	<b>Experiment title:</b> In-situ surface x-ray diffraction studies of Au electrodeposition processes	<b>Experiment number:</b> SI-1194
<b>Beamline:</b> ID32	<b>Date of experiment:</b> from: 15/06/2005 to: 24/06/2005	<b>Date of report:</b> 30/08/2005
<b>Shifts:</b> 24	<b>Local contact(s):</b> Dr. Frank Renner	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): <b>O.M. Magnussen*, J. Stettner*, A. Ayyad, K. Krug*</b> <b>Institut für Experimentelle und Angewandte Physik, Universität Kiel,</b> <b>Leibnizstrasse 19, D-24118 Kiel, Germany</b>		

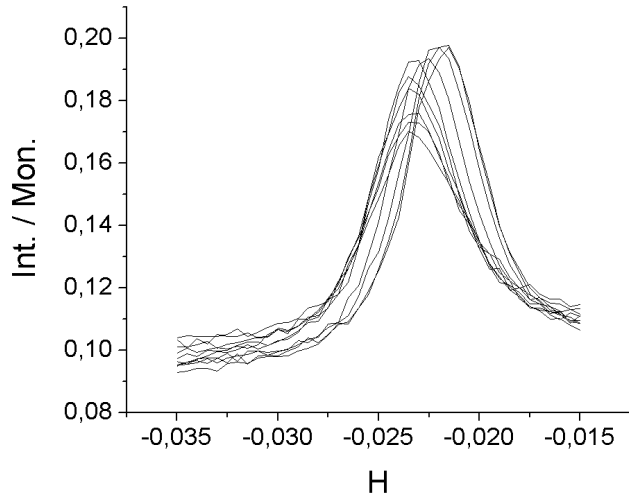
## Report:

To obtain a better fundamental understanding of electrodeposition processes the homoepitaxial growth of Au on Au(111) and Au(100) electrodes in aqueous electrolyte solutions was studied by grazing incidence diffraction (GID) and x-ray reflectivity measurements at ESRF beamline ID 32 using a photon energy of 18 keV. The experiments employed a “hanging meniscus” transmission x-ray cell, where the beam passes through 5-6 mm of electrolyte solution. The minimized cell resistance and nearly unrestricted mass transport in this cell allows to combine in-situ surface x-ray diffraction studies of rapid structural changes with high quality electrochemical measurements. In addition, a remote-controlled pump system allowed to exchange the electrolyte during the diffraction experiments. To distinguish the effects of the interface structure on the deposition process from effects caused by different deposition rates the Au electrode surface structure was studied under diffusion-limited deposition conditions (at rates up to several monolayers per minute).

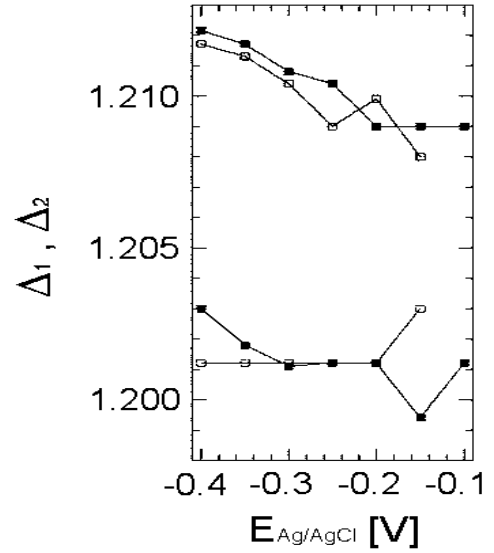
Au(111) and Au(100) are particularly interesting for such studies due to the complex, potential-dependent in-plane structure of these surfaces [1]. As shown in previous experiments at ID 32, the in-plane peaks characteristic for the Au ( $p\sqrt{3}$ ) surface reconstruction exhibit a substantial potential-dependent shift relative to those observed in Au-free solution ( $p \approx 22$ ), indicating an enhanced surface compression [2]. In the new experiments the peak shift after exchanging the electrolyte (Fig.1) or after potential steps could be directly followed as a function of time. These kinetic studies provide valuable insight into the origin of this deposition-induced compression. In addition, a similar effect was found for homoepitaxial electrodeposition on the “hex”-reconstructed Au(001) surface, where deposition resulted in an additional uniaxial compression that increased linearly with decreasing potential (Fig.2).

