Probing the Hydration of Ultrathin Antifouling Adlayers using Neutron Reflectometry

by

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A thesis submitted in conformity with the requirements for the degree of Master of Science
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Abstract

Adverse interaction and subsequent adsorption of biomolecular species (i.e. fouling) pose a great hindrance for medical and clinical applications (e.g. biosensors). Research into the mechanism behind antifouling coatings have shown a strong link between surface hydration and antifouling behaviour due to the existence of a ‘water barrier’ which prevents proteins from adsorbing onto the surface. In a previous study, a short, mono(ethylene-glycol) silane adlayer (MEG-OH) showed significantly different antifouling behaviour in comparison to its homolog – lacking the internal ether oxygen (OTS-OH). In the present work, neutron reflectometry (and modeling) was used to investigate the water density profiles at MEG-OH and OTS-OH silane adlayers on quartz and Si/SiO₂ to determine whether the internal ether oxygen affects the adlayers’ interaction with water. Despite the limitations of studying such ultrathin organic films, the two systems showed different hydration profiles supporting the link between surface hydration and antifouling.
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# Table of Contents

Acknowledgments ........................................................................................................ iii

Table of Contents ........................................................................................................ iv

List of Tables ................................................................................................................ vii

List of Figures ................................................................................................................. viii

List of Appendices .......................................................................................................... xii

1 Introduction .................................................................................................................. 1

1.1 Biofouling ................................................................................................................. 1

1.1.1 Surface Hydration and Antifouling ...................................................................... 1

1.2 Purpose of Research ................................................................................................. 4

1.3 Theory ....................................................................................................................... 5

1.3.1 Silane Chemistry ................................................................................................. 5

1.3.2 Neutron Reflectometry ....................................................................................... 7

1.3.2.1 Data Analysis: Modeling with MOTOFIT ..................................................... 13

1.3.2.2 Abeles Matrix Method ............................................................................... 15

1.3.2.3 Neutron Reflectometry Instrumentation ..................................................... 16

1.3.3 X-ray photoelectron spectroscopy (XPS) ........................................................... 18

1.3.3.1 X-ray Photoelectron Spectroscopy Instrumentation ................................ 19

2 Materials and Methodology ....................................................................................... 21

2.1 General Remarks .................................................................................................... 21

2.2 Substrate Preparation ............................................................................................... 22

2.2.1 Quartz Cleaning .................................................................................................. 22

2.2.2 Silicon Wafer Oxidation and Cleaning ............................................................ 23

2.3 Organic Film Formation ........................................................................................ 23

2.4 Analytical Techniques ............................................................................................ 24
2.4.1 X-Ray Photoelectron Spectroscopy ................................................................. 24
2.4.2 Neutron Reflectometry ..................................................................................... 25
   2.4.2.1 Instrumental Set-up ................................................................................... 25
   2.4.2.2 Calculation of Reflectivity ....................................................................... 25
   2.4.2.3 Measurement Settings ............................................................................. 27
   2.4.2.3.1 Quartz .................................................................................................. 27
   2.4.2.3.2 Si/SiO₂ ............................................................................................... 29
2.4.3 Modeling ........................................................................................................... 30
   2.4.3.1 Quartz .................................................................................................... 31
   2.4.3.2 Si/SiO₂ ................................................................................................. 33
3 Results and Discussion ............................................................................................ 36
   3.1 X-ray Photoelectron Spectroscopy: Surface Characterization ......................... 36
      3.1.1 Quartz ..................................................................................................... 36
      3.1.2 Si/SiO₂ ................................................................................................. 40
   3.2 Neutron Reflectometry Analysis ........................................................................ 44
      3.2.1 Quartz ..................................................................................................... 45
         3.2.1.1 Measurements in Air ........................................................................ 45
         3.2.1.2 Measurements in Liquid ................................................................. 47
      3.2.2 Si/SiO₂ .................................................................................................. 53
         3.2.2.1 Measurements in Air ........................................................................ 53
         3.2.2.2 Measurements in Liquid ................................................................. 57
4 Conclusion .............................................................................................................. 64
5 Future Work ............................................................................................................ 65

References .................................................................................................................. 66

Appendix A: XPS Survey Spectra for Quartz and Si/SiO₂ Surfaces ............................. 71
List of Tables

Table 1. Parameters used in MOTOFIT for measurement of quartz substrate (with and without adlayers) in air. Parameters to be ‘fit’ have lower/upper limits shown in brackets. Corresponding model with initial value(s) in Figure 21.

Table 2. Parameters used in MOTOFIT for measurement of adlayers on quartz in nCMW. Parameters to be ‘fit’ have lower/upper limits shown in brackets. Corresponding model with initial values in Figure 22.

Table 3. Parameters used in MOTOFIT for measurement of Si/SiO$_2$ substrate (with or without adlayers) in air. Parameters ‘fit’ have lower/upper limits shown in brackets. Corresponding model with initial values in Figure 23.

Table 4. Parameters used in MOTOFIT for measurement of adlayers on Si/SiO$_2$ in CMW. Parameters ‘fit’ have lower/upper limits shown in brackets. Corresponding model with initial values in Figure 24.

Table 5. ARXPS results for quartz samples.

Table 6. ARXPS results for Si/SiO$_2$ samples.
List of Figures

**Figure 1.** Schematic depicting biofouling of a surface with various biological species (e.g. proteins, fibroblasts, cells) prior to and after modification with an antifouling coating (shown in red).

**Figure 2.** Schematic depicting single EG unit as well as hydrated PEG (e.g. n ~ 100) and OEG (e.g. n ~ 6) coatings grafted onto a surface (e.g. Au, Ag).

**Figure 3.** Schematic of MEG-OH and OTS-OH adlayers on SiO$_2$ substrates in water (D$_2$O/H$_2$O mixture). Arrow indicates direction of water density gradient (toward the bulk water composed of H$_2$O and D$_2$O).

**Figure 4.** Mechanism of SAM formation on a hydroxylated SiO$_2$ substrate.

**Figure 5.** (Coherent) nuclear scattering length values of various atoms.

**Figure 6.** Reflection of neutron beam at an interface with a film between two semi-infinite media ($n_2 > n_1$, $n_3 < n_2$).

**Figure 7.** Simulated reflectivity curve for bare silicon substrate (zero roughness) in comparison to $1/q^4$. Reproduced from Fritzsche, H., *Characterization of Materials* (Ref. 38).

**Figure 8.** Simulated reflectivity curve of 30 nm Ni and Cr films on Si substrate and bare Si substrate. Reproduced from Fritzsche, H., *Characterization of Materials* (Ref. 38).

**Figure 9.** (a) Diffuse neutron scattering from a rough interface and (b) corresponding Gaussian distribution at interface, z.

**Figure 10.** SLD profile of 30 nm Ni on Si substrate (SLD$_{Ni}$ = 9.42 x 10$^{-6}$ Å$^{-2}$) with a roughness of 10 Å at both interfaces.

**Figure 11.** (a) Model of a silicon substrate with a homogenous layer (‘Layer 1’) measured in D$_2$O. (b) Model parameters chosen to be fit by the program are shown in red.

**Figure 12.** Schematic of the D3 neutron reflectometer in Chalk River, ON.

**Figure 13.** Schematic of θ-2θ geometry used for NR experiments. Red arrow indicates incoming and reflected beam.

**Figure 14.** Schematic of the photoexcitation process of an electron in 1s orbital for an F atom in sequence. Also shown is an electron from an outer shell filling the K vacancy and subsequent ejection of an Auger electron (in red).

**Figure 15.** Diagram of XPS instrumentation using Al k $\alpha$ (1486.6 eV) X-ray source.

**Figure 16.** XPS output spectra. (a) Survey (wide) scan of a clean quartz disc and (b) narrow scan (C1s ~ 285 eV).
Figure 17. Photograph comparing the size of quartz samples used for XPS analysis (left) and NR measurements (right).

Figure 18. Various NR scan components used to generate a reflectivity curve (data obtained from scan of MEG-OH adlayer on quartz in H$_2$O/D$_2$O, SLD = 4.5 x 10$^{-6}$Å$^{-2}$). Dotted lines separate low -, mid -, and high-q scan regions.

Figure 19. Cell used for measuring samples in liquid solution. (a) Photograph of cell mounted vertically on sample platform showing liquid inlet (aerial view). (b) Diagram of cell sitting flat (horizontal view). Incoming and reflected neutron beam indicated by the red arrow. *Note: cell in (b) perpendicular to orientation during measurement.*

Figure 20. Reflectivity of quartz sample in nCMW (SLD = 4.5 x 10$^{-6}$ Å$^{-2}$) showing background subtraction techniques used for the high-q region.

Figure 21. Schematic of model used for quartz samples in air, parameter to be fit is outlined in red.

Figure 22. Schematic of models used for quartz samples in liquid (nCMW). (a) Case 1 assumes no interfacial water (adlayer = layer 1) and (b) Case 2 assumes interfacial water and adlayer (layer 1). Parameters in red and green boxes fit in phases I and II, respectively.

Figure 23. Schematic of model used for Si/SiO$_2$-based samples in air. Parameters in red and green boxes fit in Phases I and II, respectively.

Figure 24. Schematic of model used for adlayers on Si/SiO$_2$ in liquid (CMW). Parameters in red and green boxes fit in Phases I and II, respectively.

Figure 25. Summary of quartz samples analyzed using XPS.

Figure 26. F1s narrow scans of a) MEG-TFA and b) OTS-TFA and corresponding hydrolyzed adlayers on quartz (take-off angle= 72.5°).

Figure 27. C1s narrow scan of OTS-TFA and OTS-OH adlayers on quartz at a take-off angle of 72.5°.

Figure 28. Summary of Si/SiO$_2$ samples analyzed using XPS.

Figure 29. Narrow scan of the Si2p orbital at various take-off angles for the (a) Si wafer and (b) thermally oxidized wafer. Si peaks correspond to elemental silicon (Si$^0$) at 99.5 eV and oxidized silicon species (Si$^{n+}$) at 103 eV.

Figure 30. C1s narrow scan of MEG-TFA and MEG-OH adlayers on thermally grown Si/SiO$_2$ at a take-off angle 72.5°.

Figure 31. F1s narrow scans of a) MEG-TFA and b) OTS-TFA and corresponding hydrolyzed adlayers on thermally grown oxide (take-off angle = 72.5°).
Figure 32. (a) Reflectivity curves and corresponding fits for quartz substrate after cleaning once (1P) and twice (2P) with piranha solution (data fit with 0-layer model). (b) Corresponding SLD profiles for the two systems (shown from quartz to air).

Figure 33. (a) Reflectivity data and corresponding fits for bare quartz and film on quartz in air. Data is fit with 0-layer model. (b) Corresponding SLD profiles for the two systems (shown from quartz to air).

Figure 34. NR data and models resulting from phase I fit. (a) Case 1: Reflectivity data and corresponding fits for bare quartz as well as MEG-OH, OTS-OH adlayers on quartz in nCMW. (b) SLD profiles for bare quartz and MEG-OH, OTS-OH films on quartz (Case 1). (c) Case 2: Reflectivity data and fits for MEG-OH, OTS-OH adlayers on quartz in nCMW. (d) SLD profiles for bare quartz and MEG-OH, OTS-OH films on quartz (Case 2). Notes: Reflectivity curves contain $\chi^2$ values in brackets. SLD profiles are shown from the direction of quartz to nCMW. Interfacial water abbreviated to ‘IW’.

Figure 35. NR data and models resulting from phase II fit. (a) Case 1: Reflectivity data and corresponding fits for bare quartz as well as MEG-OH, OTS-OH adlayers on quartz in nCMW. (b) SLD profiles for bare quartz and MEG-OH, OTS-OH films on quartz (Case 1). (c) Case 2: Reflectivity data and fits for MEG-OH, OTS-OH adlayers on quartz in nCMW. (d) SLD profiles for bare quartz and MEG-OH, OTS-OH films on quartz (Case 2). Notes: Reflectivity curves contain $\chi^2$ values in brackets. SLD profiles are shown from the direction of quartz to nCMW. Interfacial water abbreviated to ‘IW’.

Figure 36. Reflectivity data and fits for a (a) bare and (b) thermally oxidized wafer ($d_{SiO_2} \sim 180$ Å thick) measured in air.

Figure 37. Effect of 30 min immersion time in piranha solution on Si/SiO$_2$. (a) Reflectivity data and fits (b) Corresponding SLD profiles (shown in the direction from Si/SiO$_2$ to air).

Figure 38. (a) Reflectivity data with fits ($\chi^2$ value shown in brackets) (b) Corresponding SLD profiles for MEG-OH and OTS-OH adlayers on Si/SiO$_2$ measured in air (SLD$_{SiO_2}$ allowed to fit). Red and blue dotted lines indicate the approximate location of the SiO$_2$/air interfaces for each substrate.

Figure 39. (a) Reflectivity data and fit with corresponding (b) SLD profile for Si/SiO$_2$ substrate (control) in CMW.

Figure 40. Reflectivity data and corresponding fits for the (a) MEG-OH adlayer on SiO$_2$ ($\sim 163$ Å-thick) and (b) OTS-OH adlayer on SiO$_2$ ($\sim 180$ Å-thick) measured in CMW. Fits correspond to 1- and 2-phase fits generated using 1-layer model encompassing film and interfacial water ($\chi^2$ value shown in brackets).

Figure 41. SLD profiles showing for MEG-OH and OTS-OH adlayers (films) on Si/SiO$_2$ (Si substrate not shown). Profiles correspond to 2-phase fit generated using a 1-layer model encompassing the film and interfacial water (IW). Dotted lines indicate approximate location of films. ‘Layer 1’ designates region modeled for ‘$d_1$’ for both
systems. Note: For direct comparison, the SLD baseline for MEG-OH was shifted by 
$-0.1 \times 10^6 \ \text{Å}^2$ and both SiO$_2$/layer 1 interfaces were aligned at ‘0 Å’.

**Figure 42.** Schematic of hydration profiles at MEG-OH and OTS-OH adlayers based on SLD profiles in **Figure 41.** The colour gradient is representative of relative water density (assuming constant composition of D$_2$O/H$_2$O).
List of Appendices

A. XPS Survey Spectra for Quartz and Si/SiO₂ Surfaces

B. NR Modeling Results for Quartz and Si/SiO₂ Surfaces
1 Introduction

1.1 Biofouling

The interaction of biological fluids (e.g. blood, urine) with synthetic surfaces is both essential and inevitable in medical and clinical fields. The adverse effects of biofouling can be seen with both in vivo and in vitro devices ranging from surgical implants to blood filtration systems employing materials such as stainless steel, titanium and plastics. Fouling can be described as the spontaneous interaction, adsorption and accumulation of biomolecules (e.g. proteins, cells) onto a surface.\(^1-3\) A great hindrance to the advancement of implantable biosensors as well as surgical implants is the fouling of surfaces with undesirable biological species. For implants such as stents, the body’s autoimmune response to foreign objects/surfaces begins with platelet adhesion and activation of the coagulation cascade leading to thrombosis and potential death due to embolism.\(^2,4\) Although such a risk is not a main concern with implantable biosensors, fouling of the transducer surface by proteins and cells is one of the main reasons preventing its full adoption and commercialization.\(^5\) In the context of biosensors, fouling (referred to as ‘non-specific adsorption’, or NSA) often results in a reduction in sensitivity, ‘false positives’, as well as an overall decrease in sensor performance. Unlike techniques which employ fluorescent or enzymatic probes (e.g. enzyme-linked immunoassay, ELISA), the reputation of devices relying on label-free detection (e.g. surface plasmon resonance and acoustic wave sensors) suffer considerably due to NSA when operating in a complex biological matrix.\(^6\)

1.1.1 Surface Hydration and Antifouling

The development of antifouling coatings has been an effective solution in which chemical modification of the surface reduces the adsorption of proteins and other blood-borne components (Figure 1).
Various types of antifouling coatings have been developed over the last few decades including amino acid-based coatings (e.g. peptoids), zwitterionic coatings (e.g. betaines), ethylene glycol (EG)-based coatings (e.g. PEG), and more recently, hybrid coatings such as glycopeptoids employing saccharidic species (mimicking the glycocalyx). Their structures have been characterized as being comb- and brush-like to dendronic with thicknesses ranging from as low as subnanometric to 40 nm-thick.

