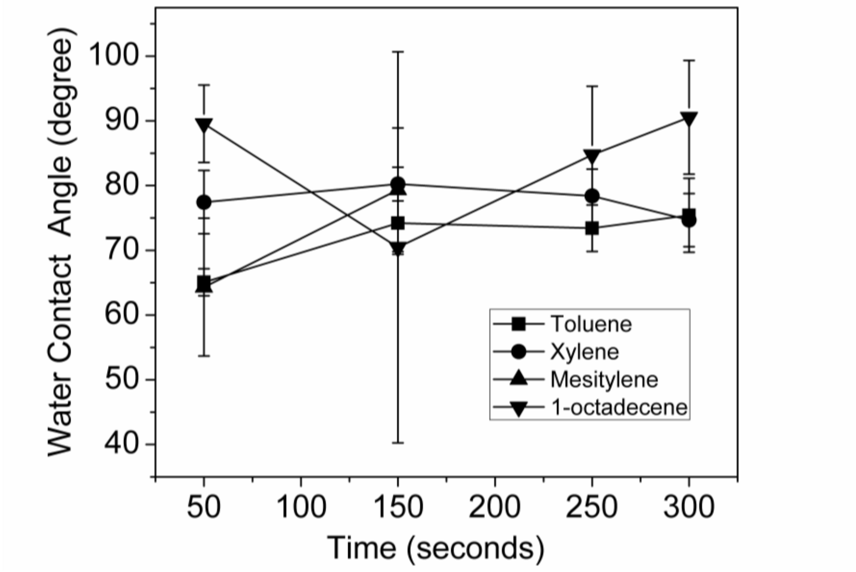


Figure 4.3. *Water contact angle measurements of perfluorosilane monolayers formed on silicon oxide surfaces by microwave synthesis at 300 W from 1 mM silane solution prepared in different solvents. The solvents are toluene, xylene, mesitylene and 1-octadecene. All data is reported for substrates that have been treated with solvent extraction. Four different positions were measured for each substrate, and data from at least two substrates were combined for each data point. The error bars were calculated as the standard deviation of at least 8 measured points from at least 2 substrates.*

The microwave reactions were monitored for changes in temperature and pressure throughout the reaction. If either property within the reaction tubes was determined to be unsafe, the reaction was terminated. This monitoring procedure resulted in only two independent reaction times being produced for the deposition of SAMs in the mesitylene solutions. The microwave reactor stopped after 150 s because the reaction conditions were reaching too high an internal pressure in the reaction tubes. It is clear that mesitylene is not a suitable solvent for long reaction times by microwave synthesis. Perfluorosilane-based SAMs formed in xylene solutions have a higher water contact angle (77° after 50 s) than those monolayers prepared in toluene and mesitylene solutions. The water contact angle of SAMs formed in toluene is almost constant over long reaction times. In comparison, the water contact angle of SAMs formed in xylene fluctuates with time. At 250 s, the water contact angle for SAMs formed by microwave processing in a xylene solution is 78.4 ± 1.5°. This value is consistent until the reaction time reaches 300 s when the water contact angle changes to 74.7 ± 4.1°. The later value is equivalent to that observed for samples prepared in toluene solutions using 300 s of reaction time. The water contact angle of SAMs formed in the xylene appears to decrease at 300 s in comparison to a reaction time of 250 s. However, based on t-test results t (14) = 1.8036, p =0.0928 (>0.05), this difference is not statistically significant. Therefore, all data points for samples produced by reactions in xylenes are consistent. Dielectric loss and tan delta values of xylene are lower than those of toluene, which indicates that xylene is a better heat sink than toluene and will help to draw extra thermal energy away from the substrate during the microwave processes. Xylene also has a higher boiling point, which might provide a more homogeneous solution during the microwave reactions. Large water contact angles and small error bars for the measurements associated with the perfluorosilane-based SAMs indicate high quality monolayers formed in the xylene solutions. Xylene could be an alternative solvent in microwave driven formation of silane-based SAMs. The monolayers formed in 1-octadecene are, however, not as high a quality. The lower quality of these films is seen in the large error bars associated with these water contact angle measurements. The molecular structure of 1-octadecene contains an unsaturated C-C bond, which might be reactive during the microwave processing. In addition, this molecule might physically adsorb more favorably onto the surfaces than the other solvents tested here.

4.4. Comparison of Conventional and Microwave Based Techniques for the Formation of Monolayers

Based on our previous experiment results (in Chapter 3), optimizing the kinetics of the reaction between the perfluoroalkylsilanes and the oxide surfaces is essential for achieving high quality SAMs. Deposition of silane-based self-assembled monolayers on oxide substrates can be time consuming (typically requiring 5h per sample). The optimized conditions for formation of SAMs on silicon oxide surfaces still require at least 5 h. In a microwave process, the microwaves couple directly with the silane molecules dissolved in the solution. This efficient coupling of energy into the molecular species of interest leads to a rapid and localized increase in temperature. The result of this process is an increased reaction rate for the silane binding with the surface silanol groups. The motivation for this work is to improve the efficiency of forming silane-based monolayers through a reduced reaction time. We compare the water contact angles and average film thicknesses of perfluorosilane monolayers synthesized by two methods: i) the conventional method using a toluene solution of silane heated to 80 °C; and ii) the microwave method using a similar solution heated by microwave reaction. For these studies, toluene is used as the solvent to keep this aspect of the work consistent for ease of comparison between the two different approaches, as well as for ease of comparing to other data reported in Chapter 3 of this thesis.

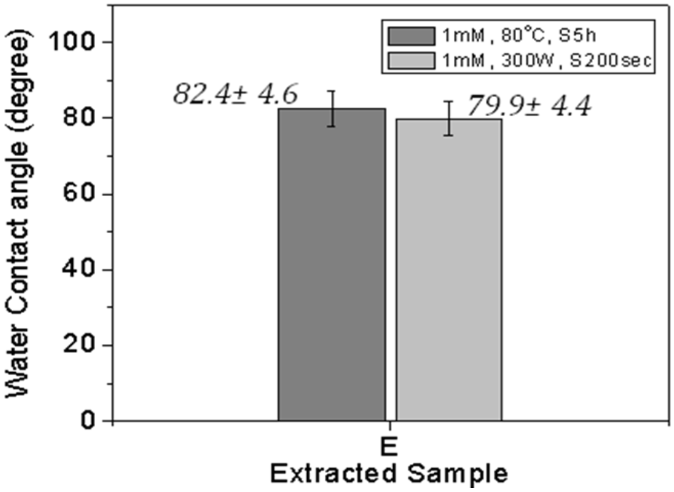


Figure 4.4. *Water contact angle measurements at perfluorosilane monolayers formed on silicon oxide surfaces from 1 mM silane solution in toluene by the conventional methods (80 °C, deposition for 5 h) and microwave synthesis (300 W, deposition for 200 s). All data is reported for substrates that have been treated with solvent extraction. Four different positions were measured for each substrate, and data from at least two substrates were combined for each data point. The error bars were calculated as the standard deviation of at least 8 measured points.*

Figure 4.4 shows the hydrophobicity of the monolayers deposited from 1mM perfluorosilane solution in toluene under the conventional method and with microwave irradiation. The substrate immersed in the silane solution at 80 °C for 5 h measured a water contact angle of approximately 82° following solvent extraction. In contrast, after only 200 s at 300 W by microwave processing, the water contact angle reached about 80°. The microwave methods approached the optimal monolayer quality within a few minutes. Microwave synthesis is very efficient, shortening the silane deposited time from 5 h to 200 s.

