



	Experiment title: Homoepitaxial copper electrodeposition under controlled mass transport: The inhibiting effect of the halide-PEG complex	Experiment number: SI-1999
Beamline: ID 32	Date of experiment: from 29/08 to 01/09/2009; from 04/11 to 09/11/2009	Date of report: 14/10/2010
Shifts: 18	Local contact(s): Jerome Roy	<i>Received at ESRF:</i>
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Report:

In this work in-situ surface X-ray scattering studies in transmission geometry at beamline ID32 ($E_{\text{ph}} = 22.5$ keV) were performed in order to investigate potential induced structural changes at Cu/electrolyte interfaces, using the “hanging meniscus” electrochemical cell employed in our previous experiments [1-3].

In detail, we studied the homoepitaxial electrodeposition on Cu(001) in 0.1 M $\text{HClO}_4 + 1$ mM $\text{HCl} + x$ mM $\text{Cu}[\text{ClO}_4]_2$, i.e. for rather high Cu concentrations ($x = 1$ and 5) resulting in deposition rates closer to industrial electroplating processes [4].

In order to achieve the improved time resolution required to monitor in-situ structural changes of the growing surface during this electrodeposition “one shot” experiment, we used for the first time our one-dimensional detector (Dectris Mythen 1k [5]) at beamline ID32 (Fig. 1).

Fig. 2a shows the time dependent integrated X-ray intensity at (1,1,0.1) during dissolution of Au(001) after a potential step to $1.09 V_{\text{Ag/AgCl}}$, i.e. deep into the dissolution regime, with a time resolution of 5 ms. The oscillations allow to verify layer-by-layer dissolution with a rate of >10 ML/s, which demonstrates the capability of this detector system for the real-time investigation of fast Cu electroplating processes.

In detail, potential step experiments at (1,1,0.1), i.e. close to the anti-Bragg position of the (1,1) rod, were carried out in order to determine the kinetic growth modes on Cu(001). For the potential of $-0.6 V_{\text{Ag/AgCl}}$ a rapid smoothening of the surface was observed, indicated by the recovery of the integrated X-ray intensity. This potential led to smooth, reproducible surfaces and hence was chosen as initial potential for the subsequent potential steps. After potential steps to potential values between $-0.55 V_{\text{Ag/AgCl}}$ and $-0.10 V_{\text{Ag/AgCl}}$ the time-dependent intensity oscillates with time, indicating layer-by-layer growth (Fig. 2b), whereas previous experiments (report SI-1530) in pure HCl-based electrolytes revealed step flow growth over a wide potential range for different Cu concentrations. The oscillation period determined by the measured X-ray intensity transients (8.1 s for $x = 1$ and 1.6 s for $x = 5$) are in good agreement with the calculated ones for diffusion limited deposition. Moreover, systematic investigations of the X-ray beam influence by recording the electrochemical current as well as the scattered X-ray intensity allow to exclude beam damage effects in $\text{HCl} + \text{HClO}_4$ based electrolytes.

