Probing the hydration of ultra-thin antifouling silane adlayers using neutron reflectometry: a study on Si/SiO_2

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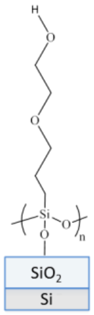

MEG-OH

OTS-OH

A follow up study on the hydration of antifouling silane adlayers (MEG-OH and OTS-OH) originally prepared on quartz was repeated using oxidized silicon wafers (*left*). In the original work, NR results and modeling (using Parratt32 software) showed that the monoethylene glycol (MEG-OH) silane adlayer seemed to have a relatively thick, less dense interfacial water whereas the model for the OTS-OH silane adlayer showed *no* physically distinct phase of water (from bulk). These results supported the hypothesis that the internal oxygen atom of the MEG-OH adlayer participates in a mechanism allowing for water molecules to create a special intrafilm zone of hydration from which the interphase of water originates. Unfortunately, studying such ultra-thin organic adlayers (< 1 nm) on quartz is not ideal considering the generated reflectivity curves are featureless at the measured q_{max} (< 0.07 $Å^{-1}$). As a result, the conclusions drawn from the NR data and corresponding models (on quartz) required further investigation.

As mentioned earlier, the work presented herein investigates the hydration of MEG-OH and OTS-OH adlayers on thermally-grown oxide (on Si wafers). By growing a thick SiO_2 layer (~160-180 Å) on Si the ultra-thin films and interfacial water were easily detected due to the presence of Kiessig fringes on the reflectivity curve. The technique of *contrast variation* was used where the SLD of the bulk solution was matched to that of the SiO_2 substrate (SLD_{SiO2} = 3.48 x 10^{-6} $Å^{-2}$) to enhance the scattering contrast of the adlayer and interfacial region.

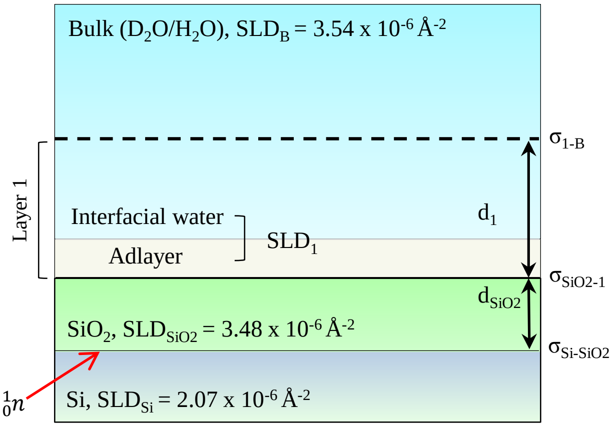

Figure 1. One-layer model schematically depicting (from bottom to top) the Si/SiO_2 substrate, the silane adlayer as well as interfacial and bulk water. Also shown are the thickness (d), roughness (σ) and scattering length density (SLD) values of the various layers. In the 1-layer model, silane adlayer and interfacial water are treated as one single medium. The arrow represents the direction of the incident neutron beam.

In order to analyze measurements performed in liquid, the samples were first scanned in air to determine the required thermally-grown oxide thickness, d_{SiO2}, as well as the interfacial roughness values, $\sigma_{Si-SiO2}$ and σ_{SiO2-1} (later used in the *liquid* models). A 1-layer model encompassing the adlayer and interfacial water was used to fit the system under investigation (Figure 1). The model-fitting program, MOTOFIT[1] was used to simulate the reflectivity curve and create an SLD profile. Modeling the reflectivity curve in liquid involved a 2-phase fitting procedure: a general fit of SLD_1, d_1 and σ_1 followed by the refinement of *all* parameters including those obtained in air and known substrate parameters. Reflectivity and the resulting SLD profiles in contrast-matched water (CMW) are shown in Figures 2a-b and 2c, respectively. Also added in Figures 2a and 2b is the reflectivity curve for bare (unmodified) SiO_2, which is noticeably featureless (*i.e.* lacks Kiessig fringes) confirming that 1) there is *no* distinguishable layer between the bulk solution and SiO_2 substrate and 2) the prepared solution of D_2O/H_2O is indeed contrast-matched.

Upon addition of the MEG-OH adlayer, fringes appear on the reflectivity curve (Figure 2a). Unlike bare SiO_2, these fringes reveal/confirm the presence of a distinguishable 'medium' sandwiched between the two contrast-matched media (SiO_2 and bulk CMW). The low amplitude of these fringes suggest that the layer is not well defined (possibly due to low contrast between adjacent media or high interfacial roughness). The resulting SLD profile (Figure 2c) showed a medium ~ 40 Å-thick with a minimum SLD of ~ 3.2 x 10^{-6} $Å^{-2}$ encompassing 'layer 1' (d ~ 20 Å) and an additional water gradient spanning over ~ 20 Å (σ_{1-B}) until bulk water resumes (χ^2 = 2.32 x 10^{-2}). A higher than normal SLD relative to other organic films[2] suggests that the MEG-OH film absorbed water[3] and corroborates with the previous hypothesis of an 'intrafilm zone of hydration'.[4] This hypothesis is also supported by a recent account of water penetrating into ethylene glycol (EG)-based films.[5]

To determine whether the internal oxygen atoms are involved with the formation of the observed interphase of water, we performed NR measurements on OTS-OH adlayer (Figure 2b). When comparing the reflectivity curves of both adlayers, it is