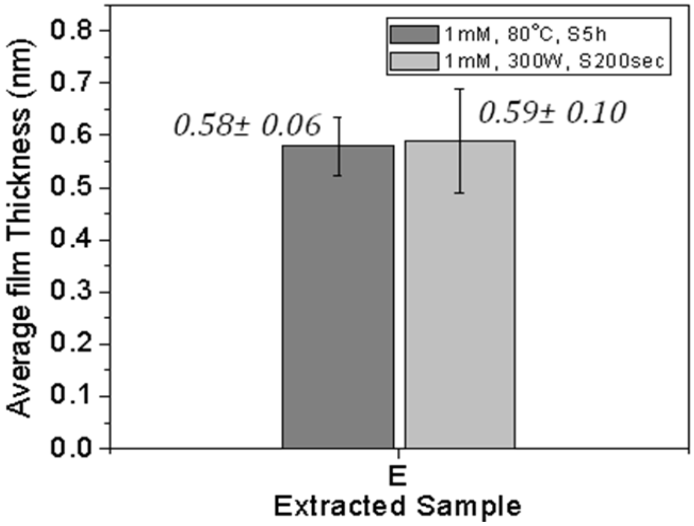


Figure 4.5. *Average thickness from spectroscopic ellipsometry measurements at perfluorosilane monolayers formed on silicon oxide surfaces from 1 mM solution in toluene by conventional methods (80 °C, deposition for 5 h) and microwave synthesis (300 W, deposition for 200 s). All data is reported for substrates that have been treated with solvent extraction. Four different positions were measured for each substrate, and data from at least two substrates were combined for each data point. The error bars were calculated as the standard deviation of at least 8 measured points.*

The average film thickness provides us further information about the quality of the monolayer. Figure 4.5 shows the average thickness of monolayers prepared by the optimized conventional methods at 80 °C (Chapter 3) and the microwave method presented in this chapter. The thickness of monolayers formed by these different methods is in very close agreement. However, the error bars associated with the average film thickness of the monolayers prepared by the microwave methods is almost double that of the conventional methods. This result suggests that the perfluorosilane monolayers are less uniform following the microwave irradiation. This result is understandable as the high energy of the microwave process increases the reaction kinetics, as well as the entropy of the system. The second law of thermodynamics states the entropy, which is a measure of disorder, will increase and is proportional to the energy put into a system. The high temperatures reached by microwave processing increases the entropy of these systems relative to that of the lower temperature processes. Consequently, the microwave process could increase disorder in the packing (e.g., molecular tilt) of the molecules within the resulting monolayers.

4.5. Conclusions and Outlook for Microwave Assisted Deposition of Alkylsilanes on Silicon Oxides

Microwave synthesis can dramatically speed up the rates of chemical reactions, thus reducing the time required for a reaction. Monolayers created from a solution of silane can be a time consuming process. However, microwave assisted deposition of alkylsilanes is a relative new method in the formation of monolayers. Different solvents were evaluated for their role in the formation of these monolayers. The choice of solvents was driven by finding those with high boiling points and low dielectric constants that are theoretically suitable for microwave processes. Another aspect that was studied included different concentrations of perfluorosilanes in a toluene solution. Through water contact angle measurements, the quality of the resulting alkylsilane-based SAMs was quickly and easily assessed. These results indicated that toluene is a suitable solvent not only in the conventional method of depositing silane-based SAMs, but also in microwave processes. Xylene is another solvent that well suited for use in microwave processes. Relatively high concentrations of silane are necessary in order to achieve high quality monolayers. The average film thickness of these perfluorosilane monolayers was also measured for substrates treated by both the conventional methods and the microwave methods. The experimental results suggest that the microwave methods can form monolayers of perfluorosilanes, shortening the reaction time from 5 h to only 200 s.

Future investigations into the microwave-assisted deposition of alkylsilane will include characterization of the surface composition and quality of the monolayers by X-ray photoelectron spectroscopy and surface topography by atomic force microscopy. Another aspect of this work will look into decreasing the microwave power (e.g., 100 W and 200 W) and assessing the impact of this change on the formation of SAMs and the quality of these films. Another possibility might be to use the microwave processes to also assist with solvent based extraction of the monolayers. The work presented here is also on silicon based substrates, but further work needs to be done to determine how applicable these results are to other silicon oxide surfaces. These and many other processes will need to be assessed in future studies for microwave-assisted formation of silane-based monolayers.

5. Measuring the Impact of Improving the Quality of Alkylsilane-Based SAMs

5.1. Importance of Preventing Non-Specific Adsorption of Biomolecules

5.1.1. Non-Specific Adsorption of Proteins

Most biological materials recognize foreign objects through their physical shape and chemical properties with remarkable precision. These processes can take place through molecular-scale interactions, which are referred to as specific binding events. On the other hand, many biological materials tend to physically adsorb onto solid surfaces without a specific recognition of a receptor. This non-selective interaction is called non-specific adsorption.[102] When artificial surfaces are in contact with a biological system or solution, such as blood, the adsorption of proteins is usually the first event to occur. Subsequent processes, such as the attachment of cells or more proteins is secondary and depends on the nature of the initially adsorbed layer of protein.[103] The protein adsorption process is a very complicated. It is driven by different protein-surface interactions, including van der Waals, hydrophobic and electrostatic forces.[104] After initial adsorption of proteins onto surfaces, the protein may dissociate from these surfaces and return back into solution. The surface-bound proteins may change their assembly orientation, or exchange with other proteins in solution. The adsorbed protein may also change its conformation, but still remain biologically active. Finally, a conformation change of the protein takes place, which can be correlated to a denatured protein structure. This change results in the irreversible adsorption and / or aggregation of the proteins onto the surfaces.[104]

A variety of parameters control protein adsorption. These include the properties of the protein, the chemical and physical character of the substrate surfaces,[105-107] the chemical composition of the solvent (e.g., pH and ionic strength)[105] and temperature. Based on internal stability, the proteins can be categorized into two groups: soft and hard proteins.[106] "Hard proteins" have high internal stability. Lysozyme and β-lactoglobulin belongs to this group. However, bovine serum albumin (BSA) and immunoglobulin (IgG) are "soft proteins", whose internal stability is low. It is more likely for soft proteins to denature on surfaces than for hard proteins.[107] As for the substrate's surfaces, it has been reported that the roughness of substrate can influence protein adsorption.[108] Also the charge on surfaces affects protein adsorption.[109] Non-specific adsorption of proteins onto surfaces is a dynamic and complex problem.