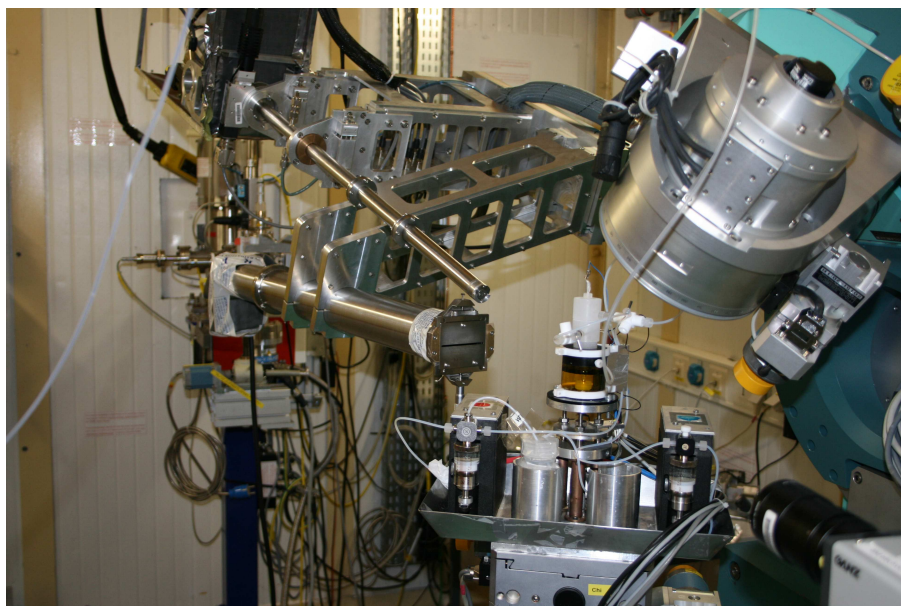


Fig. 1: Setup for the implementation of the Dectris Mythen 1k detector and its flight tube on the six diffractometer of beamline ID32. The “hanging meniscus” electrochemical cell and the remote controlled pumping system are mounted on the Huber tower.

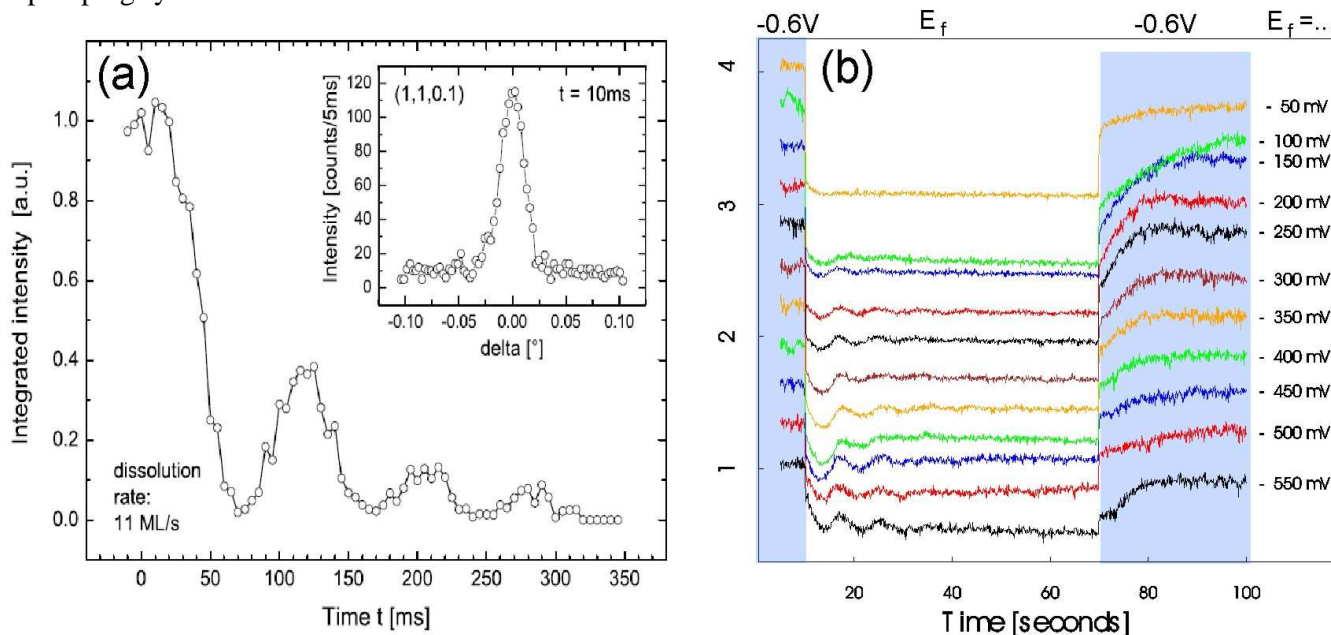


Fig. 2: (a) Integrated intensity transients at (1,1,0.1), i.e. close to the anti-Bragg position, during dissolution of the Au(001) surface after a potential step from $E = 0.6 V_{\text{Ag}/\text{AgCl}}$ to $1.07 V_{\text{Ag}/\text{AgCl}}$. The integrated intensity has been determined by frames recorded by the Dectris Mythen 1k detector with a rate of 200 Hz. The dissolution rate determined by the oscillation period in layer-by-layer mode is 11 ML/s. (b) Time dependent integrated intensity at (1,1,0.1) during Cu electroplating on Cu(001) after a potential steps from $E = -0.6 V_{\text{Ag}/\text{AgCl}}$, revealing layer-by-layer growth in 1 mM $\text{Cu}[\text{ClO}_4]_2$ containing electrolyte over a wide potential range. The curves are shifted with respect to each other.

References:

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