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Report:

In-situ time-dependent studies of the homoepitaxial growth on Au(001) and Cu(001)

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Galvanic metal plating is a widely used industrial method for the formation of metal structures with sub-micrometer dimensions. Prominent applications include dual-damascene plated ULSI microchips, magnetic storage devices, and micromechanical devices (LIGA process). To guide the trend to shrinking feature sizes an improved fundamental understanding of the underlying elementary steps is required.

To provide a deeper insight into the relationship between the atomic-scale structure of the solid-liquid interface, the growth behavior and the resulting surface morphology, the homoepitaxial growth in aqueous electrolyte solutions on metal single crystal surfaces was investigated by in-situ time-resolved surface X-ray diffraction, using Au/Au(001) and Cu/Cu(001) as examples.

Experiments were performed at 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 [1]. The electrodeposition process was initiated after exchanging the metal containing solution by a remote controlled pump system. After that potential steps were performed and the electrochemical current transient as well as X-ray intensities I(t) at selected reciprocal space positions were recorded.

The electrodeposition of Au on Au(001) electrode surfaces in HCl solution is from a fundamental point of view particularly interesting due to the complex, potential-dependent growth behavior which we found in previous experiments at ID32 [2]. Specifically, at a deposition rate of $\approx$ 4.2 ML/min after potential steps from 0.55 $V_{Ag/AgCl}$ (unreconstructed surface) in a wide potential regime intensity oscillations of the time

dependent scattered intensity of the specular truncation rod (CTR) indicate layer-by-layer growth on unreconstructed as well as "hex" reconstructed surfaces. The analysis of the CTRs for the unreconstructed surface (0.35 $V_{Ag/AgCl}$) was in good agreement with nucleation and growth of Au islands. In order to understand the complex interplay of layer-by-layer growth and the evolution of the surface reconstruction induced by the potential steps to -0.25 $V_{Ag/AgCl}$, we performed complementary grazing incidence studies. Comparison of the time dependent reconstruction reflection intensities for pure 0.1 M HCl solution (fig. 1a) and 0.5 mM $HAuCl_4$ containing solution (fig. 1b) reveals that the kinetics of the (1x1)→hex transition is during electrodeposition two orders of magnitude faster (90% of the saturation value I_0 is reached after ≈ 40 s), which can be rationalized by the strong enhancement of the Au adatom density by the deposition process. The even faster time scale (≈4 s) found in the CTR experiments can be partially attributed to the ripening of the hex domain distribution, which is demonstrated by in-plane transverse scans through the reconstruction peak (fig. 1c and d) [3]. Combining these data and the CTR results, we found that the surface reconstructs completely within few seconds, followed by layer-by-layer growth of reconstructed layers accompanied by an ordering of the hex phase.

Additionally, Cu electrodeposition on a Cu(001) single crystal has been investigated, motivated by the large industrial importance of copper on-chip connections fabricated by electroplating (e.g. Cu dual damascene technique for USLI chips). In Cu-free 10 mM HCl electrolyte the extensive characterization of the potential dependent crystalline surface structure by CTR measurements as well as intensity records during potential cycles (black lines in fig. 2 a,b) confirms the well known order-disorder phase transition of the Cl adlayer [4]. A second order transition was found, similar as reported by B. Ocko et al. for Br on Ag(100) in aqueous electrolyte solutions [5]. From detailed analysis of 8 CTRs Cl adsorption in hollow sites and a Cu-Cl bond distance of 2.47 Å were obtained. In 0.1 and 1 mM $CuSO_4$ containing electrolyte the time-dependent intensity at the (2,0,1) anti-Bragg position of the CTR reaches after potential steps from -0.2 $V_{Ag/AgCl}$ to more negative potentials very fast nonzero saturation values, indicating step flow growth (fig. 2c). Moreover, the potential dependence of these saturation values are in qualitative agreement with the order-disorder phase transition behavior found for the Cu-free electrolyte (fig.2 a,b). Diligent investigations of the X-ray beam influence by recording the electrochemical current as well as scattered intensities allow to exclude beam damage effects of Cu(001) surfaces in HCl, whereas all electrodeposition experiments performed in H_2SO_4 containing solutions (0.1 M H_2SO_4 + x mM HCl + y mM $CuSO_4$; x = 0, 0.1, 10; y = 0, 0.01, 0.1, 1), were strongly hampered by radiolytic effects at the electrolyte/metal interface, when potentials ≥0.2 $V_{Ag/AgCl}$ were chosen.

In summary, the experiments have provided new insight into the mechanism of the homoepitaxial growth on Au(001) single crystals in the potential regime of the hex reconstructed surface. First experiments on Cu electroplating on Cu(001) in 10mM HCl reveal step flow growth over a wide potential range and different concentrations. Future experiments on Cu electrodeposition will address in more detail the important influence of electrolyte composition, including the role of organic additives (inhibitors, accelerators).