5.1.2. Importance of Preventing the Non-Specific Adsorption of Proteins

Synthetic biomaterials play a significant role in the fields of biology, biotechnology and medicine. These materials are widely applied in biosensors, protein arrays,[110] drug delivery systems and tissue engineering.[110] They include materials for contact lenses, dental prostheses, cardiovascular implants, catheter coatings and vessels for storage of proteins. The surfaces of these synthetic materials are in constant contact with biological systems. Clinically, the non-specific adsorption of proteins onto the surfaces of biosensors or medical devices is often a serious problem causing the deterioration in performance of these devices in clinical settings.[111] Biosensors are miniaturized devices that generate measurable signals via biological donor-receptor interactions and can be used for biomedical diagnosis. In this application, a receptor is immobilized onto the surfaces of the biosensor to capture incoming donor species based on specific binding interactions. If a material inadvertently absorbs onto the biosensor surface through non-specific adsorption it is likely that a "false positive" response will be observed in the measurement.[112] Protein adsorption is one of the most common events that cause the loss of selectivity and sensitivity of a biosensor and, therefore, the deterioration of the biosensor's performance. In another instance, protein contamination of the solid surfaces of an implanted medical device is the beginning of microorganism colonization and an immunological reaction, which can lead to many medical emergencies and complications.[106]

Protein microarrays have prominent applications in high-throughput proteomics, biomarker research and drug discovery.[113] A microarray fabricated by Tanii et al., is produced using silane monolayers patterned by electron beam lithography on a silica substrate. These researchers immobilized target proteins selectively within a space of 100 nm. Further miniaturization could not be achieved due to significant non-specific adsorption outside the patterned regions.[114]

5.1.3. Common Strategies for Preventing Protein Non-Specific Adsorption

There is a lot of effort going into preventing the non-specific adsorption of proteins onto various surfaces. Common strategies for preventing non-specific protein adsorption include the pre-adsorption of proteins onto surfaces, or the modification of surfaces with antifouling coatings.[103] A solution concentration of 1-5% bovine serum albumin (BSA) is widely used to create a blocking agent to cover the surfaces of an immunoassay in order to resist adsorption of other proteins.[114] The biggest limitation of this strategy is that other biofunctional species (e.g., antibodies) on the surfaces might be blocked by adsorption of the BSA. Additionally, the protein may react with some surface bound antibodies.[115] In creating antifouling coatings, poly(ethylene glycol) (PEG)/poly(ethylene oxide) is one of the most effective coatings to resist non-specific protein adsorption. The PEG chain length, its density and conformation each affect resistance to protein adsorption.[116, 117] The stability of PEG is, however, compromised in aqueous environments, which can decrease this material’s ability to resist non-specific protein adsorption.[118] Silicon oxides have been widely used in the construction of biosensors and medical devices.[53] The surfaces of silica can be easily coated with silane-based SAMs, to lower the free energy of these surfaces.[13] Fluorocarbon silane-based coatings offer excellent mechanical stability, low friction, and superior resistance to proteins in comparison to other types of coatings, such as polyethylene glycol. Literature evidence suggests that coating silica surface with fluorocarbon SAMs would effectively prevent non-specific protein adsorption in biosensors and medical device applications.[108, 119]

Surface modifications with polymers or SAMs dramatically reduce non-specific protein adsorption.[119] However, these modifications can still exhibit some non-specific protein adsorption. There are a number of possible reasons for their failure to completely protect these surfaces. One possibility, which is explored here, is that the non-specific adsorption is the results of defects in the SAMs (Figure 5.1). Our research focuses on how to improve the quality of SAMs, decreasing the number of defects in these films and assessing the impact of these changes to the resistance of the monolayers to non-specific adsorption of proteins. The following results test the hypothesis on the adsorption of proteins into defects within the SAMs.

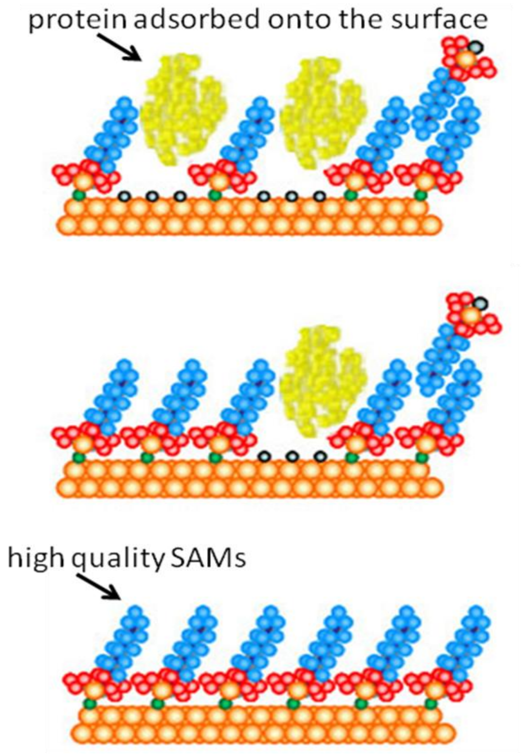


Figure 5.1. *Non-specific adsorption of proteins could be correlated with defects in self-assembled monolayers.*

5.1.4. Methods of Measuring Protein Adsorption on Surfaces

Various analytical techniques have been used to measure protein adsorption onto surfaces. In biology, radiolabelling, enzyme-linked immunosorbent assay (ELISA) and fluorescence spectroscopy are common methods for tracking the interactions of proteins.[106] Surface plasmon resonance (SPR) spectroscopy measures the changes in dielectric properties of an interface, and has been extensively used for monitoring protein adsorption on gold substrates coated with SAMs.[110,120] This technique, however, requires a metal surface that exhibits surface plasmon resonance in order to monitor the adsorption events. This technique is not applicable to silicon oxides. Quartz crystal microbalances (QCMs) can measure the changes in resonance frequency of a piezoelectric material.[103] Other techniques for monitoring protein adsorption onto surfaces include spectroscopic ellipsometry, neutron scattering and Fourier transform infrared spectroscopy (FTIR).[121]

In this research project, X-ray photoelectron spectroscopy (XPS) will be applied to monitoring protein adsorption onto surfaces. XPS is a very surface-sensitive technique. Theoretically, the nitrogen or other specific elements in the proteins can be monitored in order to determine protein adsorption on various surfaces (e.g., oxides, polymers, and metals). This technique has been used in the analysis of specific deposition of proteins to functionalized surfaces such as antibiotics and bonding agents.[122] Recent studies by Zangmeiste used both the nitrogen (N 1s) signal originating from mAb proteins and an iodine heteroatom label to confirm protein adsorption.[123] So it is practical to monitor non-specific protein binding by XPS for checking the protein-resistance of surfaces.

5.2. Methods and Materials

Preparation of Silicon Oxide Surfaces. The same procedure is used as described in Chapter 3 for cleaning the silicon oxide surfaces prior to formation of the monolayers.

