	Experiment title: *In operando* GISAXS and reflectivity studies of homoepitaxial electrodeposition on Au(001)	**Experiment number:** SI-2524
Beamline: ID03	**Date of experiment:** from: 05 Dec 2012　　　　　to: 12 Dec 2012	**Date of report:** 28 Feb 2013
Shifts: 18	**Local contact(s):** Dr. Francesco Carlà	*Received at ESRF:*

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Report:

Electrochemical deposition has a wide field of applications, especially in micro- and nanoscale fabrication. Due to its technological importance it is subject of substantial research. Nevertheless, there is still a lack of basic understanding on how the complex structure of the electrochemical interface affects the microscopic nucleation and growth processes. A well-suited model system for such studies is the homoepitaxial electrodeposition of Au(001), which exhibits a complex potential-dependent growth behavior [1]. In a previous experiment at beamline ID32 (SI-2282) we performed first pioneering *in operando* grazing incidence small angle X-ray scattering (GISAXS) studies on the temporal evolution of the nanoscale lateral structure of Au(001) electrodes during deposition in the potential regime of multilayer growth. We found that the evolution of these structures on the unreconstructed Au(001) surface is isotropic and determined by a well-defined power law. The coarsening exponent obtained in these experiments was comparable to values found in various publications, which describe crystal growth or erosion under vacuum conditions.

In experiment SI-2524 we systematically developed and optimized this method for our studies of homoepitaxial electrodeposition in 0.1 M HCl with different $HAuCl_4$ concentrations in the range 0.5 to 2.0 mM. Furthermore, we obtained for this deposition system complementary information on the vertical structure size by X-ray reflectometry (XRR). In addition, first studies in Br^- containing electrolyte were performed to elucidate the influence of the anion species on the homoepitaxial electrochemical growth of Au(001).

As in former beamtimes we performed the *in situ* surface scattering measurements in our "hanging meniscus" transmission X-ray cell using a photon energy of 22.5 keV. For GISAXS studies we used the Dectris Pilatus 300K-W, which was installed at a distance of 2 m behind the sample. Reflectivity and GID measurements we performed with the Maxipix detector which is mounted on the diffractometer in EH1 at ID03 at 1 m distance from the sample.

In operando reflectivity studies during growth are currently hampered by the slow motor movement of the diffractometer, which currently prevents obtaining a full XRR dataset within a few seconds. In order to study the evolution of the vertical surface morphology with a sufficient time resolution for our investigations of the fast roughening process during multilayer growth we adapted an approach demonstrated in previous studies of layer-by-layer growth by our group [2]: Here, the specularly reflected intensity at a constant L-value was measured as a function of time after a potential step from 0.6 $V_{Ag/AgCl}$, where the high Au surface mobility leads to a well-defined atomically smooth surface, to a potential in the regime of multilayer growth. These measurements were highly reproducible, allowing to obtain full XRR datasets with a time resolution of 0.5 to 1 Hz by recording such intensity transients for different L-values. Specifically, the use of a 2D detector resulted in significant improvements in signal-to-noise ratio and background correction as compared to our previous studies, where a simple scintillation counter was used [2]. We performed such experiments for L-values up to 0.9 and five deposition potentials between 0.0 and 0.2 $V_{Ag/AgCl}$. As an example, figure 1 shows selected reflectivity curves for deposition at 0.0 $V_{Ag/AgCl}$ in 0.1 M HCl + 0.5 mM $HAuCl_4$, revealing a clear decrease of the intensity with time. Detailed quantitative analysis of these data (currently in progress) will provide first insight into the roughness evolution during electrochemical multilayer growth.

In the *in situ* GISAXS studies of this system the time-dependent evolution of the lateral structure size was systematically studied by corresponding potential-step experiments as a function of potential and $HAuCl_4$ concentration. As in the former beamtime SI-2282 we separate the diffuse scattering caused by the growth of 3D Au islands from the static scattering contributions (resulting from the long-range step morphology of the sample) by averaging over the detector frames taken at 0.6 $V_{Ag/AgCl}$ and substracting this intensity contribution from the detector frames taken at a potential in the regime of multilayer growth. Figure 2 shows a selection of the resulting intensity distribution for three different concentrations after different times in the multilayer growth regime. An isotropic intensity distribution with a characteristic lateral structure size is found in all cases. The temporal evolution is governed by a scaling law that depends on potential, but not on the $HAuCl_4$ concentration, i.e., the Au flux to the growing interface (figure 3). However, the surface roughness increases with the concentration, as also indicated by the decreasing amplitude of the intensity distribution maximum with concentration (see figure 2).

