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Structural accelerating effect of chloride on copper electrodeposition

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The addition of small amounts of Cl ions into a sulfate-based plating solution is known to accelerate copper deposition [1,2]. It is widely accepted that the accelerating effect is due to the formation of Cu(I)-Cl complexes in the solution, which are then reduced to metallic copper more easily than the Cu(II) ions. On the other hand, studies of anion adsorption on Cu single-crystal surfaces of different orientations under electrochemical control, using various structurally-sensitive techniques, have shown that the adanions can have a strong influence on the structure of the top-most Cu layer [3-5].

Using our home-built high-speed electrochemical scanning tunneling microscope (EC-STM) that is equipped with a flow-cell [6], we image the Cu surface with atomic resolution *during* the deposition process. We obtain evidence that there is a direct connection between the accelerating effect of Cl and the structural changes on the Cu surface due to Cl adsorption. Firstly, we show that the deposition of Cu from a sulfuric acid electrolyte (without Cl) proceeds in building blocks of over 40 atoms, see Fig. 1. Secondly, we show that, if Cl is added to the solution during deposition, it replaces sulfate that is adsorbed on the surface. This leads to a strong structural change of the growing Cu surface, see Fig. 2. Finally, we show that this structural change is accompanied by the reduction of the size of the building block of growth. In turn, the reduction of the size of the building block leads to an acceleration of Cu deposition [7].

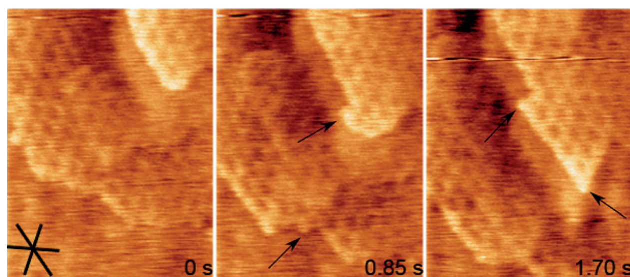

Figure 1. Consecutive STM images that were acquired during Cu electrodeposition from a sulfate-based, Cl-free electrolyte. The corrugation on the surface of the terraces corresponds to the moiré pattern, which is formed due to adsorption of sulfate on Cu(111) surface. One can see that the smallest stable growth unit, the building block of growth, is the unit of the moiré pattern. Hence, the step propagation appears "quantized" in the images. Please note that structures, smaller than the building block, can be found in the images (marked by arrows).

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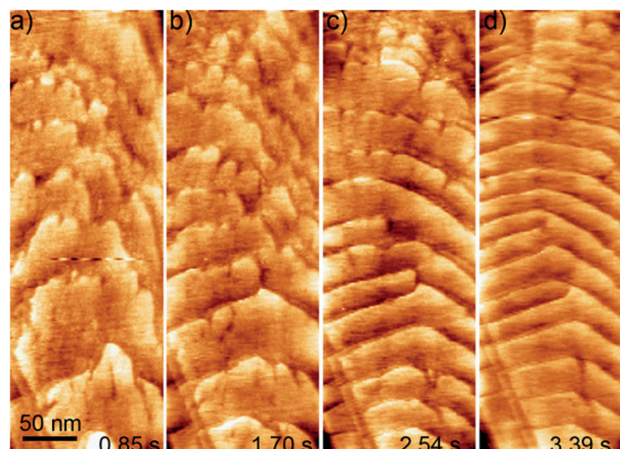

Figure 2. Consecutive STM images of the Cu(111) surface during growth after the addition of 0.3 mM HCl into a sulfate-based electrolyte. Adsorption of Cl on the surface leads to strong morphological changes, such as the straightening of the steps and a change in the step orientation. Please note that also the density of the steps as well as the step propagation rate are increased, from which we get evidence for a structural acceleration of Cl.