Preparation of SAMs on Silicon Oxide Surfaces. The cleaned silicon substrates were coated with monolayers by immersion into a solvent containing dissolved silane molecules at 20 or 80°C for 3 h. The silane of choice is 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane (product #L16582, 90%, Alfa Aesar), which is used to prepare a 1 mM solution of perfluoroalkylsilanes in toluene (product #9466-03, J.T. Baker CMOS grade, distributed by Anachemia Science) in a glass vessel.

Solvent Extraction of SAMs. The same extraction procedure is used here as described in Chapter 3.

Protein Adsorption on Substrates Coated with SAMs. Bovine serum albumin (BSA) was chosen as the adsorptive protein. It is a relatively sticky protein and is commonly used as a blocking agent in immunoassays. An aqueous solution of 1 mg per mL BSA was prepared by dissolving 60 mg of BSA (Albumin from bovine serum further purified fraction V; Sigma-Aldrich) into 60 mL of phosphate buffered saline (PBS) solution at pH 7.4. This PBS solution is prepared from an initial 10X PBS premixed powder (#6508, EMD4 Biosciences). In brief, the premixed powder was weighed out to 1.00 g and added into 1 L of 18.2 MΩ water (prepared using a Barnstead DIamond Nanopure water filtration system) to make a 0.1X PBS solution. This solution contains 137 mM NaCl, 2.7 mM KCl and 10 mM disodium phosphate. The surfaces coated with SAMs, either as deposited or solvent extracted, were immersed in the BSA solution for 1 h. These samples were rinsed with at least 500 mL of 18.2 MΩ water and dried under a stream of filtered nitrogen gas.

Characterization of SAMs and Adsorbed Proteins. The samples were analyzed by XPS using a Kratos Analytical Axis ULTRA DLD system with a monochromatic aluminum source (AlKα of 1486.7 eV). Each sample was analyzed over at least three regions of the sample, each with an area of 700 μm x 200 μm. Survey scans were acquired using electron beam energies of 160 eV with a dwell time of 100 ms. High resolution spectra were obtained using a pass energy of 20 eV and a dwell time of 300 ms. The XPS peak centered at 399 eV is associated with N1s. This peak was used to estimate the quantity of BSA adsorbed onto the surfaces coated with the perfluoroalkylsilane-based SAMs. In addition, the XPS spectra are normalized according to their Si2p peak area, using the silicon from the substrate as an internal reference. Three different positions were measured for each substrate, and data from two substrates were combined for each data point. The error bars were calculated as the standard deviation of at least 6 measured points.

5.3. Discussion about Protein Resistant Films from Alkylsilane-Based SAMs

X-ray photoelectron spectroscopy is a powerful tool for surface analysis. This technique has been successfully used to assess the quality of perfluoroalkylsilane-based

SAMs in Chapter 3. Bovine serum albumin is a single polypeptide chain consisting of about 583 amino acid residues, which contains at least 583 nitrogen atoms per molecule. It also contains 17 intrachain disulfide bridges and 1 sulfhydryl group (from Sigma product information). Potentially the nitrogen and sulphur can be traced by XPS to detect protein adsorption onto monolayer protected surfaces. The sulphur concentration is, however, too low by empirical studies to properly detect by XPS. Therefore, these studies will focus on the use of the nitrogen peak to track non-specific protein adsorption events. Bovine serum albumin is dissolved in a phosphate buffered saline (PBS) solution. The solution pH 7.4 is equivalent to human blood levels, and protein adsorption is thus monitored under physiological pH. Following a typical procedure for immunoassay fabrication, bovine serum albumin is widely used as a blocking agent to cover all the exposed surfaces of a substrate. The incubation time is generally 1 h,[124, 125] which indicates that the non-specific protein adsorption will occur within this time period, and should be sufficient for our experiments. Therefore, we chose a BSA deposition time of 1 h in these experiments.

Figure 5.2 shows the high resolution XPS spectra for the N1s region, corresponding to BSA adsorbed onto perfluoroalkylsilane-based SAMs assembled onto silicon oxide surfaces. The black curve in Figure 5.2 corresponds to surfaces protected with monolayers deposited at 20 °C; the N1s peak intensity is near 3200 cps. The light gray curve corresponds to monolayers formed at 80 °C; the N1s peak intensity is near 1200 cps. Both surfaces had been immersed into separate BSA solutions following solvent extraction of the SAMs. The smaller area under the grey peak indicates that less protein is adsorbed onto these surfaces. These results suggest that the SAMs formed at 80 °C can resist non-specific adsorption of proteins better than those samples prepared at 20 °C. Based on the results discussed in Chapter 3, the mono-reactive perfluoroalkylsilane-based SAMs formed at 80 °C have a higher coverage of molecules and less physically absorbed species than the SAMs prepared at 20 °C. The high quality of monolayers prepared at 80 °C can better resist protein adsorption.

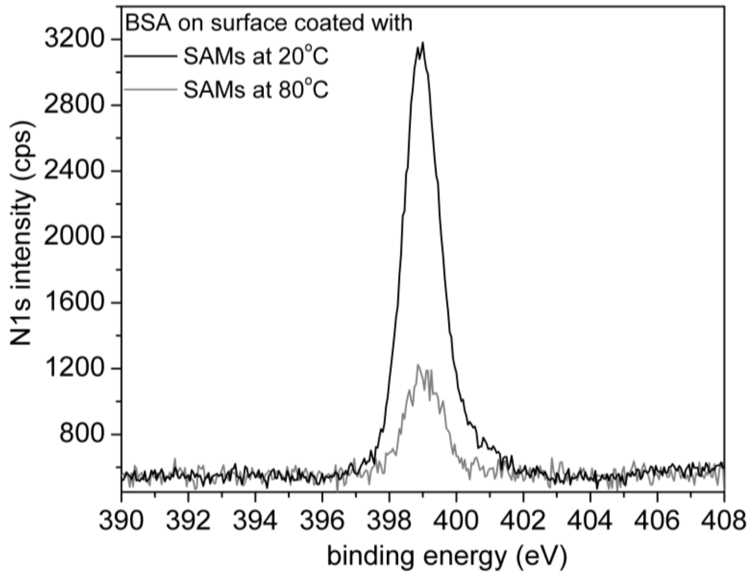


Figure 5.2. *High resolutions XPS spectrum of N1s from BSA proteins adsorbed onto silicon oxide surfaces coated with perfluoroalkylsilane-based SAMs prepared by conventional methods at 20 and 80 °C. These SAMs have been treated with solvent extraction for 1 h to remove physically adsorbed species prior to immersion in aqueous solutions containing the BSA proteins.*