In addition, first in-situ studies of homoepitaxial growth at an electrochemical interface were performed. Time-dependent measurements of the x-ray intensity at selected positions along specular and non-specular crystal truncation rods indicated a complex potential-dependent behavior for Au(100) homoepitaxy (Fig. 3a,b): With decreasing potential transitions from step-flow deposition to layer-by-layer growth, manifested by layering oscillations in the x-ray intensity, then to 3D growth (additionally confirmed by diffuse scattering measurements, see Fig. 3c), and finally back to layer-by-layer growth were observed. The latter occurred parallel to the formation of the “hex” reconstruction on the Au(100) surface. This growth behavior can be explained by the effect of Cl adsorbates and the Au surface structure on the mobility of Au adatoms.

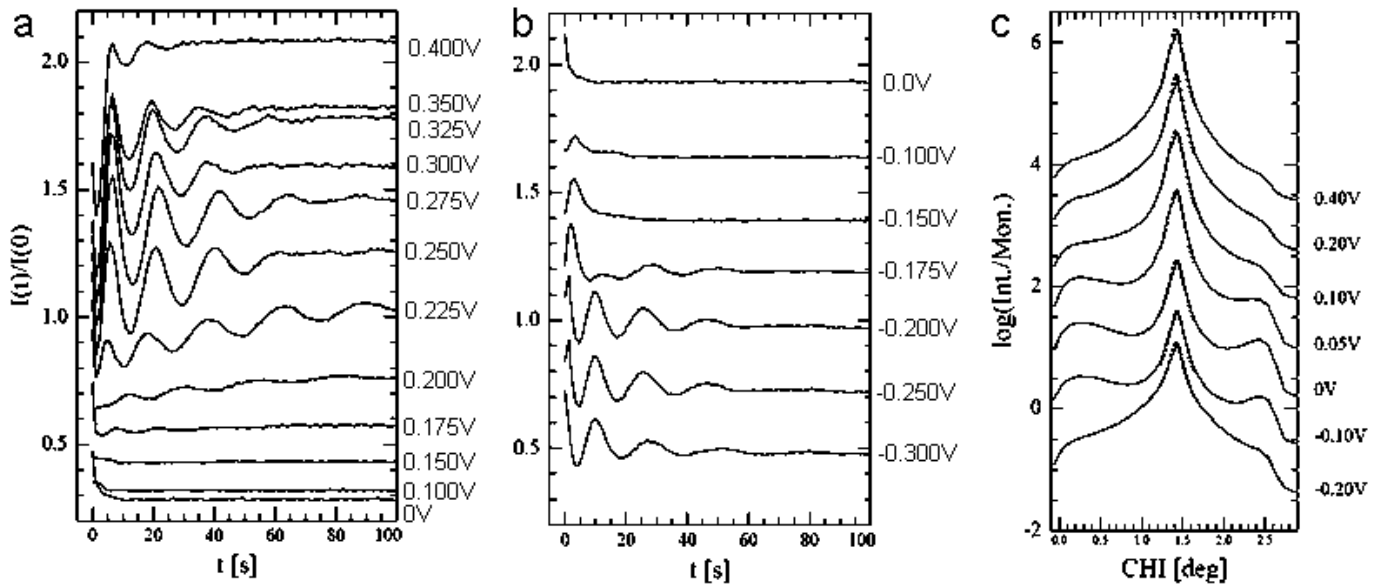
- [1] J. Wang, B.M. Ocko, A.J. Davenport, H.S. Isaacs, *Phys. Rev. B* **46**, 10321 (1992).  
 [2] A. Ayyad, J. Stettner, O.M. Magnussen, *Phys. Rev. Lett.*, **94**, 066106 (2005).



**Fig.1:** In-plane scans through the Au(111) reconstruction peak during an exchange from 0.1M HCl to 0.1M HCl + 50  $\mu$ M HAuCl<sub>4</sub> at -0.3V, showing a gradual peak shift from  $p=22$  to  $p=24$ .



**Fig.2:** Potential-dependence of the in-plane lattice vectors (in units of  $\sqrt{2} \cdot a_{Au}^*$ ) of the Au(001) “hex” reconstruction in 0.1M HCl + 50  $\mu$ M HAuCl<sub>4</sub> (solid symbols).



**Fig.2:** (a,b) Time-dependent intensity of the (1,1,0.15) peak after potential steps from 0.60  $V_{Ag/AgCl}$  to various potentials in the potential regime of the unreconstructed (-0.1 to 0.4 V) and reconstructed ( $< -0.1$  V) Au(001) surface during electrodeposition from 0.1M HCl + 50 $\mu$ M HAuCl<sub>4</sub> solution. (c) Diffuse scattering of the Au(001) surface after the deposition experiments shown in (a,b). For clarity, curves measured at different potentials are offset with respect to each other.