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Report:

In-situ surface X-ray diffraction studies of Cu(001) homoepitaxial electrodeposition in organic additive containing electrolytes

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Since several years, Cu electrodeposition is used for the defect-free filling of trenches with dimensions <100 nm on ultra large scale integrated (ULSI) microchips [1]. In this “damascene copper electroplating” process, multicomponent electrolytes containing organic additives, so-called inhibitors and accelerators [2], are used which cause a faster growth at the bottom of the trench than at the upper walls resulting in a void-free filling of the trench (“superconformal deposition”, “superfilling”). Current superfilling electrolytes for Cu deposition typically contain three components, a polyether (usually polyethylene glycol, PEG), chloride or other halide ions, and an organosulfur compound, e.g. 3-mercapto-1-propanesulfate (MPSA).

Even though the influence of the additive combinations on the shape evolution of the Cu deposit was subject of numerous studies on Cu superconformal electrodeposition [3-5], the precise influence of the additives on the elementary steps of this deposition reaction is largely not understood, mostly due to the difficulty of making direct experimental observations of the growth mechanisms on the atomic scale. In-situ surface X-ray diffraction measurements were carried out at ID32 ($E_{\text{ph}} = 22.5$ keV) using a “hanging meniscus” transmission cell. This cell geometry with minimized cell resistance and nearly unrestricted mass transport allows to combine in-situ surface X-ray diffraction studies of rapid structural changes simultaneously with high quality electrochemical measurements [7].

Kinetic growth investigations, basing on previous experiments (SI-1530), were performed in 1 mM HCl + 0.1 M H₂SO₄ + 0.1 mM CuSO₄, after the electrodeposition process was initiated by exchanging from the metal-free to Cu-containing solution by a remote controlled pump system. In subsequent potential step experiments, in which the electrochemical current transient as well as time-dependent X-ray intensity I(t) at the (1,1,0.1) anti-Bragg position of the CTR were recorded, we observed reproducible potential dependent intensities for potentials between -0.7 V_{Ag/AgCl} (hydrogen evolution) and -0.3 V_{Ag/AgCl}. The potential dependence of the initial intensities after each potential jump was in qualitative agreement with the order-disorder phase transition behavior found for the Cu-free electrolyte during the last beamtime (figure 1 (a)).

For the potential of -0.65 V_{Ag/AgCl} a smoothing of the surface was observed, indicated by a constant increase of the intensity with time (figure 1 (b)). This potential led to smooth, reproducible surfaces and hence was chosen as initial potential for the subsequent potential steps. After potential steps to potential values between -0.6 V_{Ag/AgCl} and -0.5 V_{Ag/AgCl} the time-dependent intensity reaches immediately non-zero saturation values, indicating step-flow growth in this regime. After jumps to more positive potentials than -0.5 V_{Ag/AgCl} a decrease in intensity with time is observed, hence a slight roughening seems to occur, presumably due to 3D growth.

To provide deeper understanding of the Cu nucleation and growth behaviour in the presence of organic additives, first experiments were carried in PEG-containing solution, i.e. in 0.1 M H₂SO₄ + 1 mM HCl + 0.01 mM PEG. Measurements before and after exchanging to the PEG-containing electrolyte revealed that the c(2x2) Cl⁻ adlayer still exists (figure 2 (a)). Furthermore, our investigation of the dynamics of the c(2x2) Cl⁻ formation, performed by recording the intensity at (1,0,0.1) on the Cl⁻ superstructure rod during potential cycles, revealed a scan rate dependent hysteresis in PEG-containing electrolyte. Hence, whereas for the PEG-free as well as the PEG-containing case the order to disorder phase transition is fast, the reverse process of Cl⁻ adsorption or ordering is hindered in presence of the PEG layer (cf. figure 2).

In summary, our experiments provided new insight into the mechanism of the homoepitaxial growth on Cu(001) single crystals in 1 mM HCl + 0.1 M H₂SO₄ + 0.1 mM CuSO₄ electrolyte. First experiments on Cu electrodeposition under the influence of the organic additive PEG revealed pronounced influence of the PEG layer on the dynamics of the c(2x2) Cl⁻ formation.