We also investigated the bare silicon without SAMs resisting the BSA proteins adsorption. The N1s peak intensity of XPS is around 2300 cps, which is higher than the substrate treated at 80 °C (1200 cps), but lower than at 20 °C (3200 cps). The results indicated that less protein is adsorbed onto bare silicon surfaces than the SAMs formed at 20 °C and that the least amount of protein adsorbed onto SAMs formed at 80 °C. The mechanism of the protein adsorption process is complicated. The reason why less protein adsorbed onto bare silicon surfaces could be due to a difference in hydrophobicity and charge interactions. The silicon substrates were washed with piranha solution, rinsed with high purity water and dried with nitrogen gas. The control sample was directly immersed into the BSA containing solution. The fresh, bare silicon surfaces are covered with hydroxyl groups. The protein adsorption was also carried out at a pH of 7.4 and the isoelectric point of BSA is 4.7, which makes the BSA is negatively charged for these deposition conditions. A hydrophilic and negatively charged substrate surface would likely repel some of the protein adsorption. Substrates coated with SAMs prepared at 20 °C were subject to high temperature solvent extraction for 1 h. For the latter surfaces, the silanol groups could be condensed to form Si-O-Si and the surfaces would be covered with adsorbed toluene, which increases the hydrophobicity of these surfaces and increases the possibility of protein adsorption onto these surfaces. In the future work, the control sample should be prepared by the following procedure: a bare cleaned silicon substrate is put into toluene for 5 h, subsequently extracted with toluene for 1 h, and subjected to the test for protein resistance. From the current studies, the best surface coating for resisting the non-specific adsorption of proteins are SAMs formed at 80 °C. As discussed in Chapter 3, this result is attributed to the higher density and quality of monolayers prepared at 80 °C in comparison to the other temperatures evaluated in this work.

A comparison of the ability of both as-deposited and solvent-extracted SAMs to resist non-specific protein adsorption is shown in Figure 5.3. For each temperature, the experiments were repeated on three separate occasions. Slightly more BSA adsorbed onto the solvent extracted SAMs for samples prepared at both 20 and 80 °C. During solvent extraction, the toluene removes physically adsorbed silane molecules and exposes unreacted sites on the silicon substrate. Thus the extracted monolayers contain more pinhole defects in the SAMs, which provide more opportunities for protein adsorption onto these surfaces. Additionally, the non-homogeneous surfaces of the extracted samples can also attract more protein adsorption. From these results, protein adsorption correlates with defect density in the monolayers. Monolayers of mono-reactive perfluoroalkylsilanes with a higher quality, and thus an improved protein resistance, could be achieved using relatively moderate reaction conditions. Further improvements to the quality of these monolayers remain the focus of future work in this area, and are outside of the scope of this thesis.

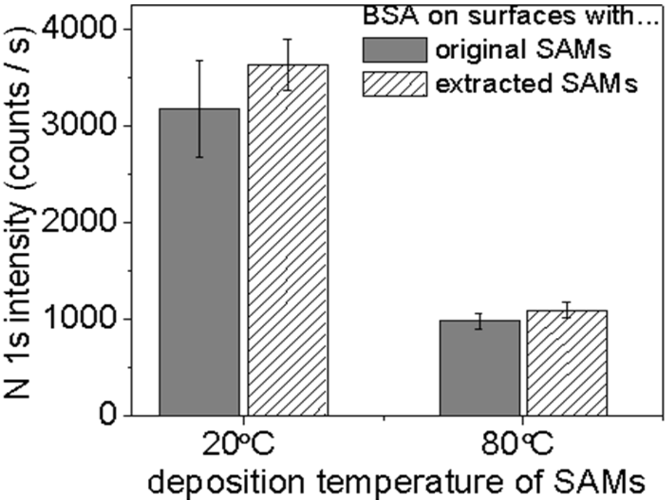


Figure 5.3. *A plot summarizing BSA protein adsorption onto the perfluoroalkylsilane monolayers as measured by the integrated XPS peak area for N1s. The SAMs were deposited at 20 or 80 °C, and samples were either analyzed as-deposited or following solvent extraction for resistance to protein adsorption. Three different positions were measured for each substrate, and data from two substrates were combined for each data point. Error bars were calculated as the standard deviation of at least 6 measured points.*

5.4. Conclusions and Outlook for Alkylsilanes in Resisting Non-Specific Adsorption of Proteins

Protein adsorption onto perfluoroalkylsilane-based SAMs on silicon oxide surfaces was evaluated using BSA. A comparison of monolayers prepared at 20 and 80 °C, as well as before and after solvent extraction, suggests that the protein adsorption correlates with defects in the SAMs. High quality monolayers can minimize non-specific protein adsorption. Further research is necessary to investigate this area and to determine the limits to how well the perfluoroalkylsilanes can resist protein adsorption, as well as extending this system to other monolayers. Other questions that will need to be addressed in the future include the influence of the solution pH on the adsorption of BSA or other proteins. The pH is important as it will impact the overall charge of the proteins. For example, the isoelectric point of BSA is 4.7. Since we evaluated the protein adsorption at pH 7.4 the BSA is negatively charged, which could have a significant influence on the interaction of the BSA with the exposed surfaces of the substrates.

Another challenge is to calibrate the XPS response in order to quantify the amount of BSA protein adsorbed onto these surfaces, as well as to understand the limits of detection of this technique for determining the amount of surface bound protein. Future work will also include a comparison with the monolayers prepared by microwave processing for their ability to resist the non-specific adsorption of proteins.

6. Conclusions and Outlook for Improving the Quality of Alkylsilane-Based SAMs

6.1. Conclusions

In this thesis, we investigated the optimum conditions for silanization of oxide surfaces on silicon substrates. Quality of these self-assembled monolayers was characterized by water contact angle, spectroscopic ellipsometry, X-ray photoelectron spectroscopy and atomic force microscopy measurements. Monolayers of mono-reactive alkylsilane molecules demonstrated an increased surface coverage at higher processing temperatures and relatively low concentrations. In the study, monolayers prepared by heating 1 mM toluene solution of silane molecules to 80°C for 5 h had a higher overall quality than at 20°C. Though monolayers prepared at 20°C had a lower surface coverage, the perfluoroalkylsilane molecules within these SAMs packed with a high molecular density on the oxide surfaces. Solvent extraction is necessary for minimizing physically adsorbed molecules, in order to appropriately assess quality of the monolayers. The result indicates that the kinetics of the reaction must be optimized with dissolution of the physically adsorbed perfluoroalkylsilanes from the surfaces of the silicon oxides. Sufficient thermal energy in the system is necessary to achieve high quality SAMs.

Chemical reaction rates can be increased dramatically by microwave irradiation, which can dramatically decrease the reaction times. The investigation of microwave-assisted deposition of alkylsilanes demonstrated it can be applied in mono-reactive alkylsilane monolayer formation. The quality of the perfluorosilane monolayers are determined by water contact angle measurements and average film thickness. Compared with monolayers formed by more conventional methods, microwave methods give a similar quality monolayer, but reduce the reaction times from 5 h to only 200 s.

In the study on BSA protein adsorption onto the mono-reactive perfluoroalkylsilane based SAMs on silica substrates, X-ray photoelectron spectroscopy was used to characterize the amount of BSA coverage. Less protein non-specifically adheres to monolayers formed at high temperatures with a higher coverage of covalently bond silanes and less physically absorbed species. The monolayers extracted by solvent lead to an increase in protein adsorption. The results agree with the hypothesis that protein adsorption is related to the density of defects of SAMs. High quality SAMs can minimize the non-specific adsorption of proteins onto surfaces.

