	Experiment title: In-situ X-ray diffraction studies of the hydrogen induced superstructure at the copper/electrolyte interface	Experiment number: SI-2075
	Beamline: ID 32	Date of report: 01/09/2010 <i>Received at ESRF:</i>
	Date of experiment: from: 30/06/2010 to: 06/07/2010	
Shifts: 18	Local contact(s): Parasmani Rajput	
Names and affiliations of applicants (* indicates experimentalists): F. Golks* ² , Y. Gruender* ¹ , J. Stettner* ¹ , O. M. Magnussen* ¹ ¹ Institut für Experimentelle und Angewandte Physik, Universität Kiel, Leibnizstr. 19, D-24089 Kiel, Germany ² European Synchrotron Radiation Facility, 6, Rue Jules Horowitz, F - 38000 Grenoble		

Report:

The experiment was performed at the beamline ID32 ($E_{ph} = 22.5$ 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. Furthermore, we used our one-dimensional detector (Dectris Mythen 1k) in order to record peak profiles of rod cross sections with a time resolution of 1/10 of a second. From these profiles we determined transients of integrated peak intensities and widths, respectively.

In the first part of the experiment we investigated the Cu(001) electrode surface structure during the hydrogen evolution regime (HER) in 0.1 M HClO₄ by *in situ* SXRD experiments. Previous *in situ* video STM studies of our group revealed the formation of a $c(px8)$ surface reconstruction of Cu(001) in the potential range of the HER [1]. In detail, we recorded the diffracted intensity close to the anti-Bragg position on the specular crystal truncation rod (CTR) while sweeping the potential to more negative potentials where the reconstruction is supposed to be stable. Within the statistical errors the diffracted intensity in the HER regime potential is independent, which is in contradiction to the transition from an unreconstructed surface to a hydrogen induced reconstruction. Our finding is supported by the fact, that a detailed search for reconstruction reflections in reciprocal space did not show evidence for the formation of this reconstruction. Further electrochemical studies are planned in order to resolve this contradiction.

Second, we investigated the complex interplay of the inhibitor polyethylene glycol (PEG) and chloride during copper electrodeposition as well as the influence of PEG on the atomic scale growth process. This is of major interest as modern copper electroplating bathes, which are commonly used in industry for the fabrication of metal interconnections in today's microelectronic devices [2], contain beside chloride and copper ions diverse organic additives, e.g. the mentioned polyethylene glycol. We applied two different techniques: a) a potentiodynamic method, in which the potential is swept at a constant scan rate (also called x-ray voltammogram); b) a potentiostatic approach, in which the potential is stepped to a different value. In parallel to these electrochemical experiments, the scattered intensity is recorded close to anti-Bragg position on the CTR [(1,1,0.1), related to the ordering state independent overall Cl coverage] and on the superstructure rod [(1,0,0.1), sensitive to Cl $c(2 \times 2)$ coverage] which allows to study the substrate and the Cl superstructure, respectively. In order to determine the influence of PEG on the anion adlayer structure, we began as reference

with the characterization of the Cu(001) surface in pure chloride and perchlorate containing aqueous electrolyte (0.1 M HClO₄ + 1 mM HCl). Afterwards, we exchanged the PEG-free by PEG-containing electrolyte by using our remote controlled pump system and performed identical measurements. As can be seen in Fig. 1, the Cl disordering and desorption shows in principle the same behavior in 0.1 M HClO₄ + 1 mM HCl (black curve) as in presence of 0.1 mM PEG (red curve). However, a slight difference in the potential dependence can be observed between -0.38 V and -0.6 V: the presence of the inhibitor seems to destabilize the full covered c(2x2) Cl adlayer as indicated by a decrease of intensity at (1,0,0.1) in comparison to the PEG free case. Furthermore, the intensity recorded at (1,1,0.1) shows a more pronounced increase of intensity with PEG for decreasing potentials, revealing that the adsorption and desorption processes take place at more positive potentials. These findings, however, are not completely consistent with previous, preliminary experiments and are currently subject of discussion.