References

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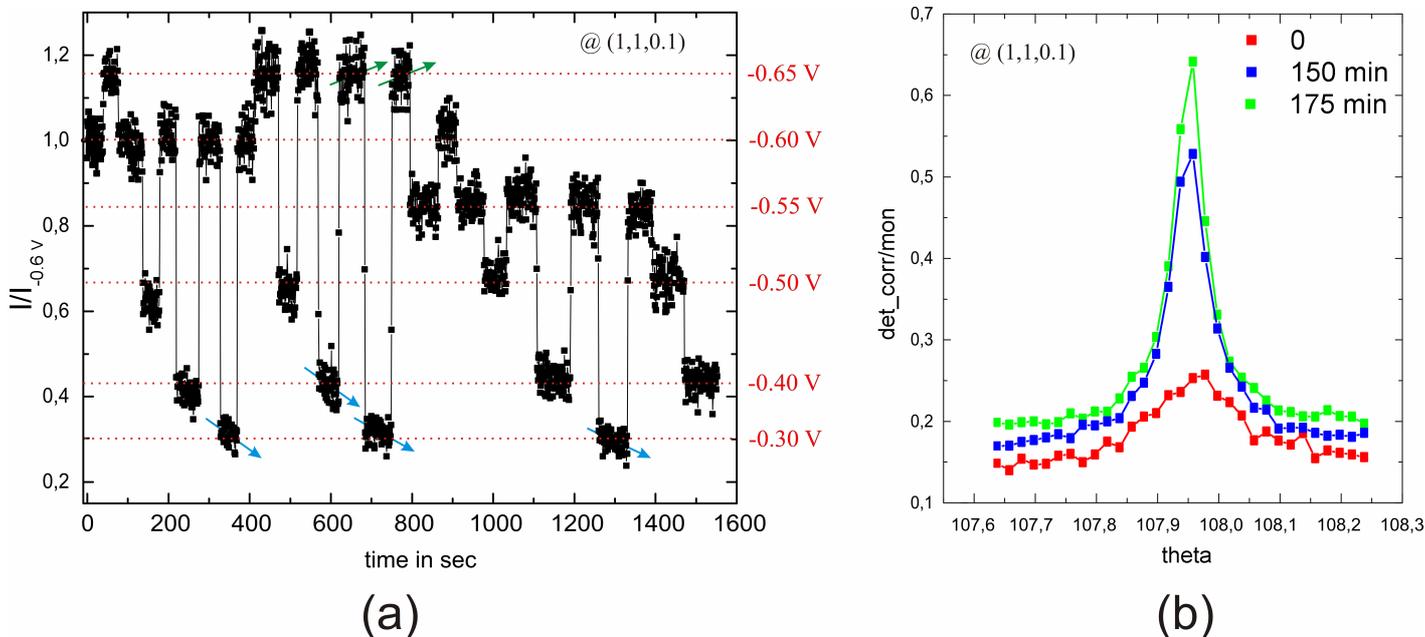


Fig 1: (a) Time-dependent intensity I at $(1,1,0.1)$ anti-Bragg position during potential jump experiments in $1 \text{ mM HCl} + 0.1 \text{ M H}_2\text{SO}_4 + 0.1 \text{ mM CuSO}_4$, normalized to the intensity before the potential step at $-0.6 \text{ V}_{\text{Ag}/\text{AgCl}}$. Green arrows indicate the smoothening of the surface at $-0.65 \text{ V}_{\text{Ag}/\text{AgCl}}$, blue arrows the roughening at potentials more positive than $-0.5 \text{ V}_{\text{Ag}/\text{AgCl}}$. (b) shows an in-plane transverse scan ($L=0.1$) through the $(1,1)$ -rod at anti-Bragg at a potential of $-0.65 \text{ V}_{\text{Ag}/\text{AgCl}}$ after 0 min (red), 150 min (blue) and 175 min (green) after the exchange to Cu-containing electrolyte.

