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| | **Experiment title:**<br>In-situ surface x-ray diffraction studies of Au electrodeposition processes | **Experiment number**:<br>SI-1042 |
| **Beamline**:<br>ID32 | **Date of experiment**:<br>from: 07/04/2004 to: 16/04/2004 | **Date of report**:<br>27/08/2004 |
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## Report:

The electrochemical deposition of metals is a subject of substantial basic research, motivated by current technologies as well as future applications. To obtain a better fundamental understanding of electrodeposition processes we have studied metal electrode surfaces in-situ during deposition in aqueous electrolytes by surface x-ray diffraction, using the homoepitaxial growth of Au on Au(111) electrodes as an example. In contrast to most previous diffraction studies of electrochemical interfaces, which were performed in a "thin layer geometry" where the mass and current transport is strongly impeded, we employed a newly developed "hanging mensicus" 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 our experiments we first investigated the Au(111) surface in Au-free solution by grazing incidence diffraction (GID) at ID32, using a photon energy of 20 keV to minimize x-ray absorption by the electrolyte. In accordance with previous results obtained in "thin layer geometry" [1] we find a hexagonal pattern around the integer crystal truncation rods, indicative for the well-known ($p\times\sqrt{3}$) surface reconstruction ($p \approx 22$),

negative of a critical (electrolyte-dependent) potential (Fig. 1, left). Subsequently the electrolyte was exchanged by solution containing 5-200 µM $HAuCl_4$, resulting in the diffusion-limited electrodeposition of Au with deposition rates of 0.25 to 1 ML/min, and the in-plane structure was monitored by GID. As before, reconstruction peaks are found, however, shifted outwards by up to 20% (Fig. 1, right). This corresponds to a commpression of the recontructed surface layer down to $p \approx 19$ or a surface strain $\varepsilon = -p^{-1} = -5.3\%$, respectively. A similar deposition-induced Au(111) surface compression has up to now neither been reported in electrochemical environment nor under UHV conditions.

Systematic studies revealed a prononunced potential-dependence of this effect (Fig. 2). At potentials in the vicinity of the $(p\times\sqrt{3}) \rightarrow (1\times1)$ phase transition the surface compression is close to that in Au-free electrolyte (i.e., $p \approx 22$). This behavior was observed in HCl, KCl, and $H_2SO_4$ solution, indicating that cation and anion species as well as $HAuCl_4$ concentration (i.e., deposition rate) do not substantially influence the compression. With decreasing potential $p$ decreased approximately linear. The change of surface strain with potential $d\varepsilon/d\phi$ is 0.013 to 0.019 $V^{-1}$ in the investigated electrolyte solutions. To explain this phenomenon we suggested that the surface compression observed during Au deposition corresponds to the true equilibrium value in electro-chemical environment, whereas it is kinetically limited to $p \geq 22$ in Au-free electrolyte. Using a simple thermodynamic model, the slope $d\varepsilon/d\phi$ can be rationalized by the potential-dependent change in surface stress, found at the Au(111) - electrolyte interface [2].


[1] J.Wang, B.M.Ocko, A.J.Davenport, H.S.Isaacs, *Phys. Rev. B* **46**, 10321 (1992).

[2] C.E.Bach, M.Giesen, H.Ibach, T.L.Einstein, *Phys. Rev. Lett.* **78**, 4225 (1997).


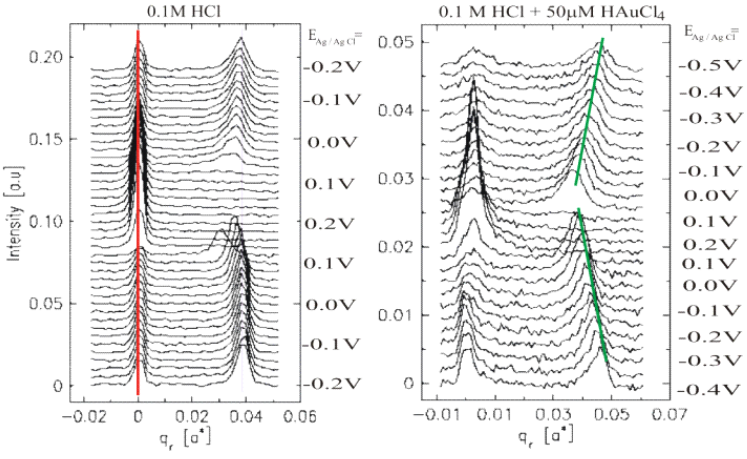


***Fig.1:*** *In-plane scans for Au(111) surfaces in 0.1M HCl (left) and 0.1M HCl + 50 µM $HAuCl_4$ (right) at different potentials. The left and the right peak are the (0,1) ($q_r$=0) and the reconstruction reflection, respectively.*

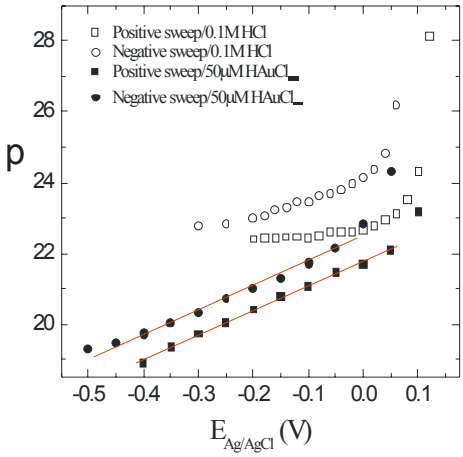


***Fig.2:*** *Potential-dependent surface compression p for reconstructed Au(111) surfaces in 0.1M HCl (open symbols) and 0.1M HCl + 50 µM $HAuCl_4$ (solid symbols).*