It has been generally accepted by the scientific community that the mechanism of antifouling is strongly linked to surface hydration. In summary, it is hypothesized that near the coating surface there exists a tightly bound layer of water forming a physical and energetic barrier preventing the adsorption of proteins on the surface. In order for adsorption to occur, water must be expelled from both the coating and the protein resulting in an overall reduction in free energy. Although several factors can influence antifouling capability, the primary factor is the strength of surface hydration. The most prevalent studies in this field are based on EG-based coatings (Figure 2), with some of the first antifouling studies focused on poly(ethylene glycol) (PEG). For such long chains, flexibility (affected by length and density) was used to argue that the ability to resist proteins has to do with steric repulsion – where compression of the polymer chains by the protein caused an unfavourable decrease in entropy. Due to the susceptibility of PEG to oxidation, the research community moved onto short-chain oligo(ethylene glycol) OEG-based coatings which were also shown to exhibit antifouling behaviour. Numerous studies
Figure 2. Schematic depicting single EG unit as well as hydrated PEG (e.g. n ~ 100) and OEG (e.g. n ~ 6) coatings grafted onto a surface (e.g. Au).

have since been performed on coatings incorporating OEG tails chemically bonded to long alkyl chains in the form of R–(CH₂)₁₁EGₙX, forming self-assembled monolayers (SAMs) (Figure 2). Protein resistance was studied as a factor of varying the following: (1) number of EGₙ units (n = 1-6), (2) terminal groups, X = –OH, –OMe, –OBu, (3) packing density, as well as (4) substrate type (e.g. Au vs. Ag).¹¹⁻¹³ A hydrophilic terminal group and longer EG chain (beyond the required minimum number of n > 2 EG units) in OEG SAMs were generally associated with improved the protein resistance.¹⁴ Overall, the combination of internal and terminal hydrophilicity along with a lower packing density were thought to maximize antifouling behaviour. Studies looking at the effect of Au and Ag substrates on the conformation of the OEG chains (e.g. planar, helical) found that OEG-SAMs on gold were more protein resistant due to a helical and ‘amorphous’ conformation (vs. all-trans structure on Ag).¹⁵ In all cases, however, the conditions (or physical properties) of the system resulting in the highest protein resistance were those which improved coating hydration: lower packing density, internal hydrophilicity, and conformational freedom. Despite all the evidence, the actual mechanism behind antifouling behaviour is still not entirely understood; thus, deeper investigation into the interfacial phenomena at such coatings is essential.

Interest in the solid/liquid interface of thin organic films has spawned extensive research employing a variety of analytical techniques such as atomic force microscopy (AFM)¹⁶, sum-frequency vibrational spectroscopy (SFM)¹⁷ and X-ray reflectivity (XRR).¹⁸ Among these, neutron reflectometry (NR) was particularly effective at elucidating interfacial effects of hydrophilic and hydrophobic surfaces in aqueous systems.¹⁹⁻²¹ In the past, NR has also been used
to study biologically relevant systems such as lipid bilayers, concentration profiles of surface-grafted DNA, as well as interactions of biomimetic materials with biological membranes. Neutron reflectometry is a technique used to probe layered materials with buried interfaces, providing information about their composition and distribution in space. Reflectivity from an interface is based on the neutrons interaction with the nuclei of the material and results in a measurement of the neutron refractive index profile normal to the surface. This refractive index is related to a property of the material called the scattering length density (SLD). Since the SLD is dependent on the atomic species and their distribution in space, it can provide information about the density of materials assuming the composition is known (e.g. H₂O). What distinguishes NR from other similar techniques (i.e. XRR), however, is its superior sensitivity to light atoms and scattering contrast between its isotopes, particularly, hydrogen and deuterium. For this reason, NR can be used to study properties of antifouling coatings relating to surface hydration as well as interfacial phenomena. Some of the first studies in this field looked at the structure, hydration and swelling of long PEG. In 2003, Schwendel et al. used NR to probe the water density profiles at various undecylthiolate SAMs terminated with EG groups. One such coating (-(CH₂)₁₁EG₃OMe) was found to have a 4 nm thick interfacial region with 85-90% bulk water density providing insight into the ‘water barrier’ theory. So far, NR has shown to be a useful technique for studying the solid/liquid interface, particularly for systems in aqueous solutions. Thus, the present technique will be used to look at several ultrathin (antifouling) coatings developed in our research group.

1.2 Purpose of Research

Recently, Sheikh and co-workers were able to monitor adsorption dynamics of serum onto various adlayers prepared on quartz using the electromagnetic piezoelectric acoustic wave sensor (EMPAS) – a device sensitive to changes in gravimetric and viscoelastic properties as well as interfacial phenomena (e.g. slip). When studying the ultrathin, monoethylene glycol-terminated adlayer (MEG-OH, Figure 3), a >15-fold reduction in frequency shift (in comparison to the bare quartz substrate) was observed. This magnitude in shift was associated with antifouling behaviour. Interestingly, its molecular homolog, which lacks the internal ether oxygen (OTS-OH), showed less dramatic results (~ 1.5 fold reduction) drawing attention to the role of this particular oxygen atom in antifouling behaviour. It was speculated that hydration of this adlayer
results in the formation of an intercalated water network or ‘special zone of hydration’ involving the internal ether oxygen and distal hydroxyl group preventing the adsorption of proteins. The purpose of the present work was to investigate the water density profiles at the MEG-OH and OTS-OH adlayers (normal to the surface) to determine the effect of the internal ether oxygen on the adlayers’ interaction with water; a schematic of the system under investigation is shown in Figure 3.

**Figure 3.** Schematic of MEG-OH and OTS-OH adlayers on SiO₂ substrates in water (D₂O/H₂O mixture). Arrow indicates direction of water density gradient (toward the bulk water composed of H₂O and D₂O).

Since neutrons are sensitive to water, a change in water density should be detected in the refractive index or, rather, in the alteration of the solutions’ SLD. From this, information pertaining to the relationship between antifouling behaviour and surface hydration could be gathered. The adlayers were first prepared on quartz followed by thermally oxidized silicon – a substrate more suitable to investigating such ultra-thin systems in water.

### 1.3 Theory

#### 1.3.1 Silane Chemistry

Functionalization of surfaces with organosilanes is usually associated with the microelectronics industry where modification of semi-conductor surfaces is performed for the purpose of micropatterning, or soft lithography. This group of molecules, however, has also been useful in
biosensor technology where they are used as platforms for the immobilization of biomolecules as well as antifouling coatings.\textsuperscript{31} Although there are many different types of organosilanes, the molecular species (or linkers) forming SAMs possess the following general structure:

$$X_3\text{Si}(\text{CH}_2)_n\text{R}$$

where X is considered to be the ‘head function’ of the molecule – usually a chloride (as in trichlorosilanes) or another reactive alkoxy group.\textsuperscript{30} The long alkyl chain is the ‘body’ of the linker and commonly contains $n=11$ repeating alkyl units which assist self-assembly process by interaction via van der Waals (VdW) forces.\textsuperscript{32} The last and most important part of the molecule, R, containing the terminal functionality and is known as the ‘tail’. Residing furthest from the surface, it tends to be functionalized in different ways depending on the desired surface properties (e.g. wettability) or application (e.g. biosensors). The chemisorption and eventual bonding of the trichlorosilane onto the substrate is a multistep process first described by Zisman\textsuperscript{33} (Figure 4) beginning with (1) the hydrolysis of the trichlorosilane in the liquid phase followed by (2) chemisorption onto the substrate via hydrogen bonding to hydroxyl (silanol) groups on the substrate. The SAMs begin forming in islands (nucleating) followed by re-organization and aggregation by VdW forces resulting in a densely packed, oriented monolayer.\textsuperscript{34} Lastly, (3) there is condensation and formation of a covalent bond to the substrate. Ideally, there is polymerization of neighbouring species via siloxane bonds resulting in a cross-linked SAM network (step B, Figure 4). Although cross-linking between individual species are known to occur, the extent of such events is limited by the terminal group (e.g. tail) due to steric effects.\textsuperscript{31-32} Many other factors affect the formation and final structure of SAMs such as the temperature, alkyl chain length, linker concentration and immersion/deposition time.\textsuperscript{30} The type of solvent as well as the amount of water within the solvent can also affect the film formation, which, in excess, can cause polymerization of linkers resulting in thick inhomogeneous films. Thus, many perform such silanization reactions under inert conditions (e.g. $N_2$ atmosphere).
**Figure 4.** Mechanism of SAM formation on a hydroxylated SiO\(_2\) substrate.

Although the molecular linkers used to prepare the MEG-OH and OTS-OH adlayers are organic trichlorosilanes, their alkyl chains are quite short (n = 3 – 6) and thus, they are not considered to be ‘SAMs’ (hence, they are referred to as ‘films’ or ‘adlayers’). The factors affecting the silanization or film formation, however, are still relevant and applicable to the systems investigated.

### 1.3.2 Neutron Reflectometry

The scattering of neutrons by matter is determined by an element’s (and its isotopes) scattering length and corresponding scattering and absorption cross section\(^{35}\). Though the relationship between these parameters is complex, the scattering length (b), in particular, has significant impact on the interaction of the incoming neutron with the nucleus. Their relationship is generally described by the Fermi pseudopotential (assuming the Born approximation):

\[
V(r) = \frac{2\pi \hbar^2}{m} b \delta(r) \quad (1)
\]

where \(r\) is the distance from the neutron to the nucleus, \(m\) is the neutron mass, and \(\hbar\) is Planck’s constant.\(^{35}\) Both, the nucleus and the neutron have a spin and thus, the Fermi potential is spin dependent – this contributes to the so-called incoherent scattering of neutrons by nuclei. The effective scattering length also includes magnetic contributions from the sample but will not be further discussed due to the use of unpolarized neutrons in the present work.\(^{35}\) Corresponding values of \(b\) for various atoms are shown in Figure 5.
Figure 5. (Coherent) nuclear scattering length values of various atoms. Values obtained from Ref. 36.

Comparing the values in the table it is evident that the b values do not necessarily follow a trend and more importantly, isotopes have differing b values (in some cases even negative).\textsuperscript{36} This is advantageous as it means neutrons are sensitive to the presence of light elements such as hydrogen (\textsuperscript{1}H) and deuterium (\textsuperscript{2}H or \textsuperscript{2}D) which are otherwise difficult to observe. It is worth stressing the significance of the opposing signs between the b values of \textsuperscript{1}H and \textsuperscript{2}D in the present section as it is essential to the understanding of the concept of contrast variation (discussed further on).

In essence, the purpose of a neutron reflectometry experiment is to measure the reflection of neutrons as a function of wave vector ($k$), perpendicular to the reflecting surface (Figure 6).\textsuperscript{25,37-38} For the specular reflection of neutrons the reflectivity is measured as a function of $q_z$, the scattering vector,

$$|q_z| = |k_s - k_o| = \frac{4\pi}{\lambda} \sin \theta_o \quad (2)$$

where $\lambda$ is the neutron wavelength (2.37 Å) and $k_o$ and $k_s$ are the wave vectors of the incoming and reflected beam, respectively. Within the typical q ranges of a neutron reflectometry experiment, reflectivity is measured as a function of incoming angle, $\theta_o$ (see equation 2) usually varying between 0 and 2°.\textsuperscript{38}
Figure 6. Reflection of neutron beam at an interface with a film between two semi-infinite media \((n_2 < n_1, n_2 < n_3)\).

Analogous to electromagnetic waves, the behaviour of the neutron beam can be explained by equations used in classic optics, in which the interaction with matter is given by the index of refraction:

\[
n = \sqrt{1 - \frac{\lambda^2}{\pi \rho}} \quad (3)
\]

where \(\rho\) designates the SLD of the interacting medium.\(^{38}\) The SLD is a product of the scattering length \((b)\) and atomic density \((N)\), which, for mixed media is defined by:

\[
SLD = \rho = \sum_j N_j b_j \quad (4)
\]

in which the interaction of the neutron with various nuclei \((j)\) in a given space is the principle of the NR technique. For a pure material comprised of only one type of nuclei (e.g. amorphous silicon) the SLD is a product of \(^{14}\text{Si}\)’s scattering length and its density (solid state). For more complex materials – where molecular composition and distribution in space varies, the SLD can be very similar to adjacent materials in the system under investigation. Contrast matching (or variation) is a technique used in NR where the SLD of the medium is controlled by varying \(N_j\) of the components. For \(\text{H}_2\text{O}\) and \(\text{D}_2\text{O}\) the calculated SLDs are \(-5.60 \times 10^{-7} \text{ Å}^{-2}\) and \(6.33 \times 10^{-6} \text{ Å}^{-2}\), respectively.\(^{39}\) Through mixing the two in different ratios the SLD can be varied allowing for matching of the SLD to another material, e.g. substrate. This is advantageous since improved contrast between adjacent media increases the sensitivity of neutron reflection at an interface. As
in optics, the index of refraction determines the reflection and transmission of neutrons depending on the angle of incidence:

\[ n = \frac{\cos \theta_o}{\cos \theta_s} \]  
(5)

where the angle, \( \theta_s \), denotes the angle of the *refracted* (transmitted) beam relative to the sample surface (Figure 7). As in Snell’s law, the neutron experiences total external reflection in the medium with the larger index of refraction below the critical angle, approximated by:

\[ \theta_c \approx \frac{\lambda}{\sqrt{n}} \]  
(6)

Unlike light, the neutron index of refraction is usually smaller than that of air (\( n = 1 \)) and as a result of the weak interaction between neutrons and nuclei, values of \( n \) do not deviate significantly from 1, usually \( n \approx 1 - 10^{-5} \). Thus, the critical wave vector, \( q_c \), can be simplified as:

\[ q_c \approx 4 \sqrt{\pi \rho} \]  
(7)

When \( q > q_c \) (or \( \theta > \theta_c \)) reflectivity of neutrons can be calculated using Fresnel’s reflectivity equation, which for a single interface is defined by:

\[ R = \left| \frac{\sin \theta_o - n \sin \theta_s}{\sin \theta_o + n \sin \theta_s} \right|^2 \]  
(8)

Since reflectivity drops quickly at large \( q \), \( R \) is plotted on a logarithmic scale (Figure 1.7). For a system with a single interface (between two semi-infinite media) the reflectivity curve is usually featureless and quickly drops off at high \( q \) (\( R = 1/q^4 \)).
Figure 7. Simulated reflectivity curve for bare silicon substrate (zero roughness) in comparison to $1/q^4$. Reproduced from Fritzche, H., *Characterization of Materials* (Ref. 38).

Upon addition of a homogeneous slab (layer) with thickness, $d$, the transmitted neutrons are further reflected/refracted at the next interface.\textsuperscript{25,35} For a system with a single slab, $j$, between two semi-infinite media, the reflectivity coefficient for the interface is defined by:

$$ r_{ij} = \frac{p_i - p_j}{p_i + p_j} \quad (9) $$

$$ p_i = n_i \sin \theta_0 \quad (10) $$

where the optical path length of neutron in the slab, $j$, with thickness, $d$, is:

$$ \beta_j = \frac{2\pi}{\lambda} n_1 d \sin \theta_0 \quad (11) $$

Thus, total reflectivity is defined by:

$$ R = \left| \frac{r_{01} + r_{12} e^{i\beta_1}}{1 + r_{01} r_{12} e^{2i\beta_1}} \right|^2 \quad (12) $$

Figure 8 shows reflectivity curves of various films of the same thickness on a silicon wafer. The oscillations present in the Ni and Cr reflectivity curves are called Kiessig fringes which are a
result of interference of the neutron beam reflected at the surface and a buried interface. The periodicity is largely dependent on the thickness of the slab, $\Delta q \approx 2\pi/d$. The maxima and minima of the fringes correspond to the constructive (in phase) and destructive (out of phase) interference of the reflected neutrons waves, respectively (Figure 8).\textsuperscript{38} Conversely, the amplitude of the fringes is proportional to the difference between SLDs of the adjacent layers where higher contrast results in enhanced sensitivity and distinct features in the reflectivity curve.