6.2. Outlook

Based on the research described in this thesis, the future work will focus on the following key aspects to making and characterizing high quality SAMs. These aspects are: i) the characterization of mono-reactive perfluoroalkylsilane monolayers by atomic force microscopy (AFM) or Kelvin force microscopy (KFM) to understand the sizes of the well-packed monolayer domains; ii) to optimize the microwave-assisted formation of mono-reactive perfluoroalkylsilane SAMs; and iii) further investigations into perfluoroalkylsilane monolayers as surface modifications to resist non-specific adsorption of proteins.

Atomic force microscopy (AFM) can provide a direct measure of the surface topography. Some AFM measurements were pursued in an attempt to observe the domains within the perfluoroalkylsilane monolayers coating the silicon oxide surfaces. A preliminary investigation by AFM of the samples is presented in the Appendices. For instance, Figures C1C and C1D in the Appendices show that the perfluoroalkylsilane monolayers on the silicon substrate are not uniform, but instead form island-like structures. Figures C1E and C1F show the BSA protein absorbed on silicon substrate coated with perfluoroalkylsilane monolayers. Since SAMs formed island-like structures on the substrate surface, the high density area of SAMs may resist protein adsorption. The AFM images provided a quick and clear view of the surface topography. During the sample scanning, contamination of the AFM probes was an on-going challenge. The AFM image resolution decreases after multiple uses of these AFM probes. This phenomenon is especially severe when imaging surfaces coated with the proteins.

These were part of a study that focused on developing quick and simple characterization methods to check the quality of the SAMs. Since these analyses, further optimization has been achieved in the formation of high quality alkylsilane-based monolayers. The AFM analyses can be used to provide further details on the domains within these higher quality monolayers. This analysis could provide information on how the surfaces vary as a function of time, correlating to the kinetics of the formation of SAMs at higher temperatures. This AFM analysis could, however, not provide the information on the lateral variations in surface potential, which is useful for analyzing non-uniformities in surface composition when no variations in topography are observed. Another technique that could prove useful to the study of defects in SAMs is the use of Kelvin probe force microscopy (KFM) that measures the differences in surface potential across surfaces. In this measurement, an AC voltage is applied between the probe tip and the surfaces of a sample. The resulting signal provides information on the surface potential of the sample, which changes with surface composition. It is possible that KFM could provide information on the uniformity of SAMs, both topography and surface potential.

Microwave synthesis is a relatively new strategy to deposit mono-reactive perfluoroalkylsilane SAMs. This is a very attractive method to reduce the time required to form SAMs down to a couple of minutes or even seconds. Further work is necessary to optimize the microwave power, reaction times and solvent composition to decrease the disorder in the packing of the molecules within the SAMs. Another key question for this area of research is the potential impact of microwave irradiation on the surface chemistry (e.g., changes in oxidation of the surfaces) and other potential non-uniformities in the surfaces and the SAMs. Along the lines of saving time and energy in the formation of SAMs is the same quantities put into characterizing SAMs. Future studies should also investigate the use of microwave processing to extract physically adsorbed molecules from the monolayers. It is clear that there are many possibilities for further processing of monolayers using microwave irradiation.

The ultimate goal of our research is to make defect-free alkylsilane-based self-assembled monolayers, which are able to resist non-specific protein adsorption. There is a lot work still to be done in this area of research. Further investigations might include studying the relationship between adsorption of bovine serum albumin proteins and the solution pH and charges on the unprotected regions of the surfaces (i.e., within the defects in the SAMs on silicon oxides). It will be important to establish the lowest concentration of BSA protein adsorbed onto surfaces that can be detected by XPS. This quantification will require a method to calibrate the protein adsorption. Other techniques that are also non-destructive and quick could also be beneficial to this work, such as spectroscopic ellipsometry. The correlation of defects in monolayers to non-specific adsorption events could be very important for many applications of monolayers (or other surface modifications) in constant contact with biologically relevant media.

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Appendices

Appendix A.

Control Experiments on Silicon Oxide Surfaces

For making high quality SAMs, substrate surfaces need to be cleaned and measures taken to avoid further contamination. The treatment and storage of the substrates is a very important factor in controlling the surface chemistry during monolayer formation. A number of aspects were investigated to assess the different procedures necessary to mitigate and / or minimize surface contamination. These studies relied on high resolution X-ray photoelectron spectroscopy (XPS). For example, high resolution C 1s peaks in the XPS spectrum provides information about the environment and oxidation state of the C on the surfaces.

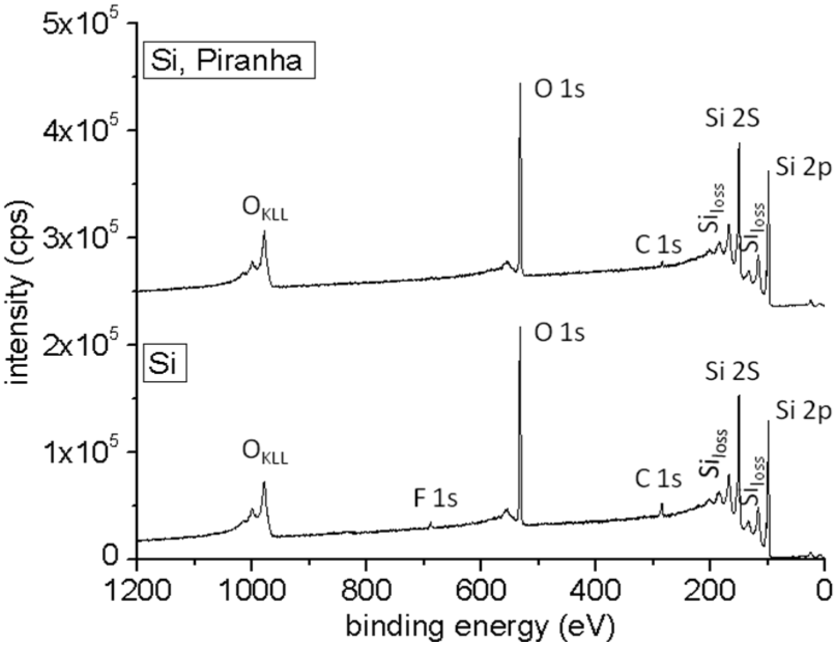

Figure A1. XPS survey scan of a native silicon substrate and a piranha-cleaned silicon substrate.

The XPS survey scans for silicon substrates are shown in Figure A1. The bottom scan line represents a typical spectrum for a bare silicon substrate as received from the supplier. The fluorine signal indicates the potential silane contamination of the surfaces, possibly from the accidental exposure to volatile silanes. The above scan line represents the surface of silicon substrate after piranha cleaning. The fluorine signal is no longer detectable. In addition, the carbon signal has decreased in comparison with the untreated substrates. The source of carbon contamination is possibly from carbonates formed in the water bound to the surfaces of the substrates, or hydrocarbons adsorbed from the air or the filtered water during the sample handling procedures following the cleaning processes. Carbon contamination is hard to avoid.

