ESRF	**Experiment title:** In-situ time-dependent studies of the homoepitaxial growth of Au on Au(001) and Au(111)	**Experiment number**: **SI-1361**
Beamline: ID-32	**Date of experiment**: from: 15 March 2006 to: 21 March 2006	**Date of report**: 12.01.2007
Shifts: 18	**Local contact(s)**: Dr. Frank Uwe RENNER (e-mail: renner@esrf.fr)	*Received at ESRF:*
Names and affiliations of applicants (* indicates experimentalists): *K. Krug*, D. Kaminski*, J. Stettner*, O.M. Magnussen**		

Report:

The investigation of homoepitaxial growth from solution is of central importance for fundamental understanding of electrochemical processes as well as for improving many current and future technological applications. A central challenge is to clarify the relationship between the atomic-scale structure of the solid-liquid interface, the growth behavior and the resulting surface morphology, which requires direct structure-sensitive investigations during the growth process.

To provide a deeper insight into this complex interplay, metal electroplating from aqueous electrolyte solutions was investigated in-situ by surface x-ray diffraction, using Au(001) homoepitaxial growth in 0.1 M HCl as an example. The results demonstrate that studies of the kinetic growth behavior at a solid-liquid interface can provide full structural information in sub-second resolution by this technique and reveal a pronounced influence of the applied electrode potential on the growth process.

Experiments were performed with reflectivity geometry (E_{Ph}= 18-20 keV) using a “hanging meniscus” transmission cell with minimized cell resistance and nearly unrestricted mass transport, which allows to combine in-situ surface x-ray diffraction studies of rapid structural changes simultaneously with high quality electrochemical measurements [1]. The electrodeposition process was initiated after exchanging the Au-solution $HAuCl_4$ 0.5 mM via a remote controlled pump system. After that the potential steps were performed.

To study the growth behavior the sample potential was first kept at 0.55 $V_{Ag/AgCl}$, where the very high surface mobility results in a rapid smoothening even of rough surfaces, and then stepped to a more negative value while the scattered intensity was monitored as a function of time at selected reciprocal space positions along specular (CTR). Specifically, in wide potential regime intensity oscillations (Fig. 1) indicating layer-by-layer growth were observed (typically only 3-4 oscillations due to imperfect 2D growth) [2]. The oscillation period is in very good agreement with the parallel electrochemical measurements, supporting the interpretation of these data as growth oscillations.

The potential-dependent growth behavior in the positive potential regime 0.35 $V_{Ag/AgCl}$, where the Au(001) surface is unreconstructed (see. Fig. 1), is in accordance with the known substantial increase in Au adatom diffusion with increasing potential, caused by the change in the electric field at the interface and the influence of coadsorbed anions [3].

At negative potentials the growth behavior can be attributed to the formation of the “hex” reconstruction on the Au(001) surface [4], which results in an enhanced Au surface mobility. The formation of the “hex” reconstruction directly after the potential step to -0.2 $V_{Ag/AgCl}$ leads to an initial increase in the scattered intensity, resulting in the noticeable "phase shift" of the curve (fig. 1) with respect to that observed on the unreconstructed surface at 0.35 $V_{Ag/AgCl}$ (blue line). Potential step measurements performed during this experiment at different reciprocal space positions allowed to obtain the complet (00L) CTR as a function of time or coverage, respectively at a time resolution of 1 s. The analysis of these data was in good agreement with a simple layer-by-layer growth for growth on the unreconstructed surface. For potential steps into the regime of the "hex" reconstruction they revealed rapid reconstruction of the topmost Au layer within the first seconds, followed by subsequent layer growth of the fully reconstructed surface (fig 2b).

In summary, these experiments demonstrate that by surface x-ray scattering in transmission geometry direct in-situ studies of the kinetic growth mode as well as determination of the electrode surface structure changes during electrochemical growth with sub second time resolution is possible, making this technique a promising new tool for future fundamental and applied studies of galvanic deposition processes.

References

[1] A.H. Ayyad, J. Stettner, O.M. Magnussen, *Phys. Rev. Lett.* **94**, 066106 (2005).
[2] K. Krug, J.Stettner, O.M. Magnussen, *Phys. Rev. Lett.*,**96**, 246101 (2006).
[3] M.Giesen, et al., *Surf. Sci.* **595**, 127 (2005).
[4] B.M. Ocko, et al., *Phys. Rev. Lett.* **65**, 1466-1469 (1990).

Figure captions

Fig 1 Growth oscillations indicating layer-by-layer growth for Au(001) homoepitaxial electrodeposition in 0.1M HCl + 0.5 mM $HAuCl_4$, after steps to the potential regime of the unreconstructed (1×1) (blue line) as well as the "hex" reconstructed (red line) Au surface. The insets show high-resolution STM images of both surface structures.

Fig. 2 Structure factor amplitudes along (00) rod and the best fits for (a) potential 0.35V (unreconstructed surface) at the onset of deposition (red triangles) and after deposition of 0.5 ML (blue circle) as well as (b) after deposition of 0 ML (red circles), 0.13 ML (green circles), 0.25 ML (blue circles) and after 0.0.75 ML (violet circles).

Fig. 1

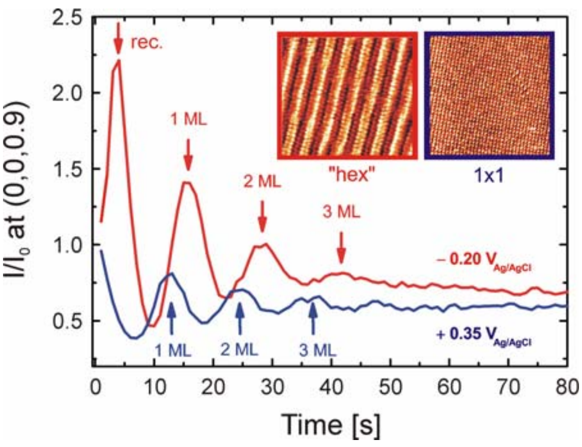

Fig. 2