



Experiment title: Structure of O-Ag(111) p(4x4) on single crystals and Ag nanoparticles investigated by in-situ surface x-ray diffraction

Experiment number:
SI-1355

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Report:

Silver is used as a catalyst for oxidation reactions on a large scale. Knowledge of the atomic and micro structure of silver surfaces is of great importance for a better understanding of its functionality. The aim of the present experiment was to study the atomic surface structure of Ag(111) and Ag nanoparticles on sapphire at oxidizing conditions. At a temperature of 280 °C and an oxygen pressure of about 100 mbar, the O-Ag(111) surface reconstructs to form a p(4x4) overlayer. By use of synchrotron X-rays, it is possible to perform scattering experiments enabling to obtain the structure with atomic resolution. Experimental access to performing in situ surface sensitive X-ray scattering experiments while maintaining the sample at the appropriate thermodynamic parameters for the oxidation, is achieved in a dedicated sample chamber, which was developed at the Max Planck Institute for Metals Research.

Although the diffractometer at BM25 is standard, due to the particular construction of the detector arm, there was not enough space for our sample chamber to freely rotate. With a few modifications on both the detector arm and the sample chamber, it was possible to have a free rotation for the sample chamber over 180 degrees, enabling to check for equivalent reflections along the Ag(111) three-fold symmetry axis.

In addition, two days of the beam time were lost, because of a poor crystal quality of the Ag sample and it was necessary to repeatedly sputter and anneal the sample in UHV at 650 °C. This resulted in sharp diffraction features enabling to continue the experiment. The experiment was planned to be performed with an X-ray energy of 18 keV, because this would allow for accessing a large part of reciprocal space. For unknown reasons, the flux was extremely low at this energy (about 10^9 photons/s in the 1mm^2 beam). By changing the energy to 12 keV we obtained a flux of $1.4 \cdot 10^{11}$ photons/s/ 0.6mm^2 @160 mA ring current, which was measured using a calibrated photodiode. However, it would be possible to gain another 25% of flux at the sample position. This could be achieved by using the signal of the beam monitor in the experimental hutch as feedback to the monochromator instead of the signal of the beam monitor in the optics hutch. It seemed that the maximum intensity found by the feedback system using the beam monitor in the optics hutch was systematically lower than the maximum intensity that could have been obtained in the experimental hutch. The beam monitor in the experimental hutch also has a very large dark current (about

10%), which should be taken into account when scaling the data. Halfway our beam time the filling mode of the ring changed from $2 \times 1/3$ to hybrid mode. With this change the beam became less stable. Although the maximum ring current does not change between the two filling modes (200 mA in both cases), the lifetime does change drastically (almost a factor of 10). The fact that the stability of the X-ray beam was much affected by this seems to be a sign of optics overly sensitive to *changes* in the heat load. Here a better feedback for the optics as discussed before would be very helpful.

The stability of the $p(4 \times 4)$ surface reconstruction was monitored by the reference reflection (0.25,0.75,0.2). At an oxygen pressure of 80 mbar, this particular reflection showed the highest intensity, indicating that with the present set up these are the ideal circumstances. The reconstruction showed not to be stable for a period longer than about 6 hours. After repeatedly preparing the $p(4 \times 4)$, it was found to be stable only for about three hours, which is an indication that the sample properties changed with time. By renewed annealing of the sample at high temperature and oxidizing the clean surface again, the stability became better again. It could be that a small leak in the sample chamber was responsible for a too high water vapour pressure, which is known to destroy the $p(4 \times 4)$ reconstruction.

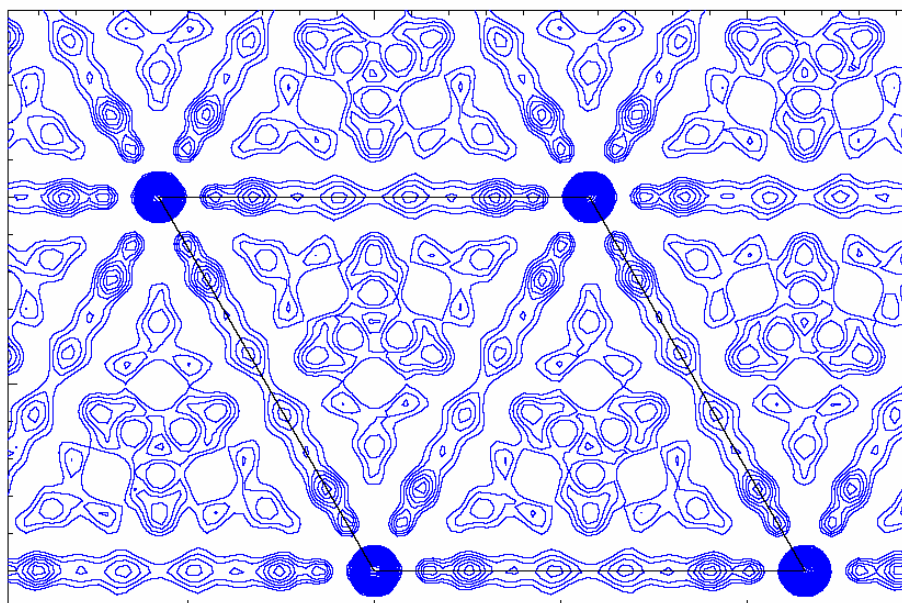


Fig. 1 Patterson map of the $p(4 \times 4)$ O-Ag(111) surface.

From the O-Ag(111) surface at 280 °C and 80 mbar oxygen pressure, about 500 points in reciprocal space were measured in situ, resulting in 20 surface rods, 3 crystal truncation rods and an in-plane data set which results in the Patterson map shown in figure 1. In addition, three CTR's of the Ag(111) surface at 500 °C in vacuum were measured.

In conclusion we can say that we have partially succeeded in meeting our goals as set for the present experiment. Due to problems with the sample and the set up, such as the sample chamber not being completely adapted to the particular diffractometer and not having enough photon flux at 18 keV, we lost too much beam time to be able to study the Ag nanoparticles. Nevertheless, we were able to obtain complete data sets of the Ag(111) surface at oxidizing conditions. The data are currently being worked out and will be helpful for obtaining a better view of the Ag(111) surface structure at oxidizing conditions and high temperatures, which are common in chemical reactions.