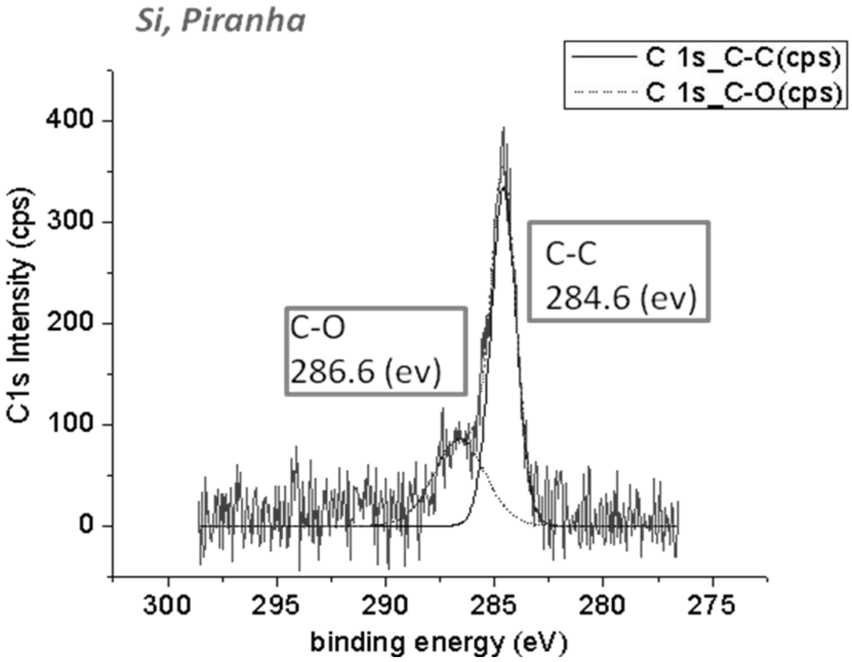

Figure A2. High resolution XPS spectrum, depicting the C 1s region, for a silicon substrate after cleaning the substrate with a freshly prepared piranha solution.

A comparison of the XPS C1s integrated peak areas (e.g., Figure A2) for substrates prepared under different conditions indicated a clear trend with how the samples are handled and stored. The smaller the peak area for the XPS C 1s peaks, the cleaner was a surface. The analyses from this study are reported in Table A1. These results suggest that the best controlled substrate is given by the following conditions.

1) The entire single side polished silicon wafer is treated by a fresh piranha solution (sulfuric acid: hydrogen peroxide 7:2 (v/v)) for 15 minutes.

2) Subsequently, the silicon wafer is cut into smaller pieces under a steady stream of high purity water.

3) The pieces of silicon substrate should be stored in a plastic petri dish (VWR International).

Table A1. ***Comparison of C 1s integrated XPS peak areas as a function of different surface treatments and storage conditions for samples***

Controlled conditions	**C 1s, C-C / Peak Area (cps)**	**C 1s, C-O / Peak Area (cps)**
Si wafer without piranha	1896.2	854.4
Si wafer with piranha	878.9	503.3
After piranha treatment:		
Si wafer cut in air	988.1	513.5
Si wafer cut under water	707.2	501.7
Si pieces stored in glass petri dish	938.8	437.1
Si pieces stored in plastic petri dish	798.3	438.0

Appendix B.

A Comparison of the Extraction Time for Soxhlet Extraction of SAMs

In the investigation of silane-based self-assembled monolayer (SAMs) formed on silicon oxide surfaces, the procedure of solvent extraction is very important to assess the quality of the SAMs. Solvent extraction removes physically absorbed molecules, which can represent a major irregularity in these SAMs. The question remains, what is a sufficient period of time that is necessary for soxhlet extraction of these surfaces? This question will be answered herein.

Herein is a comparison of extraction times used for this process. After piranha treatment, the silicon oxide surfaces were dried under a stream of nitrogen gas and then was immersed in a 1 mM solution of 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane in high purity toluene at 20°C for 3 h. These samples were placed into a Soxhlet extractor, and washed with toluene for 30 min to 4 h. The entire experiment was repeated in triplicate. The extracted samples were assessed by water contact angle measurements, spectroscopic ellipsometry measurements, X-ray photoelectron spectroscopy (XPS) analyses.

The experimental results are shown in Figure B1. The average film thickness decreases with longer extraction times, although the trend is not linear with time. After 1 h the change in monolayer thickness is minimal. A similar trend is seen for the XPS analysis. The data suggests the shorter period of soxhlet extraction, such as 30 min, is sufficient to remove all of the physically absorbed molecules. The large error bars at 30 min indicate a non-uniform density of silane molecules over the surfaces of the silicon oxide surfaces.

Water contact angle measurements are measured over an area of $2 mm^2$ from the 2μL droplets of water. Density of the molecules in these SAMs is not high, so the hydrophobicity of the samples is determined largely by the exposed regions of the silicon oxide surfaces. The trend observed by water contact angle measurements is not the same as that observed in the ellipsometry and XPS measurements (Figure B1). A longer extraction may increase the chances for contamination since the extraction system is not a completely closed system. A longer extraction time, such as 4 h, is also not necessary given the additional risk of contamination to the system.

We chose an extraction time of 1 h as our standard time for cleaning the samples. The data suggests there is a significant difference from 30 min to 1 h for solvent extraction. One hour is sufficient to remove the majority of physically absorbed species. When designing an experiment the quality of product must be considered, as well as the efficiency of the experiment. The goal is to produce high quality SAMs in the shortest period of time. Hence, the majority of experiments reported in this thesis rely upon 1 h of extraction with toluene.