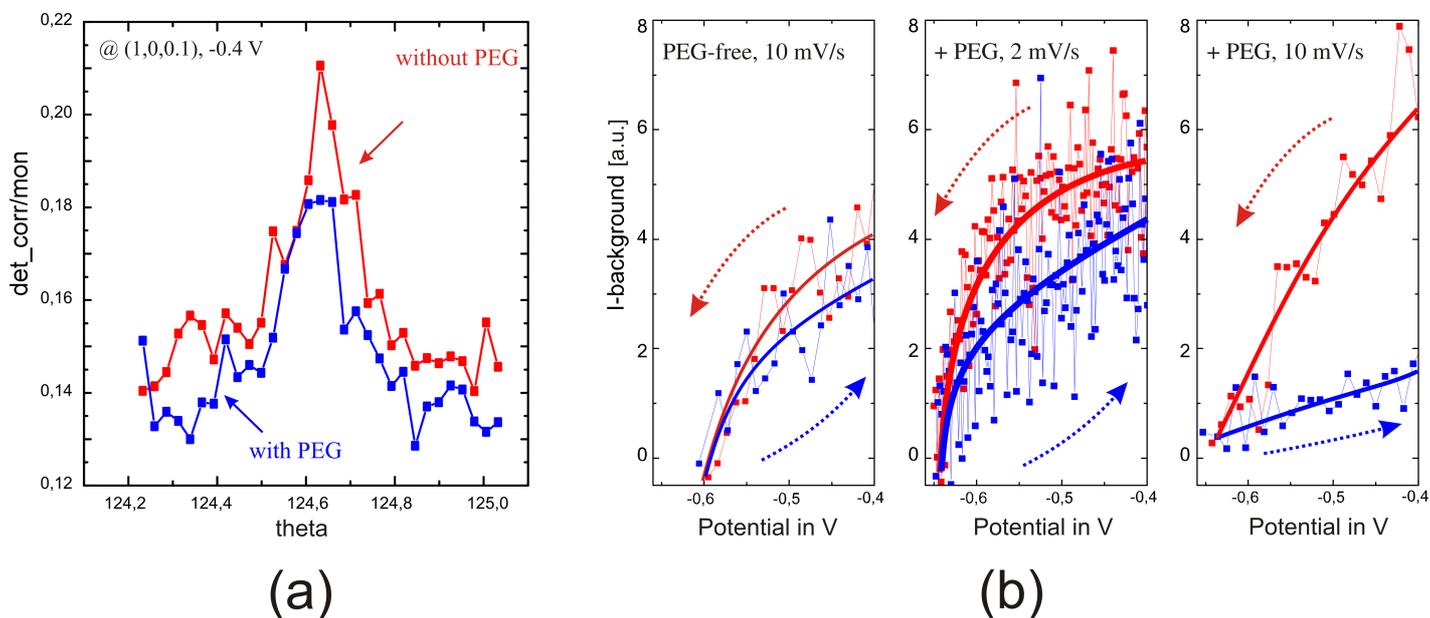


Fig 2: (a) $c(2 \times 2)$ Cl^- superstructure peak at $(1,0,0.1)$ before (red) and after (blue) exchange to 0.01 mM PEG -containing electrolyte. (b) Cyclic diffractograms recorded at $(1,0,0.1)$ on the Cl^- superstructure rod in $0.1 \text{ M H}_2\text{SO}_4 + 1 \text{ mM HCl}$ base electrolyte. The red symbols indicate the measured $c(2 \times 2)$ order to disorder phase transition, the blue symbols the reverse process (solid lines in respective colours serve as guide to the eyes). All intensities are background subtracted. Scans shown (left) without PEG, scan rate 10 mV/s , (middle) with PEG, scan rate 2 mV/s and (right) with PEG, scan rate 10 mV/s . The scan rate dependent hysteresis indicates that the Cl^- adsorption/ordering is hindered in presence of PEG.