![Figure 8. Simulated reflectivity curve of 30 nm Ni and Cr films on Si substrate and bare Si substrate. Reproduced from Fritzsche, H., Characterization of Materials (Ref. 38).](image)

The quality of the reflectivity curve can also be attributed to the quality of the sample which is crucial to the success of the NR experiment. Since the measured intensity is collected as an average, any inhomogeneity in the sample may result in misinterpretation of data, specifically (i) unequal substrate or layer thickness across the sample (large scale) and (ii) surface and/or film interface roughness (small scale).\textsuperscript{35} Roughness can be attributed to the nature of the substrate/layer (inherent) but can also vary based on the mode of deposition or treatment of the sample. For a given depth, $z$, the interfacial roughness or interdiffusion (between two layers) results in an averaged SLD value over a large surface.\textsuperscript{35} The application of the Névot-Croce factor to the interface, $j$ (assuming a flat distribution of the surface, $x$), allows for the two interfaces to be represented by a single model as an error function:
\[ \text{erf} \left( \frac{z-z_j}{\sigma_j} \right) = \frac{2}{\sqrt{\pi}} \int_{0}^{(z-z_j)/\sigma_j} e^{-t^2} dt. \] (13)

where \( \sigma_j \) is the inverse value of the slope at the point of inflection \((z_j)\) on the described curve.

This factor (essentially the root mean square - roughness) is further refined by the Debye-Waller factor, which is then multiplied by the reflectivity at a perfectly smooth surface:

\[ R_{\text{rough}} = R_{\text{ideal}} e^{-2kz_j^j k_{j+1}^j \sigma_j^j \sigma_{j+1}^j} \] (14)

Though it is unlikely that an interface is perfectly smooth, roughness is usually treated as a small deviation from layer or substrate thickness (Figure 9).

\[ \sigma \]

**Figure 9.** (a) Diffuse neutron scattering from a rough interface and (b) corresponding Gaussian distribution at interface, \( z \).

Since \( \sigma_j \) is the error function of layer \( j \), it should not be greater than \( 1/3 \)rd of the actual layer thickness \( (d) \). At low \( q \), the reflectivity curve seems unaffected. However, with increasing \( q \), the oscillations (Kiessig fringes) are dampened and details of the curve (sharpness) diminish (Figure 8).

1.3.2.1 Data Analysis: Modeling with **MOTOFIT**

Though the reflectivity curve is the main point of interest, the objective of an NR experiment is to obtain an SLD profile (Figure 10) which shows the SLD of the various layers as a function of distance (normal to the surface). The SLD profile allows for the visualization of the system under investigation in real space. It is, however, impossible to perform data inversion since the phase information is lost in the final reflectivity curve. It is, however, possible to simulate the same reflectivity curve from two completely different SLD profiles. Thus, the majority of NR data are
analyzed via modeling, using models that make physical sense and take into account additional information such as the material properties.

**Figure 10.** SLD profile of 30 nm Ni on Si substrate (SLD$_{Ni} = 9.42 \times 10^{-6}$ Å$^{-2}$) with a roughness of 10 Å at both interfaces.

*MOTOFIT* is a model-fitting program which aids in the fitting of X-ray and neutron reflectivity data. Though it offers several computational advantages over other fitting software/programs, its greatest feature is the simple graphical user interface (GUI) - which allows less experienced users to exploit its features. Analogous to other such programs, the interpretation of reflectivity data is achieved by simulating a reflectivity curve through the generation of a model followed by comparison to the experimental reflectivity data (chi – squared analysis, $\chi^2$). Figure 11 shows a typical model of a layered system and corresponding parameters used to simulate a reflectivity curve (and SLD profile).

<table>
<thead>
<tr>
<th>Layer</th>
<th>d (Å)</th>
<th>SLD (x 10$^{-6}$ Å$^{-2}$)</th>
<th>σ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>$\infty$</td>
<td>6.33</td>
<td></td>
</tr>
<tr>
<td>Layer 1</td>
<td>$d_1$</td>
<td>SLD$_1$</td>
<td>$\sigma_b$</td>
</tr>
<tr>
<td>Substrate</td>
<td>$\infty$</td>
<td>4.18</td>
<td>$\sigma_Q$</td>
</tr>
</tbody>
</table>

**Figure 11.** (a) Model of a silicon substrate with a homogenous layer (‘Layer 1’) measured in D$_2$O. (b) Model parameters chosen to be fit by the program are shown in red.
In *MOTOFIT*, a minimum of five variables/parameters are used to calculate a reflectivity curve - they include the SLD \((\rho)\), thickness \((d)\), and roughness \((\sigma)\) values of the substrate and experimental medium (e.g. air, \(D_2O\)) as well as the instrumental scale factor and sample background. The parameters listed are usually known while the parameters of the layer(s) (e.g. \(SLD_1, \sigma_{1-B}\) and \(d_1\)) are varied by the program to fit the data in the experimental reflectivity curve (minimize \(\chi^2\)).\(^{40}\) The process of ‘fitting’ data allows for inferring about the physical parameters of the actual sample through comparison of reflectivity curves. Like most other software, *MOTOFIT* allows the user to select the parameters to be fit, however, it also allows the user to set lower and upper limits for the values of each parameter providing the advantage of a more realistic fit. The method of fitting the simulated curve to the experimental curve is difficult and becomes significantly more complex upon addition of a second layer. Thus, assumptions must be made about the parameters of that layer to provide a reasonable starting point for the program to begin fitting. Ultimately the direction of the fit depends on the initial parameters, the lower and upper limits set by the user as well as in which order and combination the parameters are fit. For this reason, several plausible models may exist for the same reflectivity curve. Regardless, the user should be able to recognize and reject an unlikely model irrespective of the \(\chi^2\) value.

1.3.2.2 Abeles Matrix Method

*MOTOFIT* uses the Abeles Matrix method\(^{41}\) to calculate specular reflectivity (of neutrons or X-rays) from a stratified medium.\(^{40}\) This package provides results identical to those produced by L.G. Parratt’s recursion formula\(^{42}\) - the most commonly used algorithm by various reflectivity software.\(^{38}\) In the Abeles method, the system is split into \(n\) layers. The wave vector of the incident neutron beam, \(k_n\), for each layer is defined by:

\[
k_n = \sqrt{k_0^2 - 4\pi (\rho_n - \rho_0)} \quad (15)
\]

where \(k_0 = q/2\) is the wave vector perpendicular to the surface which, together with \(z\) constitutes the phase of the neutron wave in space. Reflectivity at the \(n, n+1\) interface is described by the Fresnel coefficient,

\[
r_{n,n+1} = \frac{k_{z,n} - k_{z,n+1}}{k_{z,n} + k_{z,n+1}} e^{-2k_{z,n} k_{z,n+1} \sigma_{n,n+1}^2} \quad (16)
\]
The present algorithm also incorporates the previously described roughness within individual reflectivity coefficients, \( r_{n,n+1} \). A phase factor, \( \beta = ik_n d_n \), takes the thickness, \( d_n \), into account and is included in each layer. With this, a characteristic matrix \((c_n)\) is calculated (for every layer):

\[
c_n = \begin{bmatrix}
e^{\beta_n} & r_{n,n+1} e^{\beta_n} \\
r_{n,n+1} e^{-\beta_n} & e^{-\beta_n}
\end{bmatrix}
\] (17)

The resultant matrix, \( M \), is defined as the product of \( c_n \) – from which the reflectivity, \( R \), is calculated:

\[
M = \prod_{n=0}^{N} c_n \quad (18)
\]

\[
R = \frac{|M_{21}|^2}{|M_{11}|} \quad (19)
\]

1.3.2.3 Neutron Reflectometry Instrumentation

The D3 neutron reflectometer uses neutrons generated at the National Research Universal (NRU) reactor located in Chalk River, ON, Canada. Neutrons are generated by nuclear fission of uranium \((^{235}\text{U})\) upon collision with a slow-moving neutron. Each fission releases \( \sim 200 \text{ MeV} \) of energy, distributed between heavy fragments and a number of neutrons (on average 2.5). A fission reaction generally takes the following form:

\[
^1\text{n}_{\text{slow}} + ^{235}\text{U} \rightarrow ^{236}\text{U} \rightarrow ^{141}\text{Ba} + ^{92}\text{Kr} + 3^1\text{n}_{\text{fast}}
\]

where the fission products include two new nuclei, barium and kryptonite, along with 3 fast neutrons.\(^{43}\) The ejected (fast–moving) neutrons, however, are required to lose energy in order to restart the process of nuclear fission. Slow–moving neutrons are produced following multiple collisions with heavy (deuterated) water, which is used as a moderator in the CANDU (CANada Deuterium Uranium) reactor.

A diagram of the D3 set up (Figure 12) shows the pathway of the neutron beam from the source to the detector.\(^{38}\) The neutrons first hit a pyrolitic graphite monochromator (M) directing them with a wavelength of 2.37 Å towards the first and second set of slits (S1, S2) which determine beam collimation and establish the beam footprint on the sample. The instrument
operates with vertical sample mount (i.e. horizontal scattering plane) with the sample and detector setup in a θ-2θ geometry (Figure 13) in order to measure the specular reflectivity.

**Figure 12.** Schematic of the D3 neutron reflectometer in Chalk River, ON.

**Figure 13.** Schematic of θ-2θ geometry used for NR experiments. Red arrow indicates incoming and reflected beam.

The angular resolution and wavelength resolution (dependant on crystal mosaicity) determine the error in \( \mathbf{q} \), which defines the overall instrumental resolution.

\[
\left( \frac{\Delta q}{q} \right)^2 = \left( \frac{\Delta \lambda}{\lambda} \right)^2 + \left( \frac{\Delta \theta}{\theta} \right)^2 \tag{20}
\]
where $\Delta \theta$ is determined by the distance $D$ between slits 1 and 2 and their individual opening width (S1, S2).  

\[
\Delta \theta = \frac{S1 + S2}{2D} \quad (21)
\]

The detection of the reflected beam intensity is monitored by slits 3 and 4 (S3, S4) which are used for background reduction (Figure 12-13). The reflected intensity is measured by means of a 32-wire $^3$He gas proportional detector allowing for observation of the signal distribution. Upon interacting with neutrons, the $^3$He gas is ionized (below).

\[
n + ^3\text{He} \rightarrow ^3\text{H} + ^1\text{H} + 0.764 \text{ MeV}
\]

The application of a potential allows for the electrons to travel toward the anode resulting in the production of an electronic signal. The proportional counter operates at a higher applied potential which increases ionization resulting in amplification of the ion current. The current is then recorded as ‘neutron count’, which is the basis of the reflectivity measurement. Although there are multiple wires/anodes (exactly 32), usually 3 wires are chosen to record the actual signal (depending on the S3 and S4 slit settings). The spatial distribution of these neutron counts can be described with a Gaussian curve with a full width at half max (FWHM) of about 1.5 mm.

### 1.3.3 X-ray photoelectron spectroscopy (XPS)

Though the discovery of the photoelectric effect by Hertz occurred more than a century ago, it was Siegbahn and co-workers who pioneered the development of XPS as an analytical technique in the late 1950’s. Today, contributions of this surface sensitive technique can be seen in the fields of physics, corrosion chemistry, materials chemistry and more recently, biotechnology. The diverse applications of XPS are a consequence of the various levels of information that can be obtained, including: elemental composition (accurate to 0.01–0.3 atomic % depending on the element), depth profiles and chemical/electronic states of atoms. It is considered to be highly surface-sensitive with an effective probing depth of 1-10 nm across an area on the micrometer scale up to 1 cm$^2$. The basic principle of XPS is rooted in the photoelectric effect where interaction of an X-ray photon with a sample causes the excitation and subsequent ejection of a core-level photoelectron, shown in Figure 14.
Figure 14. Schematic of the photoexcitation process of an electron in 1s orbital for an F atom in sequence. Also shown is an electron from an outer shell filling the K vacancy (dotted line) and subsequent ejection of an Auger electron (in red).

Though the relaxation process of Auger emission is a natural occurrence, XPS is focused mainly on determining the atomic binding energy of the species, $E_B$, which is the energy required (relative to the Fermi level) to remove an electron from a solid.\(^46\) In treating the event as an elastic collision, the kinetic energy of the photoelectron, $E_K$, can be related to $E_B$ by the conservation of energy equation:

$$E_K = h\nu - E_B - \phi \quad (22)^{46}$$

where $h\nu$ is the X-ray photon energy and $\phi$ is the spectrometer work function, both which are known. The binding energy of the electron is then determined by measurement of the kinetic energy upon correcting for the spectrometer work function. Although the $E_B$ value is inherent and essentially identifies an atomic species, it is susceptible to small shifts due its local electronic environments providing insight into the chemical surroundings of the target atom (i.e. bonding).\(^{46}\)

1.3.3.1 X-ray Photoelectron Spectroscopy Instrumentation

An example of an XPS set-up and individual components is shown in Figure 15. The X-ray source is usually designed with twin anode configuration utilizing either Al or Mg producing a
Kα beam with radiation energy of 1486.6 eV or 1253.6 eV, respectively. The photon beam passes through a quartz monochromator and hits the sample - which is contained in an ultra-high vacuum (UHV) chamber.

**Figure 15.** Diagram of XPS instrumentation using Al Kα (1486.6 eV) X-ray source

The sample lies on a platform which can be rotated (for ARXPS). This can be utilized such as for angle-resolved XPS, which is used to determining distributional information of atoms or for depth profiling. The ejected photons pass through a series of lenses (allowing for determining the area to be analyzed) after which they are directed toward the hemispherical sector analyzer (also in UHV environment). By varying the voltage applied to the hemispheres, it is possible to select the energy of the electrons that will reach the channel electron multiplier (detector). The detected electrons are then recorded in counts/s as a function of binding energy and can be used for quantitative analysis based on individual peak areas determining the relative atomic concentration. Figure 16 shows the type of data output from a typical XPS experiment - both spectra display electron count/peak intensity as a function of binding energy (eV). The survey (wide scan) is a summary of all the elemental species present in the sample (within the measured range) while the narrow scan provides individual peak spectra (e.g. C1s in Figure 1.16 b) allowing for extraction of more detailed information about the particular elemental species. This
will mainly be utilized for characterization of surface modification via silane chemistry as well as Si/SiO₂ substrate characterization.

![Figure 16. XPS output spectra. (a) Survey (wide) scan of a clean quartz disc and (b) narrow scan (C₁s ~ 285 eV).](image)

2  Materials and Methodology

2.1  General Remarks

Glassware for silanization was pre-treated overnight with a 1/20 (v/v) solution of octadecyltrichlorosilane (OTS) in anhydrous toluene. Preparation of 100 mm-diameter samples was performed in large Pyrex petri dishes (125 mm in diameter, 65 mm deep). Concentrated sulfuric acid was purchased from ACP Chemicals Incorporated. Hydrogen peroxide (30%), methanol and chloroform were purchased from Fisher Scientific and chemicals including methanol, toluene, anhydrous toluene, and OTS were purchased from Sigma-Aldrich®. MEG-TFA and OTS-TFA silane linkers were synthesized and provided by Dr. Christophe Blaszykowski (available in Ref. 1). Heavy water (D₂O) used to prepare the testing solutions for neutron reflectometry measurements was provided by Chalk River Laboratories, Atomic Energy Canada Limited. Quartz discs [AT-cut, 100 mm in diameter and 5000 mm thick (± 500 µm)] were purchased from Laptech Precision Inc., Bowmanville, ON, Canada. Quartz silanization was performed at the University of Toronto using a glovebox maintained under inert (N₂) and anhydrous (P₂O₅) atmosphere. Silicon wafers [(111) ± 0.5°, n-type, phosphorus-doped, R = 20-40 Ω-cm, 100 mm in diameter and 5000 µm thick (± 500 µm)] were purchased from University Wafers, Boston, MA, USA. Si wafers were prepared at Chalk River Laboratories, Chalk River,
ON, Canada. Silanization was performed in an in-house Plexiglas® glove box maintained under inert (N₂) atmosphere. The furnace used for oxidation was manufactured by Thermolyne Corp., Dubuque, IA, USA (Model F–A1620).

