	Experiment title: Structure of solid-water interfaces at supercritical conditions	**Experiment number**: SC-5084
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Report:

We performed pressure and temperature dependent X-ray reflectivity (XRR) studies at beamline ID31 at a photon energy of 70 keV on the structure of the solid-fluid interface using water (H_2O), carbon dioxide (CO_2), and hexafluoroethane (C_2F_6) in combination with a silicon wafer coated with octadecyltrichlorosilane (OTS) as hydrophobic substrate. The aim of the experiments was to investigate the interface under supercritical conditions with regard to possible structure formation caused by adsorption. We were able to exceed the critical point (T_{crit} and p_{crit}) for C_2F_6 ($T_{crit} = 19.88\,^{\circ}\mathrm{C}$, $p_{crit} = 30.48\,\mathrm{bar}$), and CO_2 ($T_{crit} = 30.88\,^{\circ}\mathrm{C}$, $p_{crit} = 73.77\,\mathrm{bar}$) while the supercritical regime was not accessible for H_2O ($T_{crit} = 373.95\,^{\circ}\mathrm{C}$, $p_{crit} = 220.64\,\mathrm{bar}$). The critical temperature could be exceeded, however, the pressure inside the sample cell did not rise high enough under isochoric conditions. This could be due to leakage, or too low a level of water in the sample cell.

During the experiments the temperature was regulated via heating cartridges, that are connected to a temperature control unit (Eurotherm 3508). A type K thermocouple was connected to one of the two 1/4 " high-pressure ports of the sample cell, which was also connected to the temperature control unit. With this setup, high temperature stability up to 0.1 °C could be achieved in a temperature range between 20 °C and 500 °C. A bursting disc with a bursting pressure of 250 bar at 400 °C and a pressure sensor were connected to the other high-pressure port so that safe operation was ensured and the pressure could be recorded.

Before every pressure/temperature series, a wafer was cleaned in an ultrasonic bath in chloroform and ultra pure water, respectively. After placing the wafer inside the sample cell, the sample cell was sealed and mounted at the beamline. When using CO_2 and C_2F_6, the wafer was initially characterized at ambient pressure and room temperature. Gas was then introduced inside the sample volume and the pressure was increased using a cylinder pressure regulator and kept constant with a shut-off valve. Two more XRR curves were recorded until the maximum pressure of the connected gas bottle was reached. The pressure was now increased by heating the sample cell up to 300 °C and XRR measurements were taken. Another reflectivity was recorded close to room temperature after the gas was vented from the sample cell. Due to the high flux of the beam, radiation-induced damage of the wafer was already observed during the second XRR measurement

in air at the same position. We therefore moved the sample perpendicular to the beam in the horizontal plane during a pressure/temperature series. The individual reflectivities were divided into different scan ranges during acquisition, where the absorber factors were reduced at larger q_z due to the lower reflected intensity in order to maintain good statistics.

Figure 1 shows the reflectivitiy data for the pressure/temperature series with C_2F_6. The curves are shifted vertically for clarity. With increasing pressure, a shift of the first minimum to lower wave vector transfers $q_z = \frac{4\pi}{\lambda} \cdot \sin(\alpha_i)$, where λ describes the wavelength and α_i the angle of the incident beam with respect to the sample surface, is observed, indicating the adsorption of a C_2F_6 layer. Above 50 °C up to 100 °C, the minimum shifts to higher q_z again, which could be due to desorption of the C_2F_6 layer or also damage of the OTS layer. In addition, the oscillation amplitudes decrease with increasing pressure. At 300 °C the reflectivity shows no oscillations and is similar to the reflectivity of a silicon surface, indicating the destruction of the OTS film. The reference measurement in air at 37 °C after the pressure/temperature series shows weak oscillations. However, these oscillations are not related to those of the reference measurement in air before the pressure/temperature series. Therefore, it can be assumed that the OTS layer is no longer present. After the gas was drained from the sample volume, a thin adsorbed layer might have remained, causing the observed oscillations.

Figure 2 shows the reflectivities for the pressure/temperature series with CO_2. The reference measurement at air and 26 °C shows the typical oscillations of a silicon-OTS interface. By increasing the pressure at constant temperature, the oscillations are strongly damped and the first minimum shifts to smaller qz, which is indicative of a rough adsorbed layer whose thickness increases. As the temperature was increased up to 150 °C, the oscillations become more pronounced again and the first minimum shifts to higher qz, which may be attributed to alterations in the adsorbed layer and perhaps also in the substrate. At 250 °C, the oscillations are barely visible, because the OTS layer is presumably nearly defective. Based on the reflectivity after the gas has been released from the sample cell, it can be seen that the OTS layer has been irreversibly damaged.

The data is still under evaluation.

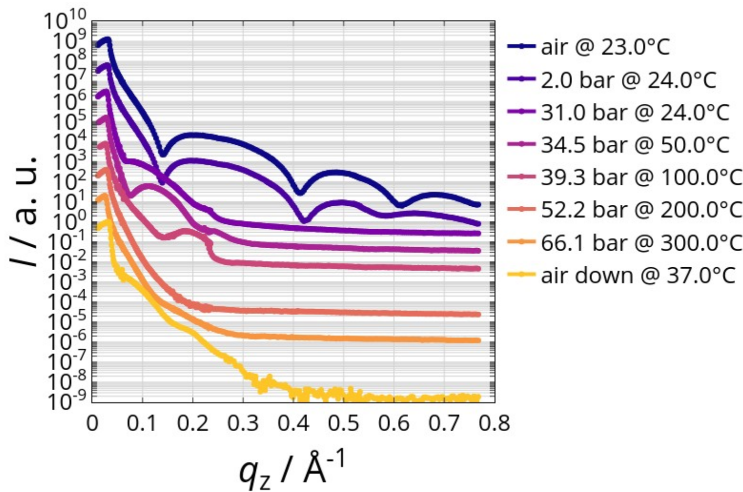

Figure 1: Reflectivity curves for the pressure/temperature series with C_2F_6.

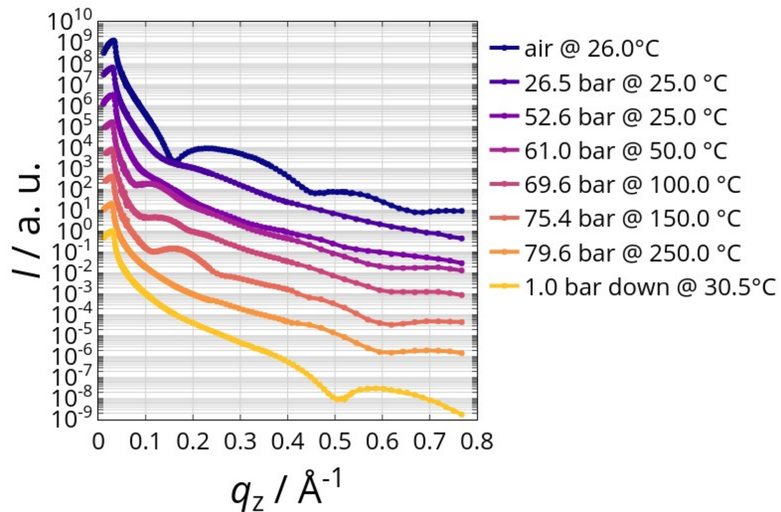

Figure 2: Reflectivity curves for the pressure/temperature series with CO_2.

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