

**Experiment title:**

Bridging the pressure gap for oxygen on Silver

**Experiment number:**

SI665

**Beamline:**

ID3

**Date of experiment:**

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**Shifts:**

21

**Local contact(s):**

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**Report:**

The aim of our experiment was to study the structure of Ag surfaces at elevated oxygen pressures and temperatures using surface x-ray diffraction as an in-situ tool. The experiment was performed on the vertical z-axis diffractometer of beamline ID3 at a photon energy of 17 keV. Micrometer thick Ag(100) and Ag(111) epitaxial films were prepared in Stuttgart prior to the experiment by Molecular Beam Epitaxy. They were transported to the ESRF in a multi-sample UHV transport chamber. From this chamber the samples could be transferred to our UHV-high pressure (HP) chamber, allowing quick sample exchange without vacuum breaking. The UHV-HP chamber is in its design similar to the ID3 one, but it allows in addition sample transportation by a battery driven ion pump. It can be attached to a sample characterization chamber in Stuttgart, which allows pre- and post-experiment sample exchange to perform auxiliary low energy electron diffraction and Auger electron spectroscopy. The epitaxial films were of high quality as confirmed by the in-plane Bragg peak rocking width of  $0.03^\circ$  for Ag(100) films. As a first step, we employed grazing incidence diffraction to measure the in-plane lattice constant with an information depth varying from 2 nm to 1000 nm as a function of the temperature and oxygen pressure. No indication of a peak shift for different information depths could be detected for the clean surface and under stationary exposure to 10 mbar  $O_2$  at  $300^\circ C$ , in agreement with the low bulk solubility of oxygen in Ag at this temperature.

To be even more surface sensitive, crystal truncation rod measurements were performed. Figure 1 summarizes the results for the Ag(100) surface. In Figure 1 a) a sequence of (20) rods is plotted, during which the oxygen pressure was varied from 0 to 10 mbar. The rod of the clean surface and after the oxygen exposure cycle are identical and correspond to the clean Ag(100) surface. It exhibits a small inward relaxation, which

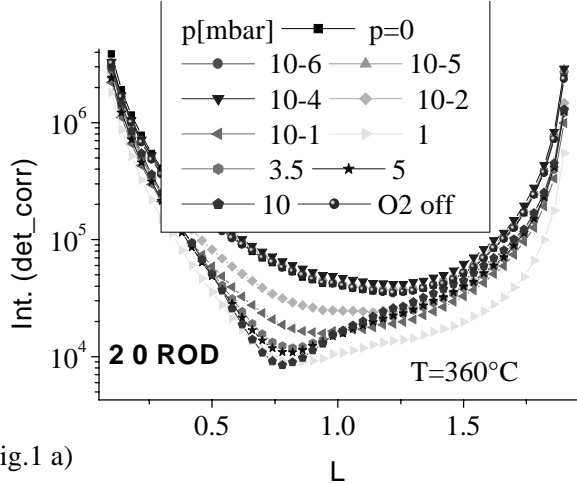


Fig.1 a)

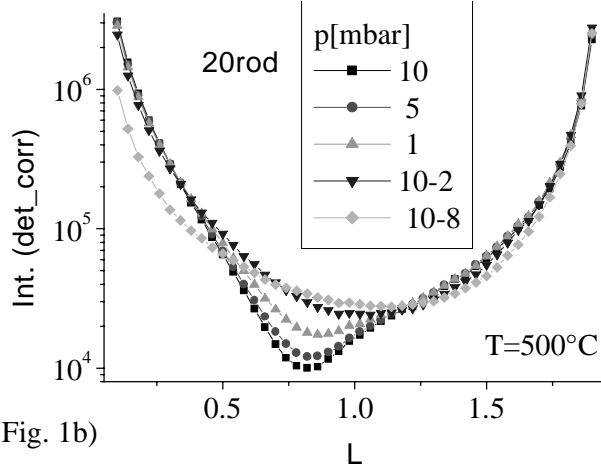


Fig. 1b)

can be readily seen from the small shift to the right from the ideal rod minimum at  $L=1$ . With increasing oxygen pressure the rod minimum starts to move to the left of the ideal minimum position and a change in the rod

shape takes place, which indicates a change in the surface structure of the first layer. It is fully established at an oxygen pressure of 10 mbar. This change in structure is completely reversible with reduction in oxygen pressure and disappears again, when oxygen is switched off. A very similar behavior is also observed at 500°C (Figure 1b)), at which the change in surface structure takes also place. From the shift to the left of the rod minimum it can be concluded in a qualitative way that the outmost Ag layer distance is increased with respect to the bulk