For practical reasons as well as restrictions on XPS sample size, small-scale quartz discs and Si wafers were used for XPS analysis (Figure 17). All samples were prepared in test tubes (13.5 mm diameter) and the volume of solvents used was scaled down accordingly. Quartz discs (AT-cut, 20 MHz, 13.6 mm in diameter) were purchased from Laptech Precision Inc. Thin Si wafers [(111) ± 0.5°, n-type, phosphorus-doped, R = 320-480 Ω-cm, 100 mm in diameter and 525 μm thick] were purchased from University Wafers and cut into 10 x 10 mm pieces (approximately) by hand using a diamond cutter. The furnace used for oxidation of the small Si samples was manufactured by Hevi Duty Electric, Milkwaukee, WI, USA (Model 321-T).

Figure 17. Photograph comparing the size of quartz samples used for XPS analysis (left) and NR measurements (right).

2.2 Substrate Preparation

2.2.1 Quartz Cleaning

Quartz cleaning was performed according to protocol in Ref. 29. Quartz discs were first sonicated in 300 mL of concentrated liquid soap for 30 min. They were then copiously rinsed with hot water followed by distilled water, then dried with forced air. Next, the discs were individually soaked in piranha solution (3:1 v/v mixture of 98% H₂SO₄ and 30% H₂O₂) pre-heated to 90°C using a water bath (CAUTION: Piranha solutions are corrosive. Handle with care). After 30 min, the discs were removed from solution, set aside to cool (30 min) then
thoroughly rinsed with distilled water (x3) followed by methanol (x3). The discs were next
sonicated in methanol for 2 min then individually transferred into an oven maintained at 150°C.
After 2 h, they were removed from the oven to cool for 15 min. Finally, the discs were
transferred into a humidity chamber (80 % RH, rt) and set aside overnight.

2.2.2 Silicon Wafer Oxidation and Cleaning

Silicon wafers were placed in a furnace maintained at 850 °C and oxidized in an ambient
atmosphere to obtain an approximate oxide thickness between 160 Å and 190 Å. The wafers
were allowed to cool at room temperature (30 – 45 min) followed by copious rinsing with
deionized water after which they were dried with ultrapure N₂. Next, the wafers were rinsed with
toluene (x3) followed by chloroform (x3) and thoroughly dried (N₂). Lastly, the wafers were
rinsed with methanol, dried with N₂, and stored in a humidity chamber (Mg(NO₃)₂ – 6H₂O, rt)
overnight.

2.3 Organic Film Formation

Silanization of the quartz and Si/SiO₂ substrates were replicated from Ref. 29 with the surface
modification protocol summarized in Scheme 1, below. The quartz discs and oxidized Si wafers
were transferred from the humidity chamber to a Petri dish and transported into the glovebox.
MEG-TFA or OTS-TFA surface modifiers (75 μL) were first diluted with anhydrous toluene (50
mL) in a graduated cylinder. The resulting solution was then poured onto the quartz disc
followed by an additional 25 mL of anhydrous toluene (used to rinse the graduated cylinder).
The Petri dish was then covered with a watch glass, sealed around the circumference using
Parafilm®, removed from the glovebox and placed on a spinning plate for 60 min. Next, the discs
were thoroughly rinsed with toluene (x3) then sonicated in another portion for 5 min. After a
final rinse with toluene, the previous procedure was repeated with chloroform. Immediately after
drying under a gentle stream of nitrogen, the discs were individually soaked in 75 mL of a 1/1
(v/v) solution of methanol and deionized water overnight at room temperature on a spinning
plate for hydrolysis of the silane (MEG-TFA or OTS-TFA). The discs were then rinsed with
methanol (x3) and dried under a stream of N₂.

For the significantly smaller XPS samples, a 10 mL solution of neat silane in toluene
[1/1000 (v/v)] was prepared in a graduated cylinder and 1 mL was transferred into the test tube
containing the sample. The volume of MeOH/H$_2$O in the hydrolysis step was also reduced to 1 mL.

Scheme 1. Protocol for the formation of MEG-OH and OTS-OH adlayers on (a) quartz (e.g. MEG-TFA silane linker) and (b) Si/SiO$_2$ (e.g. OTS-TFA silane linker).

2.4 Analytical Techniques

2.4.1 X-Ray Photoelectron Spectroscopy

Angle-resolved XPS was performed using the Thermo Scientific Theta Probe (Thermo Fisher Scientific, East Grinstead, United Kingdom) by Peter Brodersen at Surface Interface Ontario, Toronto, ON, Canada. An Al K$_\alpha$ probe (1486.6 eV) was used to investigate a 400 µm spot size at take-off angles of 27.5°, 42.5°, 57.5°, and 72.5° relative to normal. A wide (survey) scan was performed followed by narrow scans of C1s, O1s, Si2p, and F1s peaks. Data analysis was performed using accompanying Avantage software (Thermo Fisher Scientific). All binding energy peak positions were calibrated by shifting the C1s peak to 285.0 eV.\textsuperscript{46}
2.4.2 Neutron Reflectometry

2.4.2.1 Instrumental Set-up

Neutron reflectometry measurements were performed on the D3 neutron reflectometer at the National Research Universal (NRU) reactor in Chalk River, ON, Canada. To perform a reflectivity scan the sample first had to be mounted and aligned with the detector to maximize the reflected beam intensity. The instrument and sample were aligned similarly to the outlined protocol in Ref. 38. The alignment procedure is as follows: (1) the sample table is aligned so that the centre of rotation is in the centre of the neutron beam. (2) The detector is aligned (set to $\theta - 2\theta = 0^\circ$) by scanning it through the neutron beam and determining the centre of the measured curve (determined by the distribution of neutron counts). (3) Next, the sample is set to $\theta$ and the detector is moved to $2\theta$ (usually around 0.08° and 0.16°, respectively). Since the position of the sample is unknown, the sample is rotated at angles below and above $\theta$ ($\pm 0.01^\circ$) in order to find the signal maxima and establish the correct $\theta$ value. (4) Again, the sample is moved in the x-direction and ‘refined’ to maximize reflectivity now with the sample and detector in their appropriate configuration. Steps 3 and 4 are repeated until a Gaussian distribution of neutron count is obtained for all scans with lowest FWHM. (5) Lastly, the sample’s tilt angle is varied to further maximize the reflected intensity. The alignment for samples in liquid is the same as described.

2.4.2.2 Calculation of Reflectivity

To generate a reflectivity curve adequate for interpretation, additional measurements and further processing had to be performed. The reflectivity data from measurement of the sample contains high background signal and is not corrected for loss of beam intensity when the neutron beam is passing through the quartz or Si wafer (substrate). Thus, in addition to the main ‘experimental’ scan (I), a background ($I_{\text{Back}}$) and beam intensity ($I_0$) scan had to be performed (Figure 18).
Figure 18. Various NR scan components used to generate a reflectivity curve (data obtained from scan of MEG-OH adlayer on quartz in H₂O/D₂O, SLD = 4.5 x 10⁻⁶ Å⁻²). Dotted lines separate low -, mid -, and high-q scan regions.

The background reflectivity data was then subtracted from the experimental reflectivity data and normalized using the beam intensity data. Both $I_{\text{Back}}$ and $I_0$ measurements were performed with the same slit settings (S1 – S4) as a function of $q_z$. To generate the ‘true’ reflectivity of a system, the following calculation is performed:

$$R = \frac{[I/I_{\text{Back}}M_{\text{Back}}]}{I_0} \left( \frac{1}{F_{\text{Abs}}} \right) \quad (22)$$

where ‘M’ refers to the monitor beam count (a signal normalization factor representing the number of neutrons hitting the sample and collection time) which can be varied depending on the desired statistics. An absorbance factor, $F_{\text{Abs}}$ corrects for the use of a ‘neutron absorbing material’ (e.g. lucite) required during the $I_0$ scan. The $I_0$ data varies between systems depending on which side the beam is hitting the sample from (e.g. from air or the substrate side). The statistical error calculation for the reflectivity is shown below:

$$E_R = \sqrt{\left( \frac{\sqrt{I}}{M_1 I_{\text{Norm}} F} \right)^2 + \left( \frac{\sqrt{I_{\text{Norm}} M_{\text{Back}}}}{M_1 I_{\text{Norm}} F} \right)^2} \quad (23)$$

The calculated values for each data point were presented as error bars (+/-) in the reflectivity curves.
The reflectivity scan was separated into three sections (or regions, as each region required different slit settings with respect to beam collimation (S1, S2) and background subtraction (S3, S4). For all scans, the slit opening of S1 and S2 was proportional to the angle of incidence (θ), the angle between the sample surface and the incident beam. As such, the neutron beam consistently illuminated the same portion of the quartz wafer, an area of roughly 60 x 50 mm$^2$. With these slit settings, the relative resolution of $\Delta q/q$ remained constant for all angles ($\Delta q/q \approx 5\%$). At low q (small angles) reflectivity is high and S1, S2 are narrow and S3, S4 are held constant usually with S4=2S3. With increasing q, S1 and S2 were systematically widened to maintain the beam footprint on the sample along with S3, S4 which are also widened with higher q. Consequently, higher levels of background signal are observed particularly in the high q region – which is most affected by noise (Figure 18, green data points). This usually prevents scanning to higher q values, limiting the quality of the scan and, ultimately, the information obtained. Since H$_2$O and D$_2$O scatter neutrons more than air, measurements were made up to $q_{\text{max}} < 0.07 - 0.1$ Å$^{-1}$ in liquid and $q_{\text{max}} < 0.1 - 0.2$ Å$^{-1}$ in air depending on the system (quartz or Si/SiO$_2$).

2.4.2.3 Measurement Settings

For all scans performed, the detector was aligned at wire 17 (out of the 32 $^3$He wires). The overall output signal represented the average signal across wires 16-18 where the widths of slits S3 and S4 ensured that surrounding wires collected minimal or no signal.

2.4.2.3.1 Quartz

For measurements in air, the samples were scanned from the direction of air toward the quartz substrate. For the low ($q < 0.02$ Å$^{-1}$) and mid ($0.02 < q < 0.045$ Å$^{-1}$) regions, S1 and S2 were widened while S3 and S4 were held constant. For $q > 0.045$ Å$^{-1}$, S3 and S4 were allowed to vary (widen) as reflectivity decreased in this region. Background scans were performed with settings analogous to experimental ones however the sample angle was off-set by 0.3º to mimic off-specular scattering. Optimization of scan parameters in air was unnecessary since the neutrons are sensitive to this medium.

For the series of quartz experimental series, the following were investigated in air:

1) Effect of piranha cleaning on the quartz substrate (after 1 and 2 treatments).
2) Substrate roughness measurement (with/without organic film).

For measurements, in liquid the set up required for the samples to be scanned from the quartz (substrate) side to the D$_2$O/H$_2$O solution within a specialized cell (Figure 19).

![Figure 19](image)

**Figure 19.** Cell used for measuring samples in liquid solution. (a) Photograph of cell mounted vertically on sample platform showing liquid inlet (aerial view). (b) Diagram of cell sitting flat (horizontal view). Incoming and reflected neutron beam indicated by the red arrow. *Note: cell in (b) perpendicular to orientation during measurement.*

All measurements were performed in water (8-10 hrs) with a refractive index near that of quartz to enhance the scattering contrast of the various layers. Near-contrast matched water (nCMW) was prepared from a 55:20 (v/v) mixture of D$_2$O/H$_2$O with a SLD of 4.50 x 10^{-6} Å$^2$. This value (among others) was generated by the SLD calculator available through the National Institute of Standards and Technology (NIST) website taking into account atomic composition, the λ used and density, ρ, of the medium. Due to significant incoherent scattering by hydrogen and deuterium atoms, the background contribution to the signal was large. To properly subtract the background, the following procedure was applied: for $q > 0.02$ Å$^{-1}$, slits S3 and S4 were widened in order to detect the background signal in wires 15 and 19 which was later subtracted from the true reflectivity signal (collected in wires 16-18). The instrument was consistently aligned on wire 17 with a fraction of the reflected neutrons also detected in the neighbouring wires 16 and 18 due to a Gaussian distribution of recorded neutron capture with respect to the actual location of impact on the detector. This is a generic characteristic of $^3$He detectors. In this q-range, slits S3 and S4 were widened and held constant to make sure that all the wires detect the same amount of background neutrons. Figure 20 shows the effect of applying the ‘wire 15+19’
background subtraction technique in comparison to the off-set method used for the lower q regions (standard background subtraction settings).

![Graph](image)

**Figure 20.** Reflectivity of quartz sample in nCMW (SLD = 4.5 x 10^{-6} Å^{-2}) showing background subtraction techniques used for the high-q region.

For the low q regions (q < 0.02 Å^{-1}), slits S3 and S4 were narrowed since they were exposed to less background noise than the signal wires (16-18) and wires 15 and 19 could not be used for background correction. This is the same method that is used for samples in air. A background scan was performed with the sample angle consistently off-set by 0.3º to ensure that no true reflected intensity was recorded.

For the series of quartz experimental series, the following were investigated in liquid:

1) MEG-OH and OTS-OH adlayers on quartz in nCMW (bare quartz control).

2.4.2.3.2 Si/SiO\textsubscript{2}

Measurements in air were performed from the direction of air towards the Si/SiO\textsubscript{2} substrate with the same scan parameters used for quartz samples. Modeling was performed to determine the thickness of the grown oxide on the Si wafer as well as characterize the substrate roughness at both interfaces (Si and SiO\textsubscript{2}). For series of the Si wafer experiments series, the following were investigated in air:

1) Effect of piranha cleaning on the Si/SiO\textsubscript{2} substrate.

2) Measurement of oxide thickness and interfacial roughness.
Measurements in liquid were performed in the same configuration as quartz samples. The refractive index of the bulk liquid was matched exactly to SiO$_2$ (3.48 x 10$^{-6}$ Å$^{-2}$). This contrast matched water (CMW) was prepared from a 175/125 (v/v) mixture of D$_2$O/H$_2$O with an SLD of 3.54 x 10$^{-6}$ Å$^{-2}$ (calculated using NIST SLD calculator).\textsuperscript{39} In the low- and mid-q region (0.005 Å$^{-1}$ < $q$ < 0.05 Å$^{-1}$), S1 and S2 were varied with changing q to maintain a constant beam footprint on the sample (as in the air scan). In these regions, S3 and S4 were maintained at constant slit width for the low q region due to higher signal-to-noise (S/N). In the mid q region, however, they were varied at an optimal slit width (after testing various S3, S4 combinations in order to obtain the best resolved fringes). Background subtraction for these scans was performed by an offset scan, where the sample angle was consistently offset by 0.5°.

For the high-q region (q > 0.05 Å$^{-1}$), the contribution from scattering led to saturation of the signal if the same background subtraction technique was applied as for the low and mid q regions. The signal intensity was decreased in this region by holding S2 constant at 0.5 mm. To properly subtract the background, we took used wire 15 and 19 for background subtraction as for the quartz measurements in liquid (refer to Section 2.4.2.3.1).

Though this worked well for the high-q region of OTS-OH, the fringes in the MEG-OH sample were difficult to resolve (due to the nature of the sample), thus S3 and S4 were narrowed (while S1 and S2 were held at 0.5 mm) and a background scan was performed by scanning the high-q region with the sample angle consistently off-set by 0.5°. This allowed for resolving the details of the MEG-OH sample measurement while still maintaining the position and amplitude of the fringes. For the series of Si wafer experiments, the following were investigated in liquid:

1) Testing contrast variation between thermally grown oxide (SiO$_2$) and CMW.

2) MEG-OH and OTS-OH adlayers on Si/SiO$_2$ in nCMW (Si/SiO$_2$ control).

### 2.4.3 Modeling

Amongst numerous sophisticated modes of fitting available in \textit{MOTOFIT}, ‘Genetic Optimisation’ was chosen since it allows for poor initial parameter guesses while still providing a best-fit solution.\textsuperscript{40} Modeling was performed assuming constant instrumental resolution ($\Delta q/q = 5\%$) and the ‘Genetic Optimisation’ mode were used. To analyze the NR data, the simplest models were created which focused on applying minimal number of layers to represent the
system under investigation. In general, models of systems in air included no additional layers after the substrate as the SLD of organic coatings can range from ~0.4 x 10^{-6} \text{Å}^{-2} \, (48) to ~1 x 10^{-6} \text{Å}^{-2} \, (19) (depending on packing density) and the adlayers are <1 nm thick.\textsuperscript{29} The adlayers were assumed to be invisible to neutrons and an accurate measurement of substrate roughness was attainable.