Finally, we also performed first exploratory deposition studies in 0.1 M $HClO_4$ + 1 mM NaBr + 0.5 mM $HAuCl_4$. Surprisingly, Au(001) growth in this electrolyte was found to exhibit an unexpected tendency towards higher surface roughness, suggesting that the presence of Br^- decreases the Au surface mobility as compared to Cl^-.

In summary, the *in operando* electrodeposition studies previously performed by our group at ID32 could be successfully continued at ID03. Specifically, in this experiment for the first time complementary quantitative data on the nanoscale vertical and lateral structure size evolution during homoepitaxial electrodeposition could be obtained as a function of potential and metal ion concentration. These data are an important experimental basis for decribing electrochemical growth from the atomic to mesoscopic length scales and thus will provide new fundamental insight into these technologically important processes.

References

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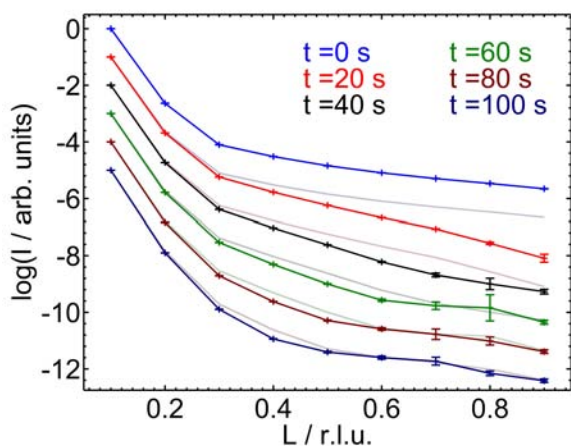
Figure 1: Measurements under reflectivity conditions during homoepitaxial growth at 0.0 $V_{Ag/AgCl}$ in 0.1 M HCl + 0.5 mM $HAuCl_4$. The curves are normalized to the intensity at L = 0.1 and shifted with respect to each other by an offset of -1. For easier comparison dashed lines show the previous reflectivity curve with offset.
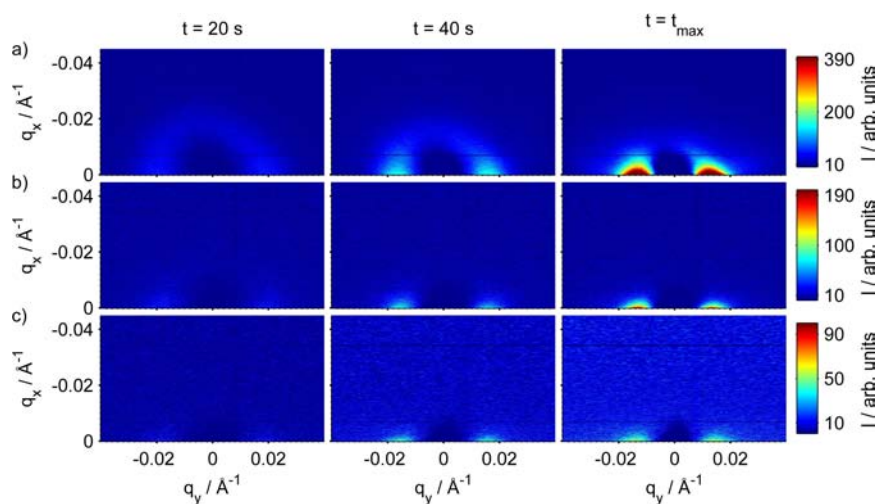

Figure 2: Distribution of separated intensity at different stages of multilayer growth in 0.1 M HCl containing **a)** 0.5 mM $HAuCl_4$, **b)** 1.0 mM $HAuCl_4$, and **c)** 2.0 mM $HAuCl_4$ after deposition at 0.1 $V_{Ag/AgCl}$ for 20 s, 40 s, and directly before the potential step back to 0.6 $V_{Ag/AgCl}$ at **a)** $t_{max} = 100$ s, **b)** $t_{max} = 80$ s and **c)** $t_{max} = 50$ s.
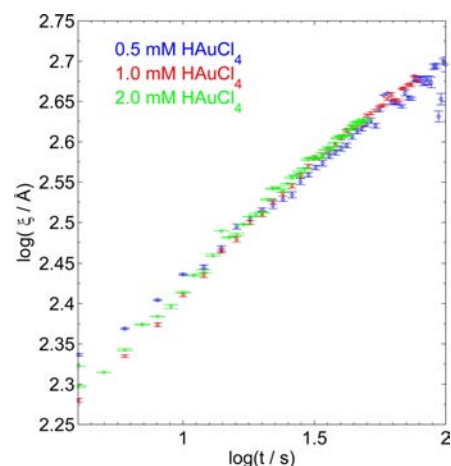

Figure 3: Temporal evolution of the characteristic lateral structure size, obtained from the data partially shown in figure 2.