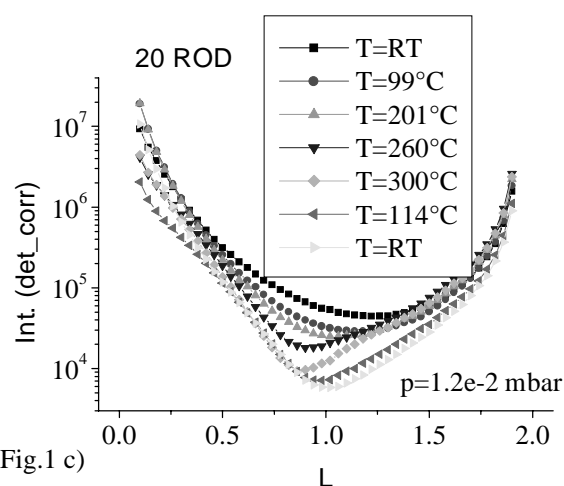


Fig.1 c)

value or that oxygen is incorporated between the first two Ag layers, giving rise to a phase shift for the scattered x-rays. The difference between these two cases will be visible in the quantitative data analysis. In Figure 1 c) is summarized the temperature dependence of the formation of the new surface structure at an oxygen pressure of  $1.2 \times 10^{-2}$  mbar, which is the onset pressure for significant changes in the surface structure. Interestingly, at room temperature the new structure is not formed but with increasing temperature a change in the surface structure takes place, which can be kinetically frozen in after reducing the temperature again to room temperature and maintaining the oxygen pressure. This demonstrates that the formation of the oxygen induced change in the surface structure is thermally activated and that it probably involves dissociation of oxygen molecules at the Ag surface.

In the second part the Ag(111) surface was examined. Figure 2 a) shows a truncation rod of the (111) surface measured at 360°C for different oxygen pressures. The (1,-1) rod is sensitive to the stacking of the Ag layers in the (111) direction and the appearance of Bragg reflections at  $L=1,2$  and  $4,5$  indicates that during the

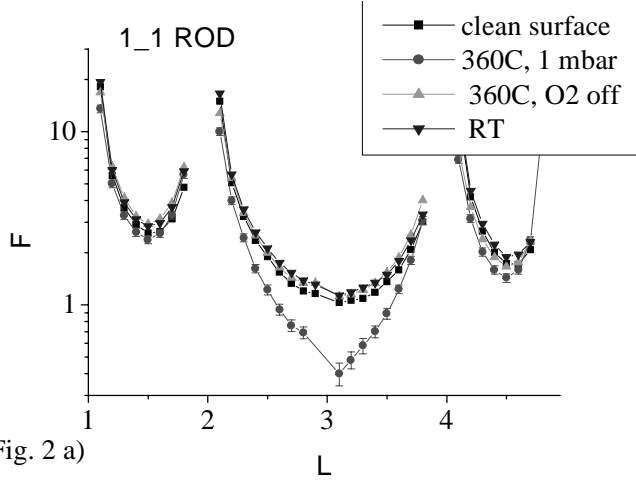


Fig. 2 a)

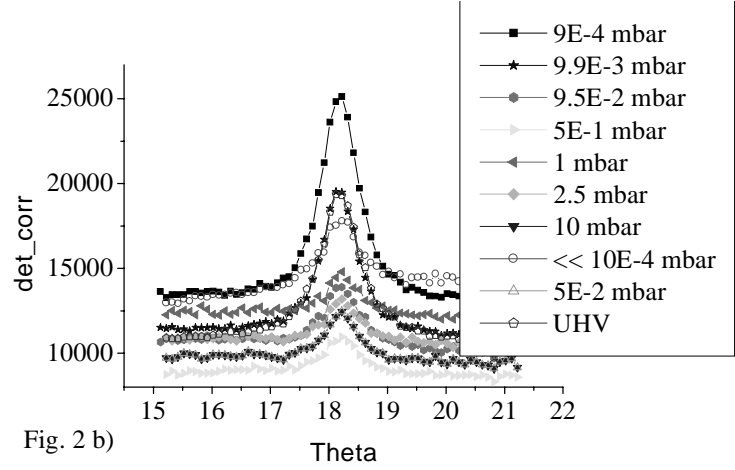


Fig. 2 b)

growth of the Ag films twin formation takes place, so ABC and CBA stacked domains coexist. Nevertheless, an oxygen pressure dependent huge reduction of the structure factor modulus on the rod minimum at  $L=3$  can be recognized. On the other hand, the minimum of the rod does not shift. A straight forward interpretation of the observation is an oxygen induced faceting of the Ag(111) surface at an oxygen pressure of 1 mbar.

Figure 2 b) shows a sequence of theta scans at  $(1,-1,3)$  for  $360^\circ\text{C}$  and different oxygen pressures. The peak intensity is reduced with increasing oxygen pressure and it reappears again, when the oxygen pressure is decreased, showing the reversibility of this process. The time constants involved in this surface restructuring is of the order of 30 min to 1 h, but to recover the original intensity the surface has to be heated to  $520^\circ\text{C}$ . The mosaicity of the (111) samples as judged from the theta scan is higher than for the (100) surface because of the growth defects mentioned above. A faceting of vicinal Ag surfaces was observed recently at oxygen pressures in the 10-8 mbar regime at room temperature, pointing of the importance of steps for oxygen induced step bunching. This interpretation could also hold to explain the data described here, because during epitaxial growth also step bunching can take place. The step bunches could act as cores for the facet growth during the oxygen exposure. On the other hand, no rods due to large facets could be detected, which indicates that the atomic rearrangement takes place on an atomic scale.

To summarize, for the Ag(100) surface a thermally activated, reversible, oxygen induced change in the surface structure was observed, taking place in the mbar regime, which was not yet reported in literature. The Ag(111) surface exhibits an oxygen induced, reversible surface roughening at elevated temperatures. Its origin is either a spontaneous or step induced change in the equilibrium surface energy by the adsorption of oxygen.