References

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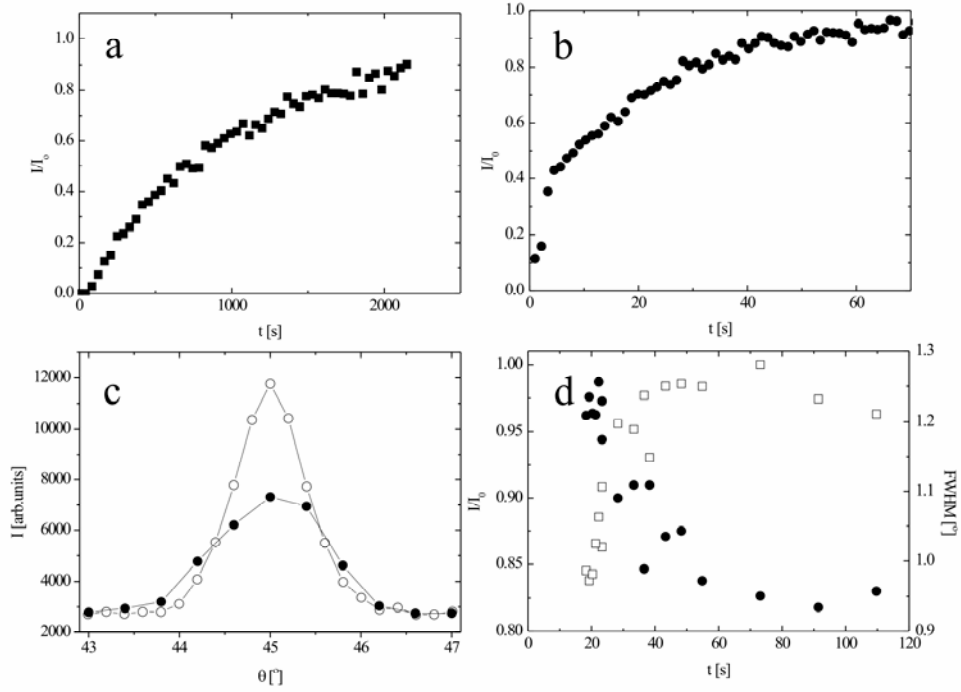[5] B.M. Ocko, X.J. Wang, T. Wandlowski, *Phys. Rev. Lett*. **79**, 1511-1514 (1997).

Fig.1: *Time-dependent intensity I at the (1.2,1.2,0.1) reconstruction reflection after potential steps from 0.55 $V_{Ag/AgCl}$ to -0.2 $V_{Ag/AgCl}$, normalized to its saturation value I_0 in (a) 0.l M HCl and (b) 0.1 M HCl + 0.5 mM HAuCl$_4$. (c) In-plane transverse scans (L=0.1) through the reconstruction peak after 20s (filled circles) and 80s (open circles). (d) Integrated intensity I/I_0 (filled circles) together with the in-plane transverse FWHM (open squares).*
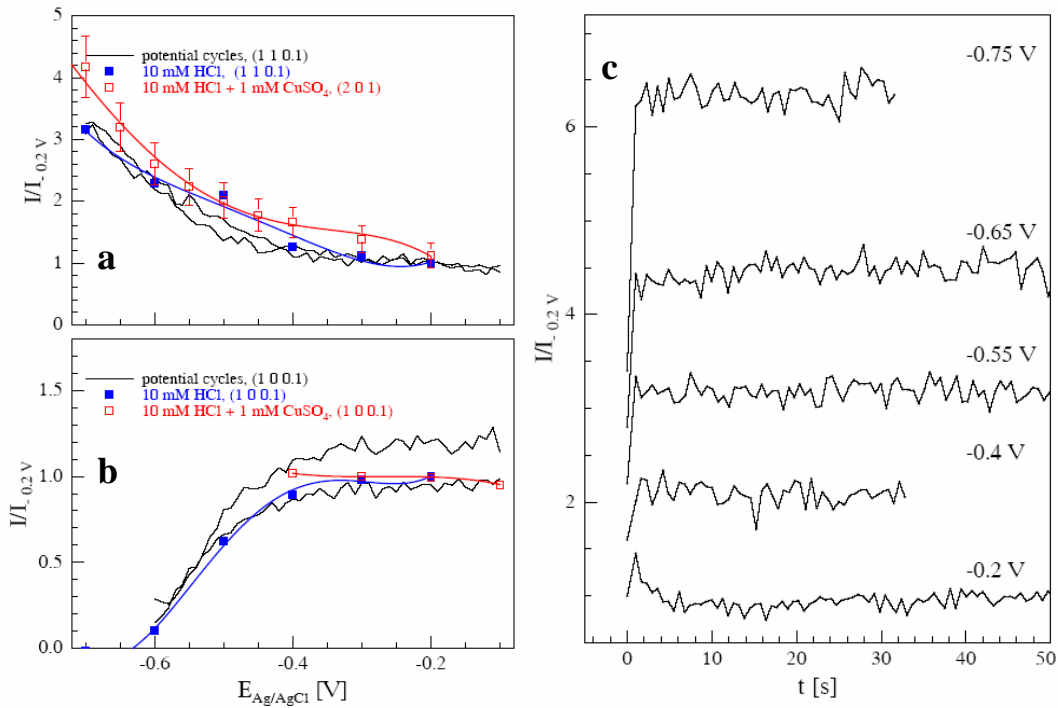

Fig 2: *(a) Potential-dependent intensity $I/I_{-0.2V}$ at anti-Bragg conditions [(2,0,1) and (1,1, 0.1), respectively] and (b) of the c(2x2) Cl adlayer reflection at (1,0,0.1), recorded by potential cycles in 10mM HCl solution (10mV/s, black lines) together with saturation values of the time-dependent intensity after potential steps from -0.2 $V_{Ag/AgCl}$ with (red symbols) and without 1mM CuSO$_4$ (blue symbols; lines in respective colours serve as guide to the eyes). (c) Time-dependent intensity $I/I_{-0.2V}$ at (2,0,1) in 10 mM HCl + 1 mM CuSO$_4$. All intensities are background subtracted and normalized to their value for -0.2 $V_{Ag/AgCl}$.*