Thin Films

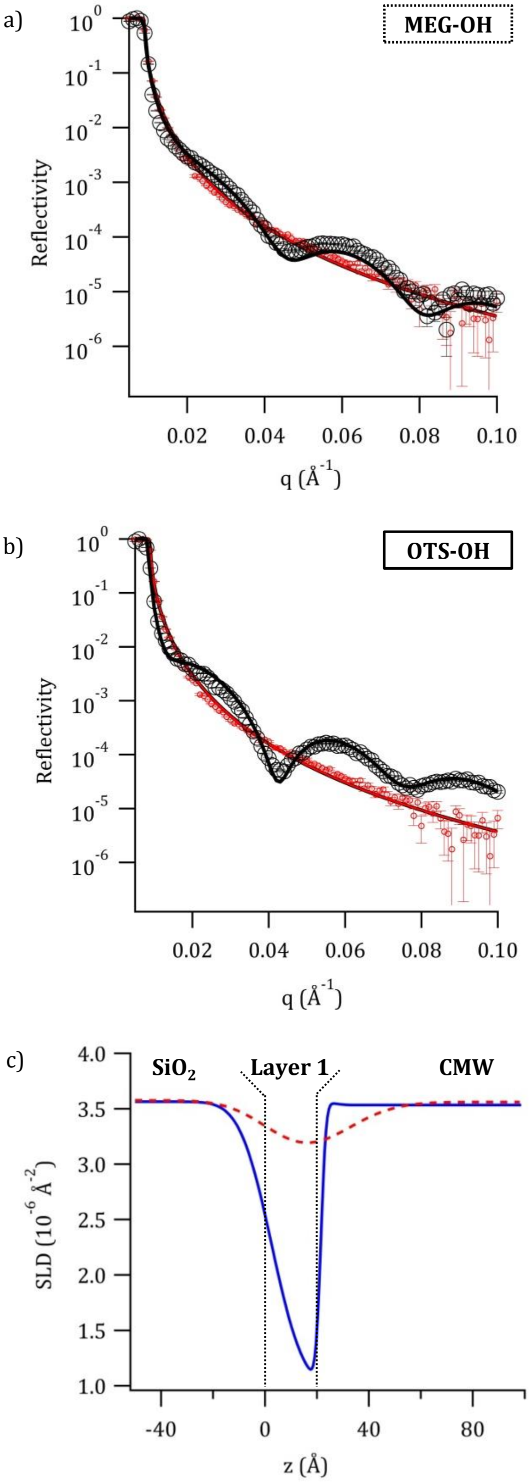

Figure 2. Reflectivity data and corresponding fits for (a) bare (red circles) and MEG-OH modified (black circles) SiO_2 (~ 163 Å-thick) and (b) bare (red circles) and OTS-OH modified (black circles) SiO_2 (~ 180 Å-thick) measured in CMW. (c) Corresponding SLD profiles for MEG-OH (dashed red line) and OTS-OH (solid blue line) systems generated using a 1-layer model (Si substrate not shown). (*Note: For 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').*

immediately evident that the absence of internal oxygen atoms in OTS-OH clearly alters the interaction of water with the adlayer. Unlike MEG-OH, the OTS-OH reflectivity curve has high, sharp amplitude fringes consistent with a well-defined layer in addition to a refractive index deviant from that of the surrounding contrast-matched media. The effect is more evident after fitting the data and generating an SLD profile (Figure 2c). For the OTS-OH system, fitting the data with a 1-layer model revealed that an interphase of water also exists but is much thinner than that of MEG-OH (confined to ~ 20 Å) with a minimum SLD of ~ 1.15 x 10^{-6} Å (χ^2 = 6.73 x 10^{-3}). This low SLD is more representative of an organic coating which is impenetrable to water.[2,6] Unlike the MEG-OH system, there is almost no transition towards bulk water (*i.e.* a sharp SLD transition) and the thickness of 'layer 1' modeled for the OTS-OH system makes up for the entire thickness of the sandwiched medium. For this system, water organization appears to be short(er) in range and more organized up to the bulk interface.

Conclusion

Collectively, NR data and modeling show distinct hydration behaviour between the MEG-OH and OTS-OH systems confirming the significance of the internal oxygen atom in determining the adlayers' interaction with water. A relatively thick, physically distinct interfacial phase/transition zone of water was observed stemming from the MEG-OH adlayer. Conversely, the adlayer lacking internal ether oxygen atoms (OTS-OH) exhibited a thinner but more organized interphase of water adjacent to the bulk solution. Another key difference between the two systems was their water uptake properties: while OTS-OH adlayers seem to be impenetrable by water, MEG-OH ones present hydrogel-like characteristics. The data support the hypothesis according to which the antifouling properties of the MEG-OH system stem from a special intrafilm zone of hydration that involves the key participation of the internal atoms of oxygen and from which the diffuse interphase of water originates. To our knowledge, this work constitutes one of the first examples studying the hydration of subnanometric EG coatings.

References

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(2) Schwendel, D.; Hayashi, T.; Dahint, R.; Pertsin, A.; Grunze, M.; Steitz, R.; Schreiber, F. Interaction of water with self-assembled monolayers: neutron reflectivity measurements of the water density in the interface region. *Langmuir* **2003**, *19*, 2284–2293.

(3) This could also be a consequence of water penetration into the substrate as a result of high surface roughness (~ 14 Å) resulting in a 'smearing' of the interface.

(4) Sheikh, S.; Yang, D. Y.; Blaszykowski, C.; Thompson, M. Single ether group in a glycol-based ultra-thin layer prevents surface fouling from undiluted serum. *Chem. Commun.* **2012**, *48*, 1305–1307.

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(6) Since the surface roughness at the SiO2/adlayer interface for the OTS-OH system (~ 10 Å) is comparable to that of MEG-OH, the possibility of it having significant effects on the interaction of the adlayer with water can be neglected (see reference 3).