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Report:

During this beamtime under proposal SI-1253, we explored the structure of octadecyltriethoxysiloxane (OTE) SAMs on Si-wafer substrates, prepared by our collaborators in the Granick group at the University of Illinois. The films are highly hydrophobic with a contact angle to pure water greater than 100°. When water is forced to be in contact with such films, the interface is frustrated and is found, in ellipsometry studies [1], to fluctuate wildly on many length- and time-scales. Neutron[2] and X-ray[3] reflectivity experiments have found evidence for a "depletion layer" of reduced density between the organic film and the bulk water. The dimensions of the depletion layer are hard to pin down because of uncertainty of the fitting, but are of order 50% density over 5Å distance.

In our measurements to date, we have been able to confirm this result for the films that were prepared.in the Granick group at the University of Illinois. They consisted of 3 20mm top-hat shaped samples of Si which are compatible with the Teflon Electro-Chemical (EC) cell of Frank Renner. These samples had been previously used for electrochemistry studies and though the Granick group attempted to clean them, it was discovered that they were seriously etched. The worst had a rms roughness of 5A. So in addition, four more samples were coated with OTE, two on 111 Si and two on 100 Si wafers approximately 2cm square. Because they were not specially polished, the wafers were feared to have potential long range waviness problems. Thin, 300micron wafers are especially challenging because they would need to be secured to the sample stage somehow. All the coated samples had contact angles between 100 and 106 degrees.

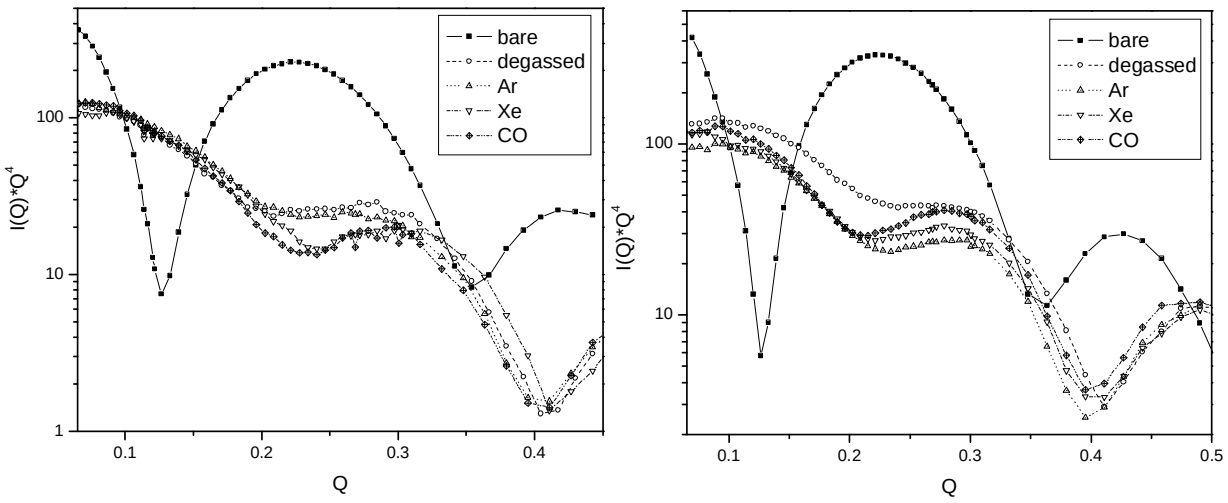
The ID-15 undulator beam was set to 71.5keV with 0.7x0.5 entrance slits. A set of 195 Compound Refractive Lenses (CRLs) were used to focus the beam and a range of motorized absorbers were used to image the various sections of the reflectivity curve. A fast shutter was installed because previous measurements of the OTE films indicated that radiation damage would be a factor in the measurements. The MPI reflectometer was used. Alignment scans were done at 0.1 degree 2*theta angles to ensure that the reflectivity scans did not stray from the specular ridge. The alignment scans also tested that the sample was flat enough to give a Gaussian drop off when imaging the slits which would prove important for some of the samples.

The Ar, Kr, Xe, and CO_2 saturated water was produced by bubbling compressed gas through millipore water contained in clean glassware with a single outlet. Given the solubility of standard gases in water, any native gas in the water would be displaced with the chosen gas once approximately 10 bars of gas had been bubbled through the water. The CO_2 water was prepared in the chemical lab and the saturated water was simply brought down in a sealed container to avoid any complications. Two types of degassed water were prepared, one by boiling and cooling and one by pumping.

The top hat samples were studied first, both wet and dry. Evidence of the hypothesized vapor layer was found in the wet sample. The dips appeared weak compared with previous studies and were found to be inconsistent, probably due to the inhomogeniety of the sample. Damage studies were done and it was found that in $1/5^{th}$ of the time it took to measure an entire wet curve, the OTE film had changed sufficiently that the dip changed in both position and magnitude. The dip position also changed in an irregular way, first shifting to lower Q with ~5 min of exposure and shifting in the opposite direction and slowly filling in at longer times. Thus it was necessary to change the sample position for each data point to ensure that all the data points were taken at a fresh spot on the sample. Differences were observed for the different gases.

The 100 Si wafer samples were then studied by putting the wafer in a flat bottomed Petri dish and securing it by placing a Teflon ring on top. This configuration proved stable enough that it did not move during the scans and could even tolerate having water put in and removed without being disturbed. The curves taken with the 100 wafers had a much stronger signal with sharper features. Similar moving scans were done with the wafers since damage was still a factor. The 111 Si samples were also tried but were found to have a Lorentzian line shape for the slit scans, indicating that they had roughness on a range of length scales and were thus not used.

The reflectivity curves which were analyzed came from the two 100 Si wafer samples. In both cases, there was a clear difference seen for the various gases and are shown below.



As can be seen, shifts in both direction were found for the different species of gas. This is very likely due to the fact that the concentration of gas within the water for the two samples was vastly different. The data from the first sample was taken when the new Petri dish / Teflon ring experimental setup was first being tested. Thus alignment times for the curves ranged from 1.5 hours to 3 hours. Having the water exposed to ambient air for such long periods of time would undoubtedly cause the gas in the water to equilibrate with the air. The second sample was done with much faster alignment times, all with less than 1 hour, thereby greatly decreasing the amount of time the desired species could outgas from the water.

Fitting of the curves was done with Parratt32. Preliminary fits have been done for the dry OTE film. Values relating to the scattering factors for the Si and SiO_2 were obtained from the NIST database. The main fitting parameters were thus the thickness and roughness of the layers. We are currently in the process of comparing the values obtained with values from the literature to assure that our fit is reasonable. Once those values are well corroborated, we can begin to fit the wet curves to determine how the thickness and roughness of the vapor layer depends on the species of gas. We will also compare with the new neutron reflectivity result for gases [4].

[1] X. Y. Zhang, Y. X. Zhu, S. Granick "Hydrophobicity at a Janus interface" Science **295** 663-666 (2002)
[2] R. Steitz et. al., Langmuir **19** 2409-18 (2003)
[3] T. R. Jensen et. al., Phys. Rev. Lett. **90** 086101 (2003)
[4] D. A. Doshi, E. B. Watkins, J. N. Israelachvili and J Majewski, "Reduced water density at hydrophobic surfaces: Effect of dissolved gases", PNAS **102** 9458–62 (2005)