	Experiment title: In operando surface X-ray diffraction studies of Ag(001) homoepitaxial electrodeposition: Effect of adsorbed chloride	**Experiment number**: CH-4308
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Report:

In this experiment we investigated the homoepitaxial growth on Ag(001) single crystal electrodes as a function of the applied electrochemical potential. The experiments were performed at 22.5 keV using our "hanging meniscus" transmission cell [1]. We used a Ag/AgCl reference electrode against which all potentials are stated. Prior to each experiment the Ag(001) crystals were cleaned by 10 cycles of chemical etching (dipping into a freshly prepared 1:1 mixture of 0.42 M NaCN and 20% H_2O_2 for about 3 seconds, followed by immersion into 0.76 M NaCN until the gas evolution stopped and the crystal had turned silver again [2]) and subsequent annealing in an induction oven at the onset of a faint orange glow for 15 minutes.

All growth experiments were performed in 0.1 M $HClO_4$ + x mM $AgClO_4$ (x = 0.1, 0.2). Before alignment the electrochemistry was checked in 0.1 M $HClO_4$. We then aligned the sample, which took about 4 hours per alignment during this run, because the hexapode was not working properly (usually the alignment procedure requires only 30 minutes). After alignment we filled the cell with the Ag containing electrolyte. Since the electrolyte is not stable under the beam, we kept the illumination to a minimum.

The potential step experiments were performed as follows: At a potential of -0.2 V, which is in the regime of smooth step-flow deposition, we exchanged 1 ml of the electrolyte at a flow rate of 5 µl/s and waited for 2 minutes. Data acquisition was started 20 seconds before initiating the step to the potential of interest. After further data acquisition during Ag growth at this potential, we stepped back to the initial potential of -0.2V and monitored the intensity until the surface smoothened again by deposition in step flow growth mode.

Prior to the studies of Ag homoepitaxial growth, the electrochemical behaviour of the Ag(001) sample surface was characterized in 0.1 M $HClO_4$ by cyclovoltammetry (Fig. 1(a)). The shape of the cyclovoltammogram is very similar to that of previous studies (e.g. [3]), verifying that clean Ag(100) surfaces were prepared and well defined electrochemical conditions were assured during the deposition experiments. The featureless double layer regime exhibits continous transitions to the cathodic hydrogen evolution regime and, at the most positiv potentials, to the onset of anodic dissolution of Ag.

X-ray measurements were perfomed by monitoring the intensity close to the anti-bragg position of the Ag(11) rod (L=0.1) where a maximum of surface sensitivity is achieved which allows to indentify different growth modes [1,4]. Fig. 1 (b) shows a selection of X-ray transients, recorded during Ag deposition in 0.1 M $HClO_4$ + 0.2 mM $AgClO_4$ for steps to different potentials -0.5 V < E < +0.20V. In accordance with previous electrochemical studies of Ag on quasi-perfect single crystal electrodes, a regime of smooth step-flow deposition could be identified, as indicated by unchanged intensity after stepping to E=-0.25V or even a significant intensity increase at E=-0.10V. Moreover, STM studies [3] of bare Ag(001) surfaces in 0.1 M $HClO_4$

show in the same potential regime large, atomically flat terraces, separated by mostly monoatomic steps, promoted by a surface- annealing process due to a high surface mobility of Ag adatoms. For even more positive potentials the intensity decreases slightly, probably indicating the onset of Ag dissolution. We assign this to slight surface roughening, in accordance to the previous STM studies, which reveal a roughening of the Ag(001) steps during dissolution. For potentials negative of E=-0.3 V, the x-ray transients exhibit a decrease in intensity followed by subsequent oscillations, as expected for layer-by-layer growth. Finally, for potentials close to the hydrogen evolution regime, strong and fast damping of the oscillations indicates increased surface rougnening, which probably marks a transition to 3D growth. These observations suggest significant changes in the Ag surface mobility with potential. In contrast, in-situ STM studies of step edge fluctuations on Ag(111) in sulfuric acid solution reported an approximately constant mobility up to -0.1 V, followed by a strong increase in the Ag dissolution regime [5].

Ag^+ ion concentration dependent studies were strongly hampered. Specifically, we found that the period of the growth oscillations were not fully reproducible. This may be caused by instability of the electrolyte under X-ray illumination and a resulting decay of the Ag concentration in the solution.

