

In situ STM study of the effect of additives on copper bulk electrodeposition

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Cu electrodeposition on copper polycrystalline as well as on single Cu(111) and Cu(100) surfaces was studied by our homebuilt electrochemical STM [1]. As a surface treatment procedure, all the samples were prepared by electropolishing in orthophosphoric acid [2].

Since the size of STM scanning area (up to 1 μm) was considerably smaller than the average grain size of our polycrystalline sample, of approximately 100 μm , each time we have studied the deposition on one particular crystallite, however with previously unknown crystal orientation. In such a case the studied surface was represented as a slice of crystallite with a high-index Miller plane. During the Cu deposition the crystal surface showed the tendency to form facets, which correspond to low-index Miller planes.

STM measurements of copper plating on Cu(111) single crystal without any additives, and with such commonly used industrial additives as Cl and SPS (bis-(3-sodium sulfopropyl)-disulfide) revealed different, additive-specific morphological changes during the bulk growth, see Fig.1. Particularly, without any additives, atomic steps have arbitrary, curved shapes. By contrast, they become immediately straight when Cl adsorbes on the surface. In addition, we have observed that even an initially rough surface has the tendency to become more flat during Cu deposition in the presence of Cl. In the case of SPS, a high density of protrusions forms on the surface, which is probably due to an increased number of nucleation sites.

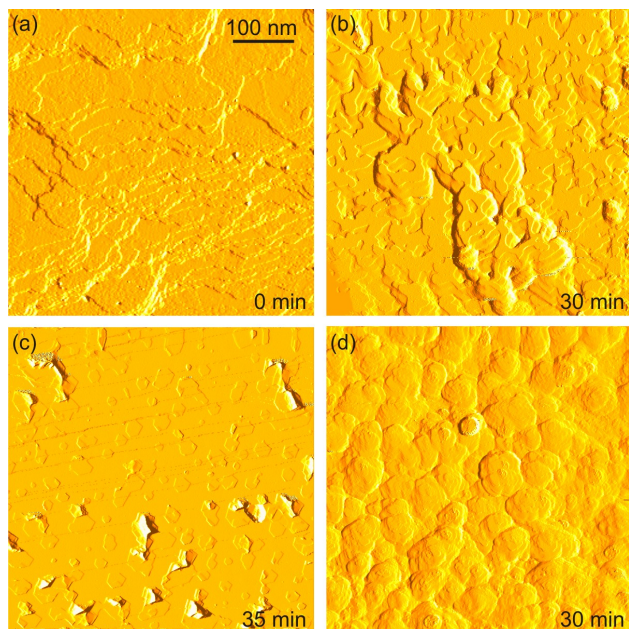


Figure 1: STM images of the Cu(111) single crystal surface a) directly after electro-polishing; b) after 30 min of Cu deposition from a 0.1M H_2SO_4 + 2 mM CuSO_4 solution; c) after 35 min of Cu deposition from a 0.1M H_2SO_4 + 2 mM CuSO_4 + 1 mM HCl solution; d) after 30 min of Cu deposition from a 0.1M H_2SO_4 + 2 mM CuSO_4 + 0.01 mM SPS solution. In all three cases b)-d) the overpotential was set to 20 mV.

Our primary data obtained during copper deposition on Cu(100) single crystal show the well-known tendency for formation of terraces with straight $\langle 001 \rangle$ oriented steps [3], which remain their orientation despite the adsorption of SPS molecules, in contrast to the case of Cu(111) surface, see Fig. 2.

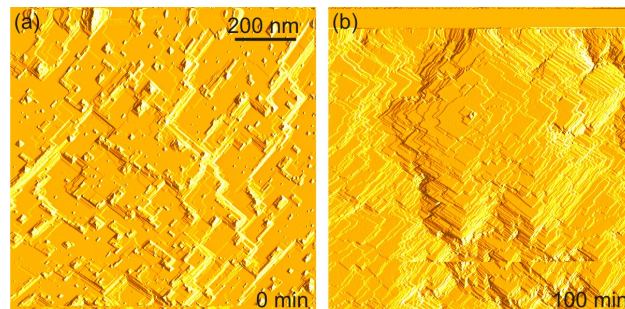


Figure 2: STM images of the Cu(100) single crystal surface a) directly after electro-polishing; b) after 100 min of Cu deposition from a 0.1M H_2SO_4 + 2 mM CuSO_4 + 0.01 mM SPS solution. The overpotential is 20 mV.

1. Y.I. Yanson, F. Schenkel, M.J. Rost, *Rev. Sci. Instr.* 84, 023702, (2013).
2. O. M. Magnussen, L. Zitzler, B. Gleich, M.R. Vogt, R.J. Behm, *Electrochim. Acta* 46, 3725, (2001).
3. M.R. Vogt, F.A. Möller, C.M. Schilz, O.M. Magnussen, R.J. Behm, *Surf. Sci.* 367, L33, (1996).