2.4.3.1 Quartz

For measurements in air, only the substrate (quartz) roughness was fit while the SLD of quartz was held constant at 4.18 x 10^{-6} \text{Å}^{-2}. A simple ‘0-layer’ model assuming a single interface was applied, shown in Figure 21 along with corresponding parameters used for modeling in \textit{MOTOFIT} (Table 1). Since the adlayer cannot be detected by the neutrons, systems with or without an adlayer were modeled with a single interface between the quartz substrate and air. This value was generated by the NIST SLD calculator\textsuperscript{39} and used by others performing studies on quartz substrate,\textsuperscript{19} thus, it is not fit throughout the entire modeling process (air and liquid).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Layer & d (Å) & SLD (x 10^{-6} \text{Å}^{-2}) & \(\sigma\) (Å) \\
\hline
Air & \(\infty\) & 0 & \\
Quartz & \(\infty\) & 4.18 & \(\sigma_{Qi} (0/30)\) \\
\hline
\end{tabular}
\caption{Parameters used in \textit{MOTOFIT} for measurement of quartz substrate (with and without adlayers) in air. Parameters to be ‘fit’ have lower/upper limits shown in brackets. Corresponding model with initial value(s) in Figure 21.}
\end{table}

\textbf{Figure 21.} Schematic of model used for quartz samples in air, parameter to be fit is outlined in red.

Since reflectivity at a single interface with \(d_{\text{Layer}}<2\pi/q_{\text{max}}\) was modelled no fringes were expected to be observed. With a ‘featureless’ curve, the program is sensitive to initial parameters from which the fitting begins as well as the limits the user sets. For measurements in liquid, the
reflectivity data was fit with two cases in order to objectively study interfacial water (if any): (1) assuming no interfacial water, and (2) assuming low-density interfacial water. Models for both cases are shown below (Figure 22).

For Case 2, the most suitable approach to assessing the presence of (and characterizing) an interfacial phase of water (distinct from the bulk solution) would be to create a 2-layer model with the adlayer and the interfacial water designated as layers 1 and 2, respectively. However, there is insufficient resolution to detect a ~ 5 Å-thick layer – particularly if the adjacent (organized) water has a lower SLD than the bulk nCMW, thereby decreasing contrast at the adlayer/interfacial water interface. Regardless, valuable information could also be obtained from a basic 1-layer model, which treats the adlayer and possible interfacial water as one single medium.

Modeling the reflectivity curve in liquid entailed a 2-phase fitting procedure where first, a general fit of layer 1 parameters was performed followed by a final refinement of all parameters including those obtained in air and theoretical/known parameters (SLD of nCMW). In the first phase, a general fit was performed where SLD$_1$, $d_1$, and $\sigma_B$ were fit while the substrate roughness ($\sigma_Q$) and SLD values of quartz and nCMW were held constant. In the second phase, a refinement of the parameters fit in phase I as well as SLD$_B$ and $\sigma_Q$ was completed. This accounts for any discrepancies between the theoretical and true values of the system and allows for the ‘unknown’ values of layer 1 to be more accurately defined. Table 2 shows the 2-phase fitting scheme with the upper and lower limits on the parameters used by the MOTOFIT program along with the starting parameter values.

![Figure 22](https://example.com/figure22.png)

**Figure 22.** Schematic of models used for quartz samples in liquid (nCMW). (a) Case 1 assumes no interfacial water (adlayer = layer 1) and (b) Case 2 assumes interfacial water and adlayer (layer 1). Parameters in red and green boxes fit in phases I and II, respectively.
Table 2. Parameters used in MOTOFIT for measurement of adlayers on quartz in nCMW. Parameters to be ‘fit’ have lower/upper limits shown in brackets. Corresponding model with initial values in Figure 22.

The upper and lower limits for the SLD of quartz and nCMW were allowed to vary by 5% from the calculated SLD value of $4.5 \times 10^{-6}$ Å$^{-2}$ and quartz roughness value of ($\sigma_Q$) was allowed to vary by a few Ångström. In both phases, the lower limit for the SLD$_1$ was set to approximately $0.8 \times 10^{-6}$ Å$^{-2}$, a value more common among EG-based organic films$^{19}$ and higher than densely packed alkyl chains.$^{48}$

### 2.4.3.2 Si/SiO$_2$

With a layer of thermally grown oxide on Si, where $d_{SiO_2} > 2\pi/q_{max}$, the thickness of the SiO$_2$ could be determined by modeling (Figure 23). Measurements of Si/SiO$_2$-based samples in air were modeled similarly to the quartz substrate (in air), except the thickness of the SiO$_2$ layer needed to be fit ($d_{SiO_2}$) along with roughness parameters at both Si/SiO$_2$ and SiO$_2$/air interfaces. The SLD of the oxide was also fit since the density of SiO$_2$ may vary from the theoretical value of amorphous silica ($3.48 \times 10^{-6}$ Å$^{-2}$) depending on oxide growth. Similar to the 2-phase fitting system, the SLD$_{SiO_2}$ was then fit along with a refinement of the previously fit parameters. Corresponding parameters for modeling in air are shown in Table 3.
**Figure 23.** Schematic of model used for Si/SiO$_2$-based samples in air. Parameters in red and green boxes fit in Phases I and II, respectively.

<table>
<thead>
<tr>
<th>Layer</th>
<th>d (Å)</th>
<th>SLD ($\times 10^{-6}$ Å$^{-2}$)</th>
<th>$\sigma$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>$\infty$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>$d_{i1}$ (100/300)</td>
<td>3.48 ($3.325/3.675$)</td>
<td>5 (0/100)</td>
</tr>
<tr>
<td>Si</td>
<td>$\infty$</td>
<td>2.07</td>
<td>10 (0/100)</td>
</tr>
</tbody>
</table>

**Table 3.** Parameters used in MOTOFIT for measurement of Si/SiO$_2$ substrate (with or without adlayers) in air. Parameters ‘fit’ have lower/upper limits shown in brackets. Corresponding model with initial values in Figure 23.

From the reflectivity curves, the approximate thickness of the oxide was deduced from the Kiessig fringes and used as the initial value (~ 150 Å). Though the SLD of the Si should not be different from its theoretical value, SLD$_{SiO_2}$ can vary from the expected value since the density of SiO$_2$ may not be exactly that of amorphous silica depending on oxide growth. This parameter, however, need not be accurately defined since it was later allowed to vary in the liquid models (along with the other parameters defined in air). Figure 24 shows the models in liquid.
Figure 24. Schematic of model used for adlayers on Si/SiO$_2$ in liquid (CMW). Parameters in red and green boxes fit in Phases I and II, respectively.

As for the quartz system, a 2-phase fitting procedure was used where, in the first phase, a general fit was performed (SLD$_{1i}$, d$_{1i}$, and $\sigma_B$) while the SLD of Si, SiO$_2$ and CMW were held constant. In phase II, all parameters were fit with the exception of SLD$_{Si}$ and d$_{SiO2}$, which remained constant in order to accurately determine d$_{1i}$. Table 4 shows the 2-phase fitting scheme with the upper and lower limits on the parameters used by MOTOFIT.

<table>
<thead>
<tr>
<th>Layer</th>
<th>d (Å)</th>
<th>SLD (x $10^{-6}$ Å$^{-2}$)</th>
<th>$\sigma$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMW</td>
<td>$\infty$</td>
<td>3.54</td>
<td></td>
</tr>
<tr>
<td>Layer 1</td>
<td>d$_{1i}$ (0/30)</td>
<td>SLD$_{1i}$ (0.80/3.54)</td>
<td>$\sigma_B$ (0/100)</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>d$_{SiO2}$ (Air)</td>
<td>3.48</td>
<td>$\sigma_{SiO2}$ (Air)</td>
</tr>
<tr>
<td>Si</td>
<td>$\infty$</td>
<td>2.07</td>
<td>$\sigma_{Si}$ (Air)</td>
</tr>
<tr>
<td>CMW</td>
<td>$\infty$</td>
<td>3.54 (3.325/3.675)</td>
<td></td>
</tr>
<tr>
<td>Layer 1</td>
<td>(I) * d$_1$ (0/30)</td>
<td>(I) * SLD$_1$ (0.80/3.675)</td>
<td>(I) * $\sigma_B$ (0/30)</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>d$_{SiO2}$ (Air)</td>
<td>3.48 (3.325/3.675)</td>
<td>$\sigma_{SiO2}$ (Air) ($\sigma_{SiO2}$ -2/15)*</td>
</tr>
<tr>
<td>Si</td>
<td>$\infty$</td>
<td>2.07</td>
<td>$\sigma_{Si}$ (Air) ($\sigma_{Si}$ -2/15)*</td>
</tr>
</tbody>
</table>

*Values obtained from ‘Phase I’ fit.

Table 4. Parameters used in MOTOFIT for measurement of adlayers on Si/SiO$_2$ in CMW. Parameters ‘fit’ have lower/upper limits shown in brackets. Corresponding model with initial values in Figure 24.
In the second phase, the upper and lower limits for the SLD of SiO$_2$ and CMW were also allowed to vary (by 5\%) from 3.5 x 10$^{-6}$ Å$^{-2}$ and to obtain a more accurate fit of the experimental data. Throughout the fitting process it was necessary to extend the upper limit of the Si/SiO$_2$ and SiO2/layer 1 interfaces to a higher value (discussed in the next section).

3 Results and Discussion

3.1 X-ray Photoelectron Spectroscopy: Surface Characterization

Angle-resolved XPS (ARXPS) was performed on quartz and Si samples, monitoring elemental and compositional changes to the substrate and surface chemistry. As previously described in Section 2.1, the samples analyzed by XPS were significantly smaller than those used for NR analysis and scaling down the protocol may have resulted in unequal surface chemistries between the two types of substrates. For this reason, the present XPS data are used for qualitative and semi-quantitative analysis of both surface modification with silane linkers as well as the substrate chemistry (of the Si-based substrates, in particular).

3.1.1 Quartz

ARXPS measurements were done on samples representing the various steps in the protocol (Figure 25) with corresponding XPS results in Table 5. Survey spectra for these samples are shown in Figures A.1 and A.2 (Appendix A). A set of 8 samples were investigated for C1s (285 eV), O1s (532 eV), Si2p (102 eV) and F1s (689 eV) peaks. The unfunctionalized, bare quartz surfaces were first studied to examine the efficacy of the cleaning procedure in removing carbonaceous contaminants (‘Clean Quartz’) and to ensure the removal of the silane adlayer (‘Re-cleaned’) since the quartz discs were re-used during the NR studies. Table 5 shows XPS results for all the quartz samples including the bare surfaces (shaded in grey). Among the species investigated, the relative amount of carbon was the most accurate indicator of surface contamination. A general trend of increasing carbon content was observed when probing closer towards the quartz surface (from 27.5° to 72.5°) supporting that contamination is likely to reside on the substrate surface. In Table 5 there is a clear decrease in % C between the uncleaned (as received) sample and remaining bare surfaces where the carbon content decreased to approximately one third the level of the ‘contaminated’ surfaces level.
Figure 25. Schematic of quartz samples analyzed using XPS.
<table>
<thead>
<tr>
<th>Sample</th>
<th>TOA (°)</th>
<th>Atomic Composition (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C1s (285 eV)</td>
<td>O1s (532 eV)</td>
</tr>
<tr>
<td>Quartz (As received)</td>
<td>27.5</td>
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<td></td>
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<td>63.5</td>
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<td>72.5</td>
<td>25.0</td>
<td>51.9</td>
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<td>4.3</td>
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</tr>
<tr>
<td></td>
<td>72.5</td>
<td>8.23</td>
<td>61.88</td>
</tr>
</tbody>
</table>

**Table 5.** ARXPS results for quartz samples.
Another important observation is that the ‘re-cleaned’ sample was comparable to other clean surfaces. This was tested by preparing a MEG-TFA adlayer and re-cleaning the sample (as described in section 2.2.1). Thus, the absence of any fluorine peaks and low carbon content demonstrates successful removal of the silane assuring that the there was no residue in subsequent samples prepared on the same substrate.

Both MEG-TFA and OTS-TFA silane linkers were successfully immobilized onto the quartz surface as demonstrated by the increase in fluorine counts (Table 5) and corresponding fluorine peaks at \( \sim 689 \text{ eV} \) (originating from the TFA head group). Figures 26 a and b show the narrow XPS scans for MEG-TFA and OTS-TFA before and after hydrolysis and subsequent removal of the TFA unit.

![Figure 26](image)

**Figure 26.** F1s narrow scans of a) MEG-TFA and b) OTS-TFA and corresponding hydrolyzed adlayers on quartz (take-off angle= 72.5°).

Evidence of this surface modification can also be seen in the narrow scan for carbon (Figure 27), where the appearance of peaks at 288 – 296 eV correspond to the –CF\(_3\) and –C=O groups which possess a higher binding energy due to covalent bonding to electronegative atoms.\(^{49}\) Overall, the present XPS results are parallel with those of Sheikh *et al.*\(^{29}\), from which the cleaning and silanization protocols were reproduced.
Figure 27. C1s narrow scan of OTS-TFA and OTS-OH adlayers on quartz at a take-off angle of 72.5°.

3.1.2 Si/SiO₂

As for the quartz samples, ARXPS measurements were performed on the silicon substrate based surfaces (Figure 28 and Table 6 below). Survey spectra for these samples are shown in Figures A.3 and A.4 (Appendix A). Substrate characterization was performed first, where confirmation of oxide formation was obtained by direct comparison of the bare Si wafer to the thermally oxidized substrate.

Figure 28. Summary of Si/SiO₂ samples analyzed using XPS.
<table>
<thead>
<tr>
<th>Sample</th>
<th>TOA (°)</th>
<th>Atomic Composition (%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C1s (285 eV)</td>
<td>O1s (532 eV)</td>
<td>Si2p (103 eV)</td>
<td>F1s (689 eV)</td>
<td></td>
</tr>
<tr>
<td>Si (As received)</td>
<td>27.5</td>
<td>6.5</td>
<td>32.0</td>
<td>61.5</td>
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<td></td>
<td>42.5</td>
<td>9.3</td>
<td>37.8</td>
<td>52.8</td>
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<tr>
<td></td>
<td>57.5</td>
<td>12.0</td>
<td>43.2</td>
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Table 6. ARXPS results for Si/SiO₂ samples.
Figure 29. Narrow scan of the Si2p orbital at various take-off angles for the (a) Si wafer and (b) thermally oxidized wafer. Si peaks correspond to elemental silicon (Si$^0$) at 99.5 eV and oxidized silicon species (Si$^{n+}$) at 103 eV.

Figure 29 shows the narrow scans for the Si atom, 2p orbital before and after oxidation. The two peaks belong to elemental silicon (Si$^0$) at 99.5 eV as well as oxidized silicon species (Si$^{n+}$) at 103 eV corresponding to the presence of native oxide on the Si wafer. As the take-off angle increases and the X-rays probe closer to the surface, the elemental Si peak height - and the ratio between Si$^0$ and Si$^{n+}$ - decreases since the native oxide resides mostly within the top most layers of the substrate.

Upon oxidation of the substrate the elemental Si peak disappears (Figure 29 b) and the oxidized elemental peak shifts to 103.5 eV corresponding to the Si belonging to the thermally grown oxide (SiO$_2$) which must be >10 nm thick, the upper limit of the X-ray probing depth. Though the kinetics of oxide growth on (111) Si crystals was described by a model formed by Deal and Grove in 1965, the uncontrolled conditions during oxidation and preparation of the wafer used in the present study prevent a prediction of oxide thickness to be made. In growing the oxide, there was no chemical pre-treatment of the wafer. Though many organic contaminants from Si wafer manufacturing process have boiling points < 850 °C (the furnace temperature used), e.g. di(2-ethylhexyl) phthalate, they are known to alter the rate of growth and the lattice structure if trapped or incorporated into the oxide layer. In comparing the % C1s between the bare Si and thermally grown oxides, Si/SiO$_2$ (Table 6, shaded grey), there was, indeed, a decrease in carbon content suggesting the removal of surface contaminants. Interestingly, % C1s was found to be highest in the control. One explanation for this could be irregular oxide porosity (due to conditions of oxide growth) allowing solvent molecules (and
other organic contaminants) to collect throughout the entire protocol and reside in the substrate. Regardless of contamination, the thermally oxidized substrates showed stoichiometric ratios of \( n(O1s):n(Si2p) \) to be \( \sim 2 \), as previously reported for thick SiO\(_2\) oxide layers\(^{50}\).

