X-ray Reflectivity Study of the Growth of Octadecyltrichlorosilane SAMs on Amorphous and Crystalline Silicon Dioxide

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Introduction:
Octadeyltrichlorosilanes (OTS, C18H37Cl3Si) SAMs consist of a hydrophobic hydrocarbon chain tail group, which is exposed, and a hydrophilic trichlorosilane head group that covalently binds to a metal oxide substrate. Our interested lies in the exact bonding scheme of these molecules to various substrates, a question that has been extensively and diversely discussed in science [1, 2, 3]. Our approach is to investigate in-situ the growth of OTS SAMs from solution via X-ray grazing incidence reflectivity for two SiO2 substrates of different nature, the native oxide of a silicon wafer (aSiO2) and single crystalline quartz (001). Thus we can deduce the surface normal structure during growth and the growth kinetics.

Experiment and discussion:
As a solvent for self-assembly we used heptane with an OTS concentration of 0.015mM. From ex-situ reflectivity measurements at our lab source we estimated a reaction time of 12h until the monolayer is fully formed. The in-situ measurements were performed at the high resolution diffraction beamline P08, using a photon energy of 25 keV. Reflectivity curves were taken at three sample position every 15 minutes (in order to reduce radiation damage), with illumination times of about 3 minutes. The experiment was terminated when no changes were observed in consecutive reflectivity curves. Thereafter the sample was taken out and measured against the air interface. The reflectivities for selected reaction times and corresponding fits are shown in fig. 1a. The corresponding scattering length density (SLD) profiles are illustrated in fig. 1b. For the modeling a four (aSiO2) / three (quartz) layer model [4, 5] in addition to the substrate was assumed: The native oxide (only on aSiO2), an interfacial layer, the hydrocarbon chain and an electron depleted region. This electron depleted region, which is enriched with hydrogens, has to be introduced in order to describe X-ray reflectivity data of systems with terminal methyl groups in contact with water or organic solvents [6, 7]. In the fitting routine each last scan was analyzed first, and the obtained parameters for the native oxide and substrate roughness were then used as fixed parameters for all other scans. Further these parameters were used to describe the reflectivity for the dry samples (fig. 1c). For aSiO2 the SAM/air reflectivity is described well for these parameters, whereas the model is not fully consistent for quartz. For both substrates the length of the chain group equals the length of a C18 chain in all trans configuration.

The coverage was calculated by multiplying the scattering length density and thickness of the chain and interface region and adding these together, which is proportional to the total number of deposited electrons. This is shown in fig. 1d. Langmuir isotherms describe this growth well, with rates of 5·10^3 l·mol⁻¹·s⁻¹ for both substrates, which is consistent with the findings of Mirji [8].

For quartz in the very early stages (up to 15 min) we observe an increasing chain length whereas on aSiO2 the chain thickness is constant. This is interpreted as island growth on the aSiO2 substrate, which is consistent with [9], and a more random growth on quartz. On aSiO2 some sites are preferred, which favors island growth. On the other hand on quartz every site is equal, which makes for a different ratio between intermolecular and molecule-substrate interactions on the two substrates, explaining the different growth modes.

References

Figure 1: a: In-situ X-ray reflectivity data and corresponding fits for OTS-SAMs at different growth stages on aSiO₂ (left) and quartz (right); b: X-ray reflectivity data against vapor interface for complete monolayers; c: corresponding scattering length density profiles for in-situ data; d: coverage vs. time and Langmuir isotherm model (red line)