In summary, the experiment demonstrated that potential dependent growth modes of homoepitaxial deposition on Ag(001) can be studied accurately in-situ in our hanging meniscus cell by combining electrochemical methods and surface X-ray diffraction.

Unfortunately, the orginally planned growth studies on Ag(100) in halide ion containing electroytes as well as GISAXS studies in both, halide-free and halide-containing electrolyte, were not possible within the experiment, because of significant time delays caused by the malfunctioning hexapode. Further thought should be put into possibilities to keep the Ag ion concentration in the solution constant when it is illuminated with the beam.
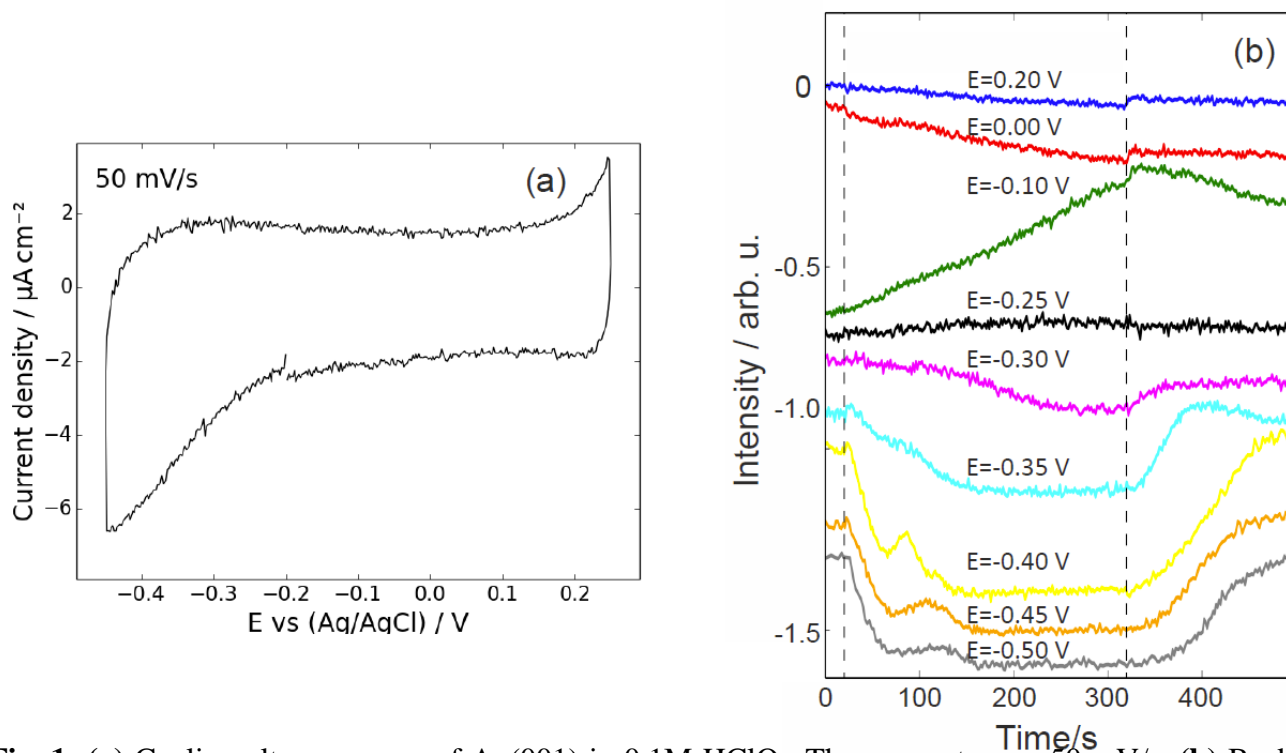

Fig. 1: (a) Cyclic voltammogram of Ag(001) in 0.1M $HClO_4$. The scan rate was 50 mV/s. **(b)** Background-corrected integrated x-ray intensity at (1 1 0.1) as a function of time during Ag deposition on Ag(001), recorded in 0.1 M $HClO_4$ + 0.2 mM $AgClO_4$ after potential steps from -0.2 V to different potentials E. The first dashed line correspond to the time at which the potential was stepped from -0.2 V to E, the second one indicates step back to -0.2 V.

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