As for quartz, successful surface modification with the silane adlayers was demonstrated by the appearance of the F1s signal after analysis of MEG-TFA and OTS-TFA adlayers on Si/SiO\(_2\) (Table 6) and C1s peak positions (Figure 30).

![Figure 30](image)

**Figure 30.** C1s narrow scan of MEG-TFA and MEG-OH adlayers on thermally grown Si/SiO\(_2\) at a take-off angle 72.5°.

Contrary to previous findings, however, the fluorine peak did not completely disappear for the OTS-OH adlayer showing incomplete hydrolysis of all the linker TFA groups (Figure 31b). Since the current chemistry functioned properly on quartz, it is possible that the present observations are an effect of the substrate. The TFA group, however, was successfully cleaved from the MEG-TFA adlayers on Si/SiO\(_2\) (Figure 31a) decreasing the likelihood of the thermally grown oxide being responsible.
Figure 31. F1s narrow scans of a) MEG-TFA and b) OTS-TFA and corresponding hydrolyzed adlayers on thermally grown oxide (take-off angle = 72.5°).

One theory for the observed differences is that the thermally grown oxides are difficult to reproduce (under present conditions) and thus, the Si/SiO₂ substrates may have had different surface properties, for example, surface hydroxylation (activation), surface roughness and overall oxide porosity. If, perchance, the silane were to covalently bind to underlying oxide layers within pores it would be difficult for them to be hydrolyzed since penetration of MeOH/H₂O may be hindered by the adlayer formed on the oxide surface.

Through XPS analysis, the substrate and surface chemistry was characterized. Further insight into the oxide properties regarding thickness, composition, and roughness (between Si/SiO₂ and SiO₂/air) was performed using NR analysis.

3.2 Neutron Reflectometry Analysis

Neutron reflectometry was used to study the hydration profiles at both, MEG-OH and OTS-OH adlayers on quartz and Si/SiO₂ substrates. The technique of Contrast variation and neutron sensitivity to ¹H and ²D-atoms was exploited, ultimately, in order to study the density of water adjacent to the two films. Recall that SLD = Nb which means that a decrease in the number density, N, results in an overall decrease in SLD, assuming the atomic composition, b, remains constant. Before measurements could be made in liquid, information about the physical parameters pertaining to the substrate had to be made. For each system (quartz and Si/SiO₂)
measurements were first performed in air followed by investigations in contrast matched solutions (D₂O/H₂O).

3.2.1 Quartz

3.2.1.1 Measurements in Air

To characterize physical parameters of the quartz substrate it was necessary to perform measurements in air. Measurements were made between $0.006 < q (\text{Å}^{-1}) < 0.2$ allowing for greater confidence in the fits since more information can be obtained at higher q values. As previously mentioned in Section 2.4.2.3.1, the quartz discs were re-used several times for NR experiments. Thus, it was pertinent to determine the effect of multiple cleaning treatments on the quality of the substrate, particularly on the surface roughness - which affects the behaviour of the adlayer with water and poses technical difficulties for NR measurements. The data was fit with a ‘0-layer’ model (Figure 21, Section 2.4.3.1) allowing for only substrate roughness to be varied (fit) between constant SLD values of quartz and air ($\text{SLD}_\text{Q} = 4.18 \times 10^{-6} \text{ Å}^{-2}$ and $\text{SLD}_\text{A} = 0 \text{ Å}^{-2}$). Figure 32 a and b show the resulting reflectivity curves and SLD profiles.

![Figure 32](image.jpg)

**Figure 32.** (a) Reflectivity curves and corresponding fits for quartz substrate after cleaning once (1P) and twice (2P) with piranha solution (data fit with 0-layer model). (b) Corresponding SLD profiles for the two systems (shown from quartz to air).
The data shown in Figure 32 a are consistent with Fresnel reflectivity at a single interface, specifically, at an air/quartz interface - as determined by the critical edge (~ 0.014 Å⁻¹). After cleaning with piranha solution, the surface roughness was measured to be 4.61 Å ($\chi^2 = 2.1 \times 10^{-3}$). This is quite low and consistent with existing values for quartz roughness. After a second 30 min cleaning, the roughness was essentially unchanged having been fit to 4.44 Å ($\chi^2=8.5 \times 10^{-4}$). Although the two reflectivity and corresponding SLD profiles are superimposed, there was a slight decrease in the quality of the fit ($\chi^2$ value) though this is minimal compared to subsequent generated models (discussed in further sections).

Often, measurement of the substrate roughness before surface modification (silanization) was not possible, thus, it was essential to determine the accuracy of the measurement with an adlayer. Measurement of a quartz substrate before and after silanization (using MEG-OH as an example) confirmed that the ultrathin organic film is ‘invisible’ to neutrons. As previously mentioned, organic films have a very low SLD (-0.4 x 10⁻⁶ Å⁻² (48) to ~1 x 10⁻⁶ Å⁻² (19)), close to that of air (0 Å⁻²); hence, it was expected that the quartz roughness would remain similar (or constant) with or without such a thin film (< 10 Å). Figure 33 shows a reflectivity curve and SLD profile for two quartz systems (with and without an organic film).

**Figure 33.** (a) Reflectivity data and corresponding fits for bare quartz and film on quartz in air. Data is fit with 0-layer model. (b) Corresponding SLD profiles for the two systems (shown from quartz to air).
For bare quartz, the fit and corresponding SLD profile generated (blue lines, Figure 33) a roughness of 7.36 Å ($\chi^2 = 5.0 \times 10^{-2}$). Upon the addition of an adlayer, the resulting model parameters showed that the roughness was essentially unchanged with a value of 7.37 Å ($\chi^2 = 1.2 \times 10^{-1}$). Though the neutrons cannot resolve a thickness one tenth or hundredth of an Ångström, the models generate specific values (with an excess number of significant digits). Although the roughness values were the same, Figure 33a shows that indeed, there is a slight difference between the two curves. A ‘1-layer model’ was attempted for fitting the ‘quartz + film’ data (assuming a film atop the substrate). However, unrealistic values were obtained and the data could not be fit within reasonable physical parameters. The slight observed differences in the shape of the curves are characteristic of differences in geometry set-up (i.e. misalignment of the sample). Still, the possibility of incoherent scattering of the neutrons by the film should be acknowledged. Thus, during the fitting of data obtained in liquid, the surface roughness was allowed to be fit (within reasonable limits).

### 3.2.1.2 Measurements in Liquid

Obtaining accurate reflectivity data in liquid for the two adlayer systems was a challenge due to the nature of the samples, i.e. the thickness of the film. Theoretically, ultra-thin films with thickness, $d<2\pi/q_{\text{max}}$ can be detected if 'sandwiched' between two contrast matched media. This is especially true for multilayered substrates where contrast between the layers enhances the detection sensitivity of thin films resulting in the appearance of Kiessig fringes. In measuring the quartz substrate with MEG-OH and OTS-OH adlayers the maximum q values which could be reached was 0.07 Å⁻¹ requiring a film thickness of at least 90 Å to be detectable. This, however, refers only to the formation of Kiessig fringes on the reflectivity curve – not for detecting reflectivity at an interface with a thickness $<90$ Å.

To investigate the hydration of MEG-OH and OTS-OH adlayers on quartz, the systems were measured in nCMW ($\text{SLD}_B = 4.50 \times 10^{-6}$ Å⁻²) to ensure enhanced neutron scattering of the ultra-thin films. Due to the lack of features on the curve, the systems in liquid were modeled using two different cases: (1) assuming no interfacial water (only adlayer) and (2) assuming a layer of interfacial water, less dense than the bulk solution (recall modeling schemes in Figure 22 and Table 2, Section 2.4.3.1). Both cases had a single layer ‘sandwiched’ between the quartz substrate, ($\text{SLD}_Q = 4.18 \times 10^{-6}$ Å⁻²) and nCMW. For case 1, the layer consisted of the organic
adlayer, whereas for case 2, the adlayer and interfacial water (if any) are treated as a single, averaged medium (‘layer 1’). Each case was subjected to a 2-phase fitting procedure where the SLD\textsubscript{1}, d\textsubscript{1}, and \(\sigma_B\) were varied (phase I) followed by a refinement of the SLD\textsubscript{B} and \(\sigma_Q\) and parameters fit (by the program) in phase I. Figures 34 a and c (next page) show the reflectivity curves of the two adlayers in nCMW and resulting SLD profiles generated by modeling for cases 1 and 2. From the reflectivity data, it is evident that the 2 adlayers have different effects on the adjacent water in comparison to the bare quartz, with the MEG-OH adlayer having the highest reflectivity across the q range (higher scattering contrast). Between the two cases (Figure 34 a and c) there is no discernible difference between the \(\chi^2\) values of the fits between each of the systems after fitting the ‘Layer 1’ parameters. The absence of Kiessig fringes emphasizes the significance of applying two different models (cases). The fits in the reflectivity curves are the product of the model parameters generated by fitting with \textit{MOTOFIT} (Table B. 1, Appendix B). Figure 34 b and d show the results of the modeling in the form of SLD profiles.

From these figures, it can be seen that both cases 1 and 2 produce similar SLD profiles for MEG-OH and OTS-OH adlayers on quartz despite the differences made in the assumptions. Just at the quartz/film interface (shown by the dotted line at 0 Å) there is a decrease in SLD resulting from the organic film (incorporated into ‘layer 1’). The transition at this interface originates from the roughness parameter of the quartz substrate which is Gaussian in distribution. In both cases, the MEG-OH profiles show a broadly distributed region (\(~30\) Å) encompassing the modeled ‘layer 1’ (d\textsubscript{1}~20 Å) followed by a transition zone towards the bulk solution (\(\sigma_B\)~10 Å) (values from Table B. 1, Appendix B). The roughness at the ‘layer 1’/bulk interface acts as an error factor and represents a gradual transition between the two media. In liquid, this is thought to be caused by a change in water density which cannot be modeled within ‘layer 1’ and is attributed to a factor of the distribution of water towards the bulk solution. Though the \(\sigma_B\) is evidence of low density water, the ‘layer 1’ thickness and SLD are also indicative of this phenomenon since the adlayers used are \(~5\) Å thick. Thus, ‘layer 1’ generated by the model encompasses the adlayer and the remaining thickness is attributed to low density interfacial water. Another important observation is the SLD minima (SLD\textsubscript{1} \(\approx\) 3 \(\times\) 10\(^{-6}\) Å\(^{-2}\)), which are higher than that of an organic coating, suggesting there may be water penetration into the film\textsuperscript{28} resulting in an averaging of the SLD between the coating and water.\textsuperscript{57-58} Initial modeling
Figure 34. NR data and models resulting from phase I fit. (a) Case 1: Reflectivity data and corresponding fits for bare quartz as well as MEG-OH, OTS-OH adlayers on quartz in nCMW. (b) SLD profiles for bare quartz and MEG-OH, OTS-OH films on quartz (Case 1). (c) Case 2: Reflectivity data and fits for MEG-OH, OTS-OH adlayers on quartz in nCMW. (d) SLD profiles for bare quartz and MEG-OH, OTS-OH films on quartz (Case 2). Notes: Reflectivity curves contain $\chi^2$ values in brackets. SLD profiles are shown from the direction of quartz to nCMW. Interfacial water abbreviated to ‘IW’.
suggests that the influence of the internal oxygen atom in the MEG-OH adlayer could be responsible for this observation. The effect of the internal oxygen atom on the interaction with water was examined using the OTS-OH adlayer, which lacks such a feature. The SLD profiles (blue lines, Figures 34 b and d) display a much thinner medium between the quartz and nCMW. Unlike the MEG-OH system, ‘layer 1’ for the OTS-OH profile is thinner (~ 10 Å) in its entirety with an SLD value closer to that of an organic film (SLD$_1 \approx 3 \times 10^{-6}$ Å$^{-2}$). More importantly, however, there is almost no transition (or interfacial) zone of low density water towards the bulk solution suggesting that perhaps the internal oxygen has an effect, not only, on water penetration but also on adjacent water organization adjacent to the adlayers.

Initial observations and analysis of the phase I fits suggest that the MEG-OH system has a thick interfacial zone of water in contrast to OTS-OH system - which seems to have indiscernible layer of water adjacent to the adlayer. Though these results present early stages of the fitting process, the present interpretation of the SLD profiles is applicable in later sections and analyses of the two systems.

Next, the modeled ‘layer 1’ parameters and SLD$_B$ and $\sigma_Q$ for each system were refined with the ‘phase II’ fit. Figure 35 shows the same reflectivity data (with new fits) along with the corresponding SLD profiles. The resulting $\chi^2$ values (Figures 35 a and c indicate an improvement in the quality of fit after decreasing by a factor of ~ 2 for the OTS-OH and MEG-OH systems (Figure 35). Though a better fit is generally indicative of a ‘more correct’ model, both phase I and phase II results were shown due to their significantly different SLD profiles for the two systems. Resulting SLD profiles from the ‘refinement’ procedure demonstrated completely opposing behaviour of water with the two adlayers (Figures 35 b and d). For the MEG-OH system a thinner layer (~ 8 Å) with no interfacial water was observed (< 1 Å) (SLD$_1 \approx 2.5 \times 10^{-6}$ Å$^{-2}$) (modeling parameters available in Table B. 2, Appendix B). The OTS-OH system showed an extended low-density water region (as previously seen for the MEG-OH system) with d$_1$ ~ 7 Å and a $\sigma_B$ ~15 Å. Between both MEG-OH and OTS-OH systems, SLD$_B$ was refined to a value less than < 2 % of the original solution (4.50 x 10$^{-6}$ Å$^{-2}$) while the quartz roughness $\sigma_Q$ was fit up to a maximum of ~ 6 Å (from 4.5 Å). In conclusion, minimal refinement of the substrate and bulk water parameters caused a complete change in the ‘layer 1’ parameters demonstrating the unreliability of interpreting systems with minute differences between them. Using MOTOFIT,
Figure 35. NR data and models resulting from phase II fit. (a) Case 1: Reflectivity data and corresponding fits for bare quartz as well as MEG-OH, OTS-OH adlayers on quartz in nCMW. (b) SLD profiles for bare quartz and MEG-OH, OTS-OH films on quartz (Case 1). (c) Case 2: Reflectivity data and fits for MEG-OH, OTS-OH adlayers on quartz in nCMW. (d) SLD profiles for bare quartz and MEG-OH, OTS-OH films on quartz (Case 2). Notes: Reflectivity curves contain $\chi^2$ values in brackets. SLD profiles are shown from the direction of quartz to nCMW. Interfacial water abbreviated to ‘IW’.
varying the individual parameters (e.g. d, SLD and σ) in a continuous mode allowed for observing the effect on the shape and intensity of the simulated reflectivity curves. For a simple 1-layer system, increasing the SLD of the layer decreased the reflectivity while the opposite occurred upon increase in the thickness of the layer (d). Initially, varying σB caused a decrease in reflectivity, however, after a certain point (roughness value) the curve began to change its shape and the intensity trend was no longer followed. Thus, it was difficult to establish a confident fit.

Further evidence of the complexity of such a system was demonstrated by the reflectivity curves and SLD profiles of the bare quartz in nCMW (black lines, Figures 34 and 35). The NR data showed much higher reflectivity in the high q region when compared to a simulation of quartz in nCMW with σQ = 4.5 Å (dotted line, Figure 35a and c). Surprisingly, for both phases (and cases) the SLD profiles remained similar – with a broad, low SLD region similar to what was observed for the MEG-OH system (phase I) and the OTS-OH system (phase II) (model parameters available in Table B. 3, Appendix B). Previous studies observed anomalies in modeling interfacial water at a quartz interface (in H2O/D2O) suggesting the existence of an enriched D2O region adjacent to quartz.55,59 This phenomenon, however, is outside the scope of the present work and was not further investigated. The deviation of NR data from the simulation could also be due to incomplete subtraction of background scattering which was less prevalent for the MEG-OH and OTS-OH systems as a result of higher scattering contrast created by the presence of the adlayer +/- interfacial water.