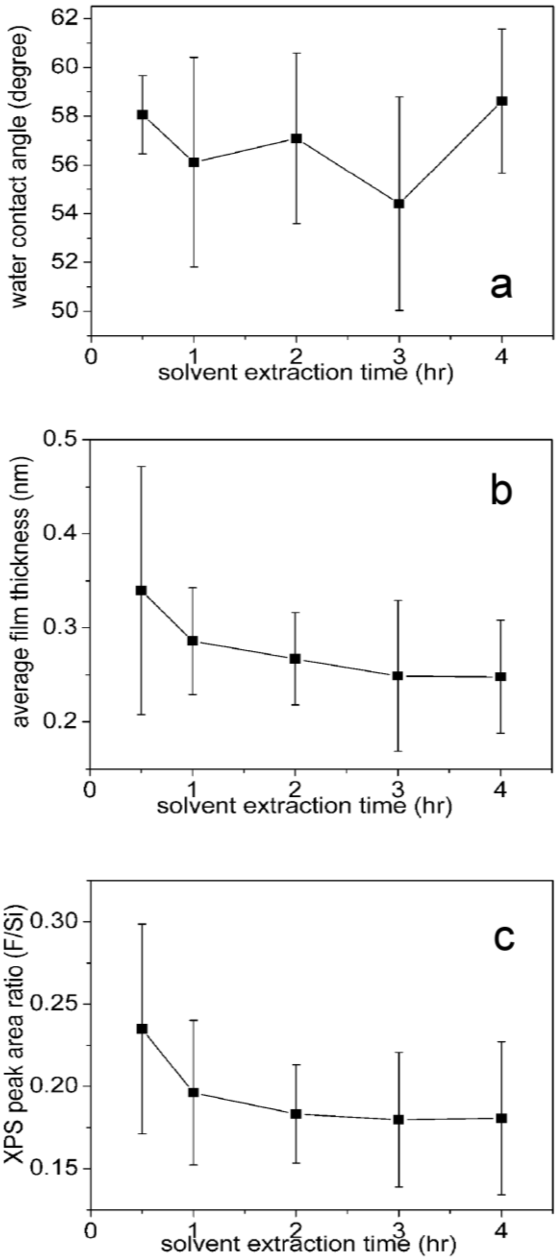

Figure B1. Perfluoroalkylsilane-based SAMs at different extraction times are assessed by (a) water contact angle measurements, (b) thickness from spectroscopic ellipsometry measurements and (c) normalized X-ray photoelectron spectroscopy (XPS) peak area for F1s. Four different positions were measured for each substrate, and data from at least three substrates were combined for each data point. The error bars were calculated as the standard deviation of at least 12 measured points.

Appendix C.

Atomic Force Microscopy (AFM) Images

Here atomic force microscopy (AFM) images are provided as a direct measure of the surface topography of samples modified with SAMs and after protein adsorption.

Before monolayer deposition, single-side polished (100) silicon wafers were cleaned by a freshly prepared piranha solution (a 7:2 (v/v) mixture of concentrated sulfuric acid and 30 % hydrogen peroxide). The piranha solution is used to remove residual organic contaminants from the surfaces of the silicon oxide coated substrate, as well as to decorate the surfaces with hydroxyl groups. Figures C1A and C1B show AFM images of the silicon substrate after piranha treatment. Figure C1B is over an area of 1μm x 1μm, which provides a higher resolution image of these surfaces.

Figures C1C and C1D show the cleaned silicon substrate was immersed into 1mM perfluoroalkylsilane toluene solution for deposition overnight at room temperature. This sample has silane deposited onto the silicon substrate and was imaged by AFM techniques without solvent extraction. The results indicate a different topography than that discussed in Chapter 3 (Figure 3.10A&C) for solvent extracted samples. The images from the non-extracted samples indicate the monolayer does not uniformly modify the surfaces, and forms island-like structures. Figure C1D is an AFM scan over an area of 1μm x 1μm.

Figures C1E and C1F show bovine serum albumin protein adsorption onto the silicon substrates coated with the perfluoroalkylsilane-based SAMs. These monolayers were not treated by solvent extraction prior to immersion in the protein containing solution. The gray regions indicate adsorbed protein. Figure C1F is an AFM scan over an area of 1μm x 1μm.

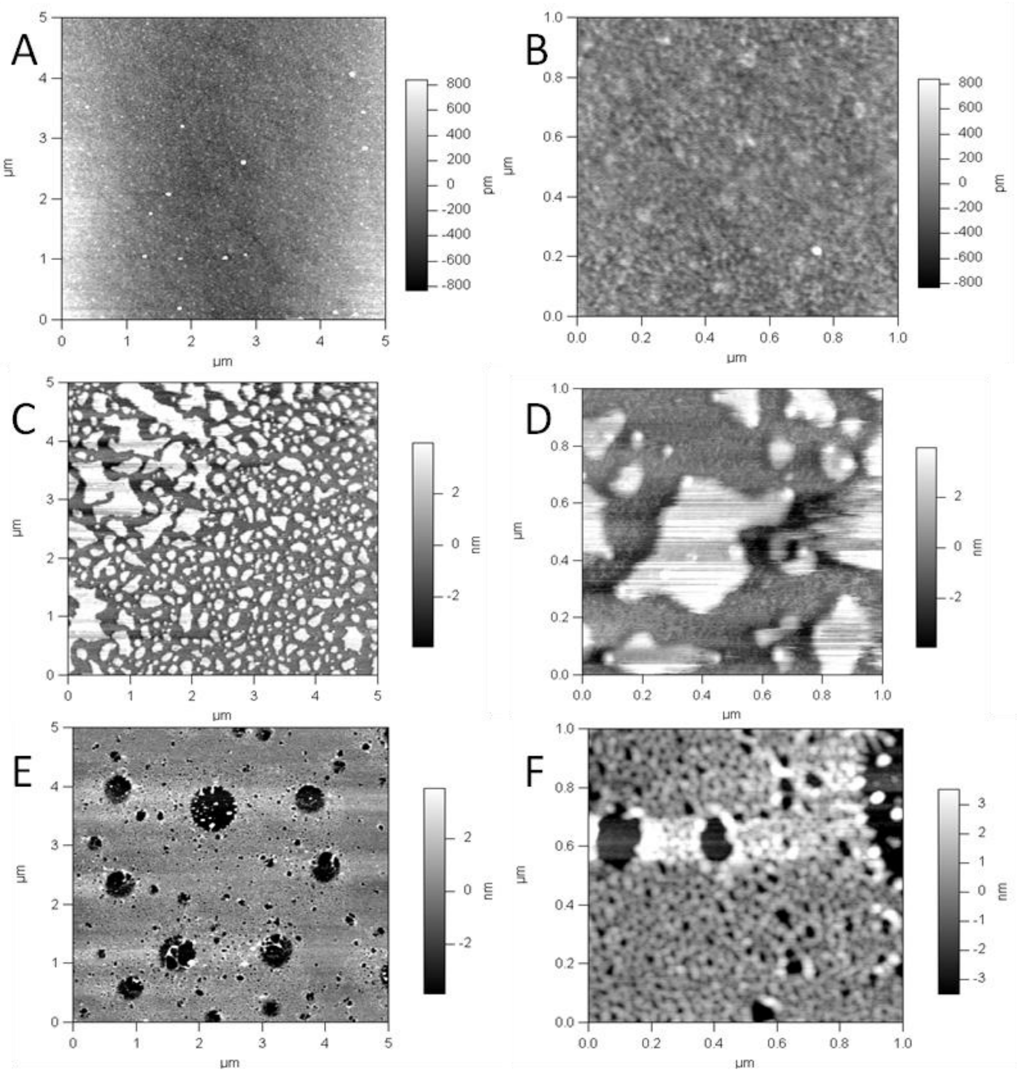

Figure C1. Atomic force microscopy images of (A) silicon substrate after piranha treatment (5μm x 5μm scan size for the image); (B) silicon substrate after piranha treatment (1μm x 1μm); (C) perfluoroalkylsilane based SAMs deposited onto the cleaned silicon substrate (5μm x 5μm); (D) perfluoroalkylsilane based SAMs deposited on silicon substrate (1μm x 1μm); (E) bovine serum albumin protein adsorption on the silicon substrate coated with perfluoroalkylsilane based SAMs (5μm x 5μm); (F) bovine serum albumin protein adsorption on the silicon substrate coated with perfluoroalkylsilane based SAMs (1μm x 1μm).