Third, we studied the electrodeposition on Cu(001) in presence of 0.1 mM PEG as a function of electrode potential in continuation of previous experiments (reports for SI-1999 and SI-2074). The deposition process was initiated prior to every potential step experiment by exchanging to fresh 1 mM CuClO₄ containing electrolyte. Fig. 2 shows a series of time dependent intensities at (1,1,0.1) upon potential steps from -0.6 V to different final potentials. For potentials up to E = -0.4 V the transients exhibit oscillations, indicating layer-by-layer growth for this potential regime. The growth rate, which has been determined from the oscillation period, is potential dependent and varies between 0.06 ML/s and 0.04 ML/s (fig. 1 inset). This is different from the growth in the inhibitor free electrolyte (with the same concentration of Cu ions), where we found a potential independent and higher growth rate (0.13 ML/s). Thus, we observed *in situ* for the first time directly on the atomic scale a deceleration of the growth process during copper electrodeposition in PEG containing electrolyte.

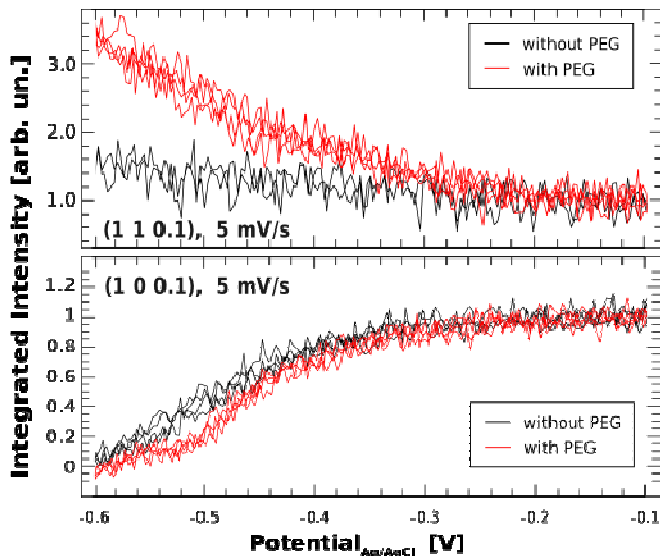


Fig. 1: Intensity at (1,1,0.1) and (1,0,0.1) during a potential cycle with a scan rate of 20 mV/s for PEG free (black curve) and 0.1 mM PEG containing electrolyte (red curve). The intensity on the superstructure rod shows a decrease at more positive potentials compared to the curve of the PEG-free case.

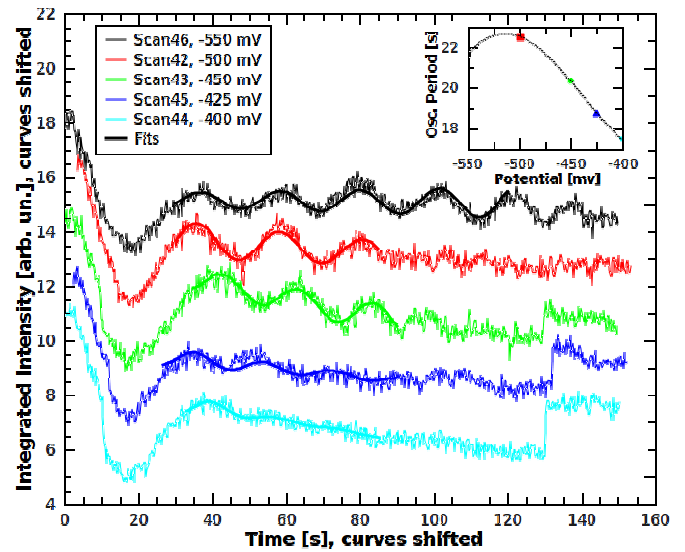


Fig. 2: Time dependent intensity at (1,1,0.1) after potential jumps from -0.6 V to indicated potentials in 0.1 M HClO₄ + 1 mM HCl + 0.1 mM PEG. Up to the potential of -0.4 V oscillations are observed, indicating layer-by-layer growth in presence of PEG. The inset shows the potential dependence of the oscillation period.

References:

- [1] H. Matsushima, A. Taranovskyy, C. Haak, Y. Gründer, O.M. Magnussen, J. Am. Chem. Soc. 131, 10362 (2009)
- [2] D. Josell, D. Wheeler, W.H. Huber, T.P. Moffat, Phys. Rev. Lett. 87, 016102-1 (2001)
- [3] M. Vogt, A. Lachenwitzer, O.M. Magnussen, R. Behm, Surf. Sci. 399 (1), 49–69 (1998)
- [4] Y. Gründer, D. Kaminski, F. Golks, K. Krug, J. Stettner, O. M. Magnussen, A. Franke, J. Stremme, E. Pehlke, Phys. Rev. B, 81, 17 (2010)