Normally, a single-layered substrate (such as quartz) has the advantage of requiring fewer fitting parameters in a model and more importantly, contains fewer interfaces from which neutrons can be incoherently scattered. This physical attribute, however, was shown to be disadvantageous in studying ultrathin layers, particularly organic films. The resulting reflectivity curves lacked defining features such as Kiessig fringes. Though both samples were measured under the same experimental settings – even a slight misalignment of the sample could have altered the reflectivity enough to change the fit. Reflectivity curves with fringes provide a feature to confidently define at least one physical parameter around which the entire model is generated. A substrate comparable to quartz (in composition) is SiO2 which can be grown atop a Si wafer to a desired thickness. Although the crystal orientation and densities differ between the two substrates, the trichlorosilane chemistry was shown to be effective on both, quartz and Si/SiO2.
Conclusively, results on quartz have shown that the MEG-OH and OTS-OH systems interact differently with water, supporting the differences in their antifouling behaviour (as shown in EMPAS studies\textsuperscript{29}). To accurately study the two adlayers, however, it was necessary to repeat the experiments on a SiO\textsubscript{2} layer thick enough to be able to observe fringes in the available q region.

3.2.2 Si/SiO\textsubscript{2}

3.2.2.1 Measurements in Air

NR measurements of the MEG-OH and OTS-OH adlayers on Si/SiO\textsubscript{2} substrate were essential in order to detect and more accurately model the ultrathin films and interfacial water. The presence of Kiessig fringes on the reflectivity curves allowed for the measurement of \(d_{\text{SiO}2}\) (in air) and subsequently \(d_{\text{SiO}2} + d_{1}\) (in liquid), where \(d_1\) = ‘layer 1’, the thickness of the adlayer and interfacial water. Thus, the change in periodicity of the Kiessig fringe from air to liquid corresponds directly to the change in thickness caused by ‘layer 1’ which can only be detected in water.

The growth of the thermal oxide was confirmed and characterized by measuring the Si wafer in air (Figure 36). Corresponding SLD profiles and generated modeling parameters are available in Figure B. 1 and Table B. 5 (Appendix B), respectively. After thermally oxidizing the substrate, the wafer was measured between 0.006 < q (Å\(^{-1}\)) < 0.12 and data was fit with an SiO\textsubscript{2} layer between the air and Si. Initially, \(d_{\text{SiO}2}\), \(\sigma_{\text{Si}}\) and \(\sigma_{\text{SiO}2}\) were fit, after which they were refined along with SLD\textsubscript{SiO}2 (while holding SLD\textsubscript{Si} = 2.07 x 10\(^{-6}\) Å\(^{-2}\) and SLD\textsubscript{Air} = 0 Å\(^{-2}\) constant). Comparing Figures 36 a and b, it is evident that the Si wafer was, indeed, oxidized due to the appearance of well-defined Kiessig fringes, suggesting good homogeneity of the SiO\textsubscript{2} film. The bare, Si substrate was modeled to have a surface roughness of ~ 7.91 Å without varying the SLD of Si (\(\chi^2 = 0.016\)). After subjecting the Si wafer to 850 °C for 45 min the oxide grew to ~ 179 Å (Figure 36 b) with interfacial roughness values of \(\sigma_{\text{Si}} = 4.3\)Å and \(\sigma_{\text{SiO}2} = 8.01\) Å (\(\chi^2 = 0.0018\)). Although the oxide was grown in a furnace without a controlled atmosphere, the thickness of the SiO\textsubscript{2} was in line with Deal and Grove’s model for ‘dry’ oxidation in pure O\textsubscript{2} atmosphere.\textsuperscript{51} As mentioned in the analysis of XPS data, the quality of the oxide can be affected during formation (e.g. pinning and islands) in the presence of contaminants as well as when forming under
uncontrolled conditions. A refinement of the SLD of SiO\(_2\) while fitting the data yielded a value of \(~3.33 \times 10^{-6} \text{ Å}^{-2}\), which is lower (by

\[\sim 5\%\]

in comparison to the theoretical value (\(3.48 \times 10^{-6} \text{ Å}^{-2}\)) but within a reasonable range considering that any air penetrating into the substrate (as a result of its porosity) would cause the SLD to decrease (SLD\(_\text{Air}\) = 0 \text{ Å}^{-2}\)).

Prior to modifying the surface with the adlayers, the effect of cleaning the Si/SiO\(_2\) substrate with piranha solution was examined by measuring the same oxidized Si wafer before and after the treatment. Figure 37 shows the reflectivity data and corresponding SLD profiles for the fits (fitting parameters available in Table B. 4, Appendix B). From the reflectivity data (Figure 37 a), it is evident that the piranha solution negatively impacts the quality of the curve with respect to the amplitude and frequency of oscillations. Recall, the periodicity of the fringes is related to the thickness of the film (in the present case, the SiO\(_2\)). The observed increase in \(\Delta q\) corresponds to a decrease in thickness by \(~12 \text{ Å}\) in d\(_{\text{SiO2}}\) (from 301 Å) as a result of etching and/or degradation of the oxide.\(^\text{61}\) More importantly, however, there is a change in overall shape and amplitude due to an increase in the roughness at the Si/SiO\(_2\) interface from \(~25 \text{ Å}\) to \(~30 \text{ Å}\) (shown in Figure 37 b). Interestingly, the roughness parameter at the SiO\(_2\)/air interface before

\[\text{Figure 36. Reflectivity data and fits for a (a) bare and (b) thermally oxidized wafer (d\(_{\text{SiO2}}\) ~ 180 Å thick) measured in air.}\]
and after the cleaning remained at ~ 0 Å which is highly unrealistic for most surfaces. This was attributed to the interference from the reflected neutrons at the rough Si/SiO\textsubscript{2} interface with those reflected from the SiO\textsubscript{2}/air interface. Such diffuse scattering at one interface may have resulted in loss of quality and clarity (sharpness) ultimately affecting parameters generated by the fit. This is an issue for multilayered systems where increasing the number of layers and interfaces leads to ambiguity in models. Unlike the quartz substrate, the present system is slightly more complex since the oxides may vary in roughness parameters and SLD values. Regardless, such detrimental effects to the interfaces would cause loss of detail from the reflectivity curve and consequently, a loss of information.

Although the oxide was grown ~ 1.8x thicker than the SiO\textsubscript{2} substrate used for MEG-OH and OTS-OH adlayer formation, the effect of the 30 min piranha treatment was expected to be more prominent on a thinner oxide (~ 160 – 180 Å). Due to the changes undergone throughout the treatment, piranha solution was not used in the preparation of the adlayers on Si/SiO\textsubscript{2} substrate. Instead, the wafers were rinsed with various solvents immediately after oxidation and stored in a humidity chamber overnight.

**Figure 37.** Effect of 30 min immersion time in piranha solution on Si/SiO\textsubscript{2}. (a) Reflectivity data and fits (b) Corresponding SLD profiles (shown in the direction from Si/SiO\textsubscript{2} to air).
MEG-OH and OTS-OH adlayers were prepared on Si/SiO$_2$ substrates for NR measurements in liquid. The thickness (and interfacial roughness) of the oxide was first determined by measuring the samples (with adlayers) in air. Reflectivity curves and corresponding SLD profiles are presented in Figure 38.

![Figure 38](image)

**Figure 38.** (a) Reflectivity data with fits ($\chi^2$ value shown in brackets) (b) Corresponding SLD profiles for MEG-OH and OTS-OH adlayers on Si/SiO$_2$ measured in air (SLD$_{SiO_2}$ allowed to fit). Red and blue dotted lines indicate the approximate location of the SiO$_2$/air interfaces for each substrate.

The two sets of reflectivity data demonstrate variability in the periodicity of the Kiessig fringes due to differences in thickness between the thermal oxide layers (shown clearly in Figure 3.13 b). Oxide formation for the OTS-OH system was reproducible with respect to previous samples, growing to ~180 Å (SLD$_{SiO_2}$ = 3.33 x 10$^{-6}$ Å$^{-2}$) while the substrate for MEG-OH was modeled at only ~163 Å (SLD$_{SiO_2}$ = 3.45 x 10$^{-6}$ Å$^{-2}$) in less time. Another staggering difference between the substrates were the modeled interfacial roughness values, particularly at the SiO$_2$/air interface where $\sigma_{SiO_2}$ $\approx$ 4.5 Å and $\sigma_{SiO_2}$ $\approx$ 14.0 Å for OTS-OH and MEG-OH systems, respectively.

The characterization of the substrate was performed mainly for the purpose of obtaining the d$_{SiO_2}$ which was held constant when modeling data in the liquid system. Remaining parameters, such as SLD$_{SiO_2}$, $\sigma_{SiO_2}$ and $\sigma_Si$, were used as guidelines and fit in liquid since they
were most likely to fluctuate between measurements in the different media. Initial values used for fitting data in the liquid system were obtained from models assuming the constant, theoretical SLD\textsubscript{SiO\textsubscript{2}} (3.48 x 10^{-6} Å\textsuperscript{2}) (data available in Table B. 5, Appendix B). Although only the refined models are shown above, the differences observed between the two sets were not significant and χ\textsuperscript{2} values did not improve significantly upon refinement of SLD\textsubscript{SiO\textsubscript{2}}.

### 3.2.2.2 Measurements in Liquid

Finally, to investigate the hydration profiles adjacent to the MEG-OH and OTS-OH adlayers the two systems were measured in a solution of D\textsubscript{2}O/H\textsubscript{2}O (CMW) whose SLD was matched to that of the SiO\textsubscript{2} substrate (SLD\textsubscript{SiO\textsubscript{2}} = SLD\textsubscript{B} ≈ 3.5 x 10^{-6}Å\textsuperscript{2}). Such contrast variation ensured maximum enhancement of neutron scattering from any layer existing between the CMW and SiO\textsubscript{2} (e.g. the adlayer + interfacial water). Unlike the quartz substrate, the reflectivity curves of the Si/SiO\textsubscript{2}-based systems had defined features (Kiessig fringes) which decreased the ambiguity in the fitting procedures. Thus, only a model assuming low-density interfacial water adjacent to the adlayer was used to fit the data (refer to Figure 24 and Table 4, Section 2.4.3.2).

The matching of the SLD\textsubscript{SiO\textsubscript{2}} to SLD\textsubscript{B} was confirmed by measuring the bare SiO\textsubscript{2} substrate in CMW (Note: Figure 36 b shows the SLD profile of this sample in air). Since the two have the same refractive index, the neutrons should not be able to detect the SiO\textsubscript{2}/CMW interface. Thus, the data was fit with a system having only a single interface, Si/(SiO\textsubscript{2} + CMW) or rather, as a system with two semi-infinite media. While holding SLD\textsubscript{Si} constant, the SLD of the SiO\textsubscript{2} + CMW medium was fit to 3.63 x 10^{-6} Å\textsuperscript{2} with a roughness of 3.61 Å between the two media (χ\textsuperscript{2} = 0.0165). The reflectivity curve for the bare Si/SiO\textsubscript{2} in CMW (Figure 39 a), however, was shown to be noticeably featureless (i.e. absent Kiessig fringes) demonstrating that: (1) there was no distinguishable layer between the bulk solution and SiO\textsubscript{2} substrate and (2) the prepared solution of D\textsubscript{2}O/H\textsubscript{2}O was, indeed, contrast-matched to the SiO\textsubscript{2}.
Figure 39. (a) Reflectivity data and fit with corresponding (b) SLD profile for Si/SiO$_2$ substrate (control) in CMW.

Upon addition of the ultrathin MEG-OH and OTS-OH films, Kiessig fringes appeared in the reflectivity curves obtained in CMW (Figure 40, next page). Unlike the bare Si/SiO$_2$ substrate, these oscillations confirmed the presence of a discernible ‘medium’ sandwiched between the two contrast-matched media (SiO$_2$ and bulk CMW), namely, the adlayer and interfacial water (‘IW’). As previously described, a ‘1-layer’ model was applied – which assumed the inclusion of the existing adlayer as well as any interfacial water whose SLD $<$ SLD$_B$ ($\sim 3.5 \times 10^{-6}$ Å$^{-2}$) (refer to model in Figure 24, Section 2.4.3.2). As for the quartz systems, ‘phase I’ of the fitting procedure allowed for the parameters associated with layer 1 to be fit first (SLD$_1$, d$_1$ and $\sigma_B$) followed by ‘phase II’, a refinement of ‘known’ parameters (SLD$_B$, SLD$_{SiO2}$, $\sigma_{SiO2}$ and $\sigma_{Si}$) as well as those fit in phase I. Both, phase I and II fits are superimposed onto the reflectivity data for both in Figure 40 (resulting parameters available in Table B. 6, Appendix B). As expected, the $\chi^2$ values for both systems decreased ($\sim$ 3-fold) after fitting in the second phase. The ‘phase I’ results, however, were quite similar to those in the second phase and thus, will not be further discussed (‘phase I’ SLD profile shown in Figure B. 2, Appendix B).
Looking at the MEG-OH reflectivity curve, some qualitative information about the system could be deduced. The low amplitude and smooth minima of the fringes suggest that the ‘sandwiched’ layer was not well defined, suggesting low contrast between adjacent media (SiO2 and CMW) and/or high roughness at the various interfaces. After performing a 2-phase fit on the data, an SLD profile for the system was obtained (red line, Figure 41, next page) showing a medium ~ 40 Å-thick with a minimum SLD of ~ 3.2 x 10^{-6} Å^{-2}.

![Reflectivity data and corresponding fits for the (a) MEG-OH adlayer on SiO2 (~ 163 Å-thick) and (b) OTS-OH adlayer on SiO2 (~ 180 Å-thick) measured in CMW. Fits correspond to 1- and 2-phase fits generated using 1-layer model encompassing film and interfacial water (χ² value shown in brackets).](image)

**Figure 40.** Reflectivity data and corresponding fits for the (a) MEG-OH adlayer on SiO2 (~ 163 Å-thick) and (b) OTS-OH adlayer on SiO2 (~ 180 Å-thick) measured in CMW. Fits correspond to 1- and 2-phase fits generated using 1-layer model encompassing film and interfacial water (χ² value shown in brackets).

Although difficult to resolve (within the SLD profile), the ‘layer 1’ thickness was fit to d₁~ 22 Å (SLD₁ of ~ 3 x 10^{-6} Å^{-2}) with an additional transition zone of water toward the bulk solution ~ 17 Å thick (represented by the bulk roughness parameter, σₜ). At the SiO₂/film interface, SLD₁ was higher than expected from an organic film. Instead, it was much closer to the SLD of CMW (~3.5 x 10^{-6} Å^{-2}) suggesting that perhaps, the MEG-OH adlayer absorbed water causing the SLDs of the organic layer and water to be averaged. With the SLD so close to the surrounding media there would be lower contrast and, hence, weak scattering from the substrate/film interface. This, however, could also be a consequence of high surface roughness (σ_{SiO2}) which
was modeled at ~ 14 Å (in both air and liquid measurements), potentially causing a reduced reflectivity intensity.

![Figure 41. SLD profiles showing for MEG-OH and OTS-OH adlayers (films) on Si/SiO$_2$ (Si substrate not shown). Profiles correspond to 2-phase fit generated using a 1-layer model encompassing the film and interfacial water (IW). Dotted lines indicate approximate location of films. ‘Layer 1’ designates region modeled for ‘d$_1$’ for both systems. Note: For direct comparison, the SLD baseline for MEG-OH was shifted by -0.1 x 10$^{-6}$ Å$^2$ and both SiO$_2$/layer 1 interfaces were aligned at ‘0 Å’.](image)

If, in fact, the water had penetrated the film, there would have been a strong basis for the existence of a special intrafilm zone of hydration involving the internal atoms of oxygen of the MEG-OH adlayer$^{29}$ exhibiting ‘hydrogel’ like characteristics. This hypothesis was also supported by recent accounts of water penetrating into EG containing films.$^{28,57,61}$ Equally as interesting, however, were the long-range effects of the adlayer on the interfacial water (‘IW’, Figure 41) as demonstrated by the presence of an additional, physically distinct transition zone of water spanning over ~ 17 Å (following the SLD minima). Theoretically, this interfacial water region could be fit into $n+1$ layers eventually diminishing the high $\sigma_B$ value, however, increasing the number of layers would require the assumption of more unknown parameters.

To conclusively determine whether the internal ether oxygen was involved with the formation of the observed interphase of water, the OTS-OH adlayer was studied next. In comparing reflectivity data from both systems (Figures 40 a and b), it is evident that the absence of internal oxygen atoms in the OTS-OH molecular species measurably altered the interaction of
water with the adlayer (assuming similar surface coverage). Unlike the MEG-OH reflectivity curve, the sharp, high-amplitude fringes shown in Figure 40b suggest the presence of a well-defined layer with a refractive index deviating significantly from the surrounding, contrast-matched media. This speculation was confirmed upon fitting the data with a 1-layer model whose fits had visibly lower $\chi^2$ values in comparison to the MEG-OH system (owing to better definition of the curve’s features). The corresponding SLD profile (blue line, Figure 41) showed a medium confined to $\sim 20$ Å with a significantly lower SLD ($\sim 1.15 \times 10^{-6}$ Å$^2$) than its surrounding media ($\chi^2 = 0.0067$). This SLD value is more representative of an organic coating suggesting, perhaps, that the adlayer was impenetrable to water and that the observed differences in hydration profiles (in comparison to MEG-OH) relate directly to water organization at the adlayer surface. Since the surface roughness at the SiO$_2$/adlayer interface for the OTS-OH system ($\sigma_{SiO2} \sim 10$ Å) was comparable to that of MEG-OH ($\sim 14$ Å), it is unlikely that its parameters could have had significant effects on the interaction of the adlayers with water.

Interestingly the modeled thickness for ‘layer 1’ made up the entire thickness of the sandwiched medium, where $d_1 \sim 19$ Å followed by a sharp transition toward the bulk water ($\sigma_B \sim 2$ Å). With the thickness of the film being $<10$ Å, the remaining portion of $d_1$ could be attributed to highly organized, low-density water up to the bulk interface. As previously mentioned, the $\sigma_B$ is an error factor interpreted as interfacial roughness. It represents/encompasses any reflectivity data that could not be included into the layer parameters (e.g. SLD, d). Contrary to the MEG-OH model, this parameter was quite small meaning that ‘layer 1’ and more specifically, the interfacial water, was well-defined/homogenous providing more confidence in the fit. Based on the models and corresponding SLD profiles, it was concluded that the interfacial water for the OTS-OH system water was short-range and more organized up to the bulk interface in comparison to MEG-OH.

As previously mentioned, it was assumed throughout the entire experimental set that the MEG-OH and OTS-OH adlayers had similar surface coverage. Although the final adlayers differ in composition by only one oxygen atom, both, MEG-TFA and OTS-TFA linkers have large, trifluoroacetic acid tail groups which influence the formation of the film. Unlike packing density, the surface coverage is an issue which must be considered as it could significantly alter the reflectivity curves and subsequently, the interpretation of the NR data. For the MEG-OH system in particular, the reflectivity data and models suggested water penetration into the adlayer
deduced from the high SLD of the modeled layer. What was interpreted as water penetration could have been a consequence of water adjacent to bare, unsilanized areas of Si/SiO$_2$. Because the reflected intensity was collected over an area of ~ 6cm$^2$, the reflectivity from the ‘bare’ areas would have been averaged with the reflectivity from the areas covered with the adlayer. For example, a substrate with 70% coverage would produce the same reflectivity curve as a 0.3 x R(0% coverage) and 0.7 x R(100% coverage). Although MOTOFIT and other fitting software allow for fitting two models simultaneously, information pertaining to the actual surface coverage would be necessary. Regardless of the coverage of the MEG-OH and OTS-OH adlayers, the behaviour of water between the two systems was observed to be vastly different. If both sets of data were averages of reflectivity from hydrated SiO$_2$ and adlayer patches (whether 40% or 60% coverage) then the adlayers’ interaction with water must have been very different in order to produce such distinct hydration profiles. A schematic representation of the two systems in water was created (Figure 42) based on the SLD profiles in Figure 41.

![Figure 42](image)

**Figure 42.** Schematic of hydration profiles at MEG-OH and OTS-OH adlayers based on SLD profiles in Figure 41. The colour gradient is representative of relative water density (assuming constant composition of D$_2$O/H$_2$O).
Through comparison of the hydration profiles of MEG-OH and OTS-OH systems, the effect of the internal oxygen on the adlayers’ interaction with water were determined. Indeed, the two adlayers were found to have different organization of water in the interfacial region supporting the link between hydration and antifouling. The data support the hypothesis stating that the internal oxygen ‘works with’ the distal hydroxyl group to encourage H-bonding within the film. While the MEG-OH system exhibited a broad transition zone of low-density water toward the bulk solution, the OTS-OH adlayer seemed to have a less extensive and highly organized interphase of water. Both exhibited some degree of structuring in the liquid phase consistent with a smooth hydrophilic surface (3-4 nm), although interfacial regions microns thick have been previously reported. Although there is no direct comparison, one of the coatings studied by Schwendel et al. (-(CH₂)₁₁EG₃OMe) similarly exhibited a 4 nm-thick low-density water region with 85-90% bulk density. The OTS-OH displayed a shorter-range but ‘highly organized’ interphase possibly due to interaction of water with exposed alkyl chains, depending on the packing density and orientation of the linkers. Such low SLD have previously been reported to exist at hydrophobic interfaces and are described as ‘nanobubbles’ or dissolved gases.

Another key difference between the two systems seemed to be their water-uptake properties: while the OTS-OH adlayer appeared impenetrable to water, the MEG-OH adlayer was believed to absorb and integrate it within an intra-molecular water network. Here, a ‘disordered’ or loosely-packed adlayer would support this speculation since the MEG-OH species would have greater flexibility – one of the conditions associated with antifouling coatings. With respect to the MEG-OH system, it is possible that once the water molecules had penetrated, the Si-OH groups in the substrate contributed to/strengthened the network of water within. Owing to the short length of the alkyl chain this would be a likely situation particularly if the packing density was low and the film was disordered. From Figures 40 and 41, it is proposed that the long-range diffuse interphase of water stems from a special intramolecular zone of hydration involving the internal ether oxygen as well as the distal hydroxyl group. Although this supports the OTS-OH system’s differing water hydration profile, it raises questions about the mechanism of antifouling. Both interfacial water regions exhibited organized, low-density water and thus, could both be considered as ‘water barriers’ preventing the adsorption of proteins. The difference between a fouling and non-fouling coating, however, is the strength of the bound water – within and/or just at the interface. In the MEG-OH system, the described
intramolecular network of water, itself, would present an energetic barrier for the displacement of water from the coating upon coming into contact with a protein. There would simply be no gain in free energy. A study done in 2009 by Skoda et al.\textsuperscript{61} used NR to look at the protein-density profiles (BSA) adjacent to OEG-based SAMs reporting protein exclusions zone between 4-5 nm. However, they acknowledged the likelihood of protein interaction with the surface and attributed differences in between reversible/irreversible binding of proteins to the strength of surface-bound water. Despite being organized/structured, the interfacial water at MEG-OH and OTS-OH adlayers is likely to be intercepted allowing for the protein to eventually come into close contact with the surface, thus, leaving the antifouling properties to be solely dependent on the hydration of the coating. Although water is an integral part of nature, it is a complex solvent whose unique behaviour should not be generalized but, rather, studied specifically within individual systems.

4 Conclusion

Collectively, NR data and modeling showed distinct hydration behaviour between MEG-OH and OTS-OH systems, confirming the significance of the internal oxygen atom in determining the adlayers’ interaction with water. Through studying the systems on quartz, the limitations of the NR technique from both technical and analytical (interpretive) angles were explored. The study was further developed after experiments performed on thermally oxidized silicon produced data which was interpreted with greater accuracy and confidence. For the MEG-OH system on Si/SiO\textsubscript{2}, a relatively thick, physically distinct transition zone of water was modeled at the adlayer interface. Conversely, the adlayer lacking internal ether oxygen atoms (OTS-OH) exhibited a thinner but more organized interphase adjacent to bulk water. The apparent water uptake properties of the two adlayers formed the basis of the antifouling properties associated exclusively with the MEG-OH adlayer. While OTS-OH adlayers seem to be impenetrable to water, MEG-OH ones showed hydrogel-like characteristics. It was hypothesized that the antifouling properties of the MEG-OH system (which the OTS-OH one lacks) stem from a special intrafilm zone of hydration involving key participation of the internal atoms of oxygen and distal hydroxyl group. Although the systems investigated are unique and comparison against other antifouling coatings is limited, the data support the link between antifouling behaviour particularly, the way in which surfaces are hydrated.
5 Future Work

Several additional studies with the MEG-OH- and OTS-OH systems on Si/SiO$_2$ would be extremely beneficial, if not necessary, in supporting the findings discussed in the present work. This includes investigating the surface coverage, which, for such thin films could be done by fluorescent- or radio-labeling of the surface species and subsequent imaging. Also, NR experiments looking at systems in several different types of liquids, other than contrast matched solutions, are generally performed in order to support existing models in one such liquid. For the present systems, if measurements of the same samples in pure $D_2O$ produced models with the same physical properties (i.e. similar SLD profile – relatively, since SLD$_B$ = SLD$_{D2O}$) then the confidence of the models developed in CMW would greatly improve.

Substrate reproducibility, with respect to surface roughness and oxide quality, was an issue due to thermal oxidation in uncontrolled conditions. Ideally, the experiments should be reproduced on professionally oxidized wafers where quality control ensures better reproducibility of substrate properties. Thus, any differences in measurements could be attributed, indefinitely, to the effects of the adlayers and not their substrates.

In addition to investigating the effect of the internal oxygen atom, it would be interesting to prepare an adlayer which is the methyl-terminated analog of the MEG-molecule (MEG-OMe). This would test the significance of the terminal hydroxyl group on the adlayers’ interaction with water. The effect of this terminal function is of great relevance particularly because it was one of the linkers studied alongside MEG-OH and OTS-OH in the original work by Sheikh et al.$^{29}$ The type of the substrate (e.g. Au vs. SiO$_2$) could also be examined since it has been previously shown to alter the antifouling behaviour of the (thiolated) MEG-OH and OTS-OH adlayers on gold.$^{66}$

Lastly, an interesting study would be to perform molecular simulations on the systems under investigation to determine (1) the structure and conformation of water within the coating as well as at the coating interface$^{67}$ and possibly (2) the forces at play upon interaction with a protein.$^{68}$ Physical analysis of water within the MEG-OH system could also be determined by polarized modulation infrared spectroscopy (PM-IRRAS), providing insight into the interactions experienced by the oxygen species within the adlayer (e.g. based on -C-O-C- stretching).$^{61}$
References


Appendix A: XPS Survey Spectra for Quartz and Si/SiO$_2$ Surfaces

Figure A.1. XPS survey scans for (a) bare quartz (b) clean quartz (c) re-cleaned quartz and (d) control.
Figure A. 2. XPS survey scans for (a) MEG-TFA, (b) MEG-OH, (c) OTS-TFA and (d) OTS-OH adlayers on quartz.
Figure A. 3. XPS survey scans for (a) bare Si, (b) thermally oxidized Si (Si/SiO₂), (c) clean Si/SiO₂ and (d) control.
Figure A. 4. XPS survey scans for (a) MEG-TFA, (b) MEG-OH, (c) OTS-TFA and (d) OTS-OH adlayers on Si/SiO$_2$. 
## Appendix B: NR Modeling Results for Quartz and Si/SiO$_2$ Surfaces

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<th>SLD ($\times 10^{-6}$ Å$^{-2}$)</th>
<th>σ (Å)</th>
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**Table B. 1.** Resulting 1-phase fit parameters for MEG-OH and OTS-OH adlayers on quartz measured in nCMW using using 1-layer model. Values for Cases 1 and 2 shown outside and inside brackets, respectively.

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**Table B. 2.** Resulting 2-phase fit parameters for MEG-OH and OTS-OH adlayers on quartz measured in nCMW using 1-layer model. Values for Cases 1 and 2 shown outside and inside brackets, respectively.
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**Table B. 3.** Resulting Case 1 and Case fit parameters for bare quartz substrate measured in nCMW using 1-layer model. Values for Cases 1 and 2 shown outside and inside brackets, respectively.

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<td>Si</td>
<td>∞</td>
<td>2.07</td>
<td>24.9 (29.9)</td>
<td></td>
</tr>
</tbody>
</table>

**Table B. 4.** Resulting fit parameters for Si/SiO₂ substrate after 30 min in piranha solution with and without varying the SLD of the SiO₂ substrate. Parameters before and after cleaning are shown outside and inside brackets, respectively.
Figure B.1. SLD profiles for (a) Si and (b) Si/SiO$_2$ substrates measured in air. Corresponding reflectivity data and fits shown in Figure 3.11.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer</th>
<th>d (Å)</th>
<th>SLD ($\times 10^{-6}$ Å$^{-2}$)</th>
<th>$\sigma$ (Å)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEG-OH</td>
<td>Air</td>
<td>∞</td>
<td>0</td>
<td></td>
<td>0.00561</td>
</tr>
<tr>
<td></td>
<td>SiO$_2$</td>
<td>163.1 (163.1)</td>
<td>3.48 (3.45)</td>
<td>14.0 (14.0)</td>
<td>(0.00564)</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>∞</td>
<td>2.07</td>
<td>6.7 (6.5)</td>
<td></td>
</tr>
<tr>
<td>OTS-OH</td>
<td>Air</td>
<td>∞</td>
<td>0</td>
<td></td>
<td>0.00132</td>
</tr>
<tr>
<td></td>
<td>SiO$_2$</td>
<td>180.1 (180.1)</td>
<td>3.48 (3.33)</td>
<td>7.3 (6.0)</td>
<td>(0.00130)</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>∞</td>
<td>2.07</td>
<td>7.8 (4.5)</td>
<td></td>
</tr>
<tr>
<td>Bare</td>
<td>Air</td>
<td>∞</td>
<td>0</td>
<td></td>
<td>0.00657</td>
</tr>
<tr>
<td></td>
<td>SiO$_2$</td>
<td>179.7 (179.3)</td>
<td>3.48 (3.33)</td>
<td>8.0 (7.1)</td>
<td>(0.00183)</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>∞</td>
<td>2.07</td>
<td>6.8 (4.3)</td>
<td></td>
</tr>
</tbody>
</table>

Table B.5. Resulting fit parameters for MEG-OH and OTS-OH adlayers on Si/SiO$_2$ substrate measured in air. Values outside and inside brackets correspond to modeling with constant and variable SLD$_{SiO_2}$, respectively.
Table B. 6. Resulting fit parameters for MEG-OH and OTS-OH adlayers on Si/SiO$_2$ substrate measured in liquid air. Phase I and II parameters shown outside and inside brackets, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer</th>
<th>d (Å)</th>
<th>SLD (x $10^{-6}$ Å$^2$)</th>
<th>$\sigma$ (Å)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEG-OH</td>
<td>CMW $\infty$</td>
<td>3.54 (3.66)</td>
<td></td>
<td></td>
<td>0.0768 (0.0232)</td>
</tr>
<tr>
<td></td>
<td>Layer 1</td>
<td>3.48 (21.7)</td>
<td>1.10 (2.97)</td>
<td>17.3 (16.5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SiO$_2$</td>
<td>163.1</td>
<td>3.475 (3.67)</td>
<td>14.0 (14.3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si $\infty$</td>
<td>2.07</td>
<td>6.7 (4.7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OTS-OH</td>
<td>CMW $\infty$</td>
<td>3.54 (3.53)</td>
<td></td>
<td></td>
<td>0.0168 (0.0067)</td>
</tr>
<tr>
<td></td>
<td>Layer 1</td>
<td>20.1 (18.7)</td>
<td>1.09 (0.90)</td>
<td>3.8 (1.6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SiO$_2$</td>
<td>180.1</td>
<td>3.475 (3.56)</td>
<td>7.3 (9.7)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si $\infty$</td>
<td>2.07</td>
<td>7.8 (15.0)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure B. 2. SLD profiles for MEG-OH and OTS-OH adlayers (films) on Si/SiO$_2$. Profiles correspond to 1-phase fit generated using 1-layer model encompassing the film and interfacial water (IW). Dotted lines indicate approximate location of films. (Note For direct comparison, both SiO$_2$/layer 1 interfaces were aligned at ‘0 Å’).
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