

The Initial Stages of Electrochemical Metal Deposition

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Metal deposition from solution has received renewed interest in microelectronics and related areas as a simple, yet versatile technique for fabricating ohmic contacts, Schottky barriers, layered structures or even nanostructures. On the other hand, metal deposition from solution remains a fascinating area of fundamental research, in which important aspects of electrocrystallization, solid-solid interactions, surface dynamics and diffusion, epitaxial growth and atom-to-solid transitions can be studied. In the following, four different topics will be briefly addressed and discussed with respect to fundamental aspects of electrodeposition on a nanometer scale.

1) *Influence of the substrate on the structure of a growing overlayer.* The substrate influence is a twofold one. Surface imperfections can play a crucial role as nucleation centers and the surface crystallographic orientation can impose its symmetry on the growing film. The influence of surface defects, such as monoatomic high steps, on the nucleation behaviour of metals is demonstrated for Pd and Co deposition onto Au(111) electrodes (Fig. 1). It is shown that Pd deposition onto Au(100) and Au(110) readily leads to alloying, while such an effect is not observed for Au(111). In the case of Cu deposition onto Ag(100) or Au(100), the lattice misfit between both metals leads to the growth of a thin bcc-overlayer, which is stabilized by the perfect fit of bcc-Cu on those (100) faces. Further growth causes a reversible transition of the bcc-structure to a wavy structure, before at much larger film thicknesses crystallites of fcc-structure emerge.

2) *Metal deposition onto semiconductors.* We have studied the initial stages of Au, Cu and Pb deposition onto hydrogen-terminated Si(111) by in-situ STM and in-situ SXS. The latter technique allows a detailed analysis of the crystallographic orientation of the emerging metal clusters with respect to the substrate. In the case of Pb and Au on n-Si(111):H preferential growth in (111)-orientation has been observed.

3) *Metal deposition onto chemically-modified gold surfaces.* Au(111) electrodes were modified by self-assembled monolayers (SAMs) of various functionalized thiols. For such surfaces, metal deposition is kinetically strongly hindered. In the case of Cu deposition, the slow formation of a monolayer at the thiol-gold interface is shown. 3-dimensional Cu-clusters are seen to nucleate at defects of the organic monolayer, grow on top of the SAM and finally, bury it.

4) *Nanostructuring of surfaces by tip-induced metal deposition.* There are several means of nanostructuring electrode surfaces by an STM. In almost all cases, the structuring consists of a tip-induced, laterally confined metal deposition. It is shown how metal clusters of nanometer dimensions can be placed precisely at predetermined positions on gold electrodes via an STM-tip. For this purpose, metal is deposited from solution onto the tip and transferred to the sample by a so-

called jump-to-contact. Various examples of a microprocessor-controlled nanodecoration of bare and thiol-covered surfaces will be presented (Fig.2). Special emphasis is placed on the unusually high stability of small, tip-generated Cu clusters, which require overpotentials of the order of 50 – 100 mV for anodic dissolution.

References

- 1) L.A. Kibler, M. Kleinert, R. Randler, D.M. Kolb, Surf. Sci. **443**, 19 (1999).
- 2) D.M. Kolb, Electrochim. Acta **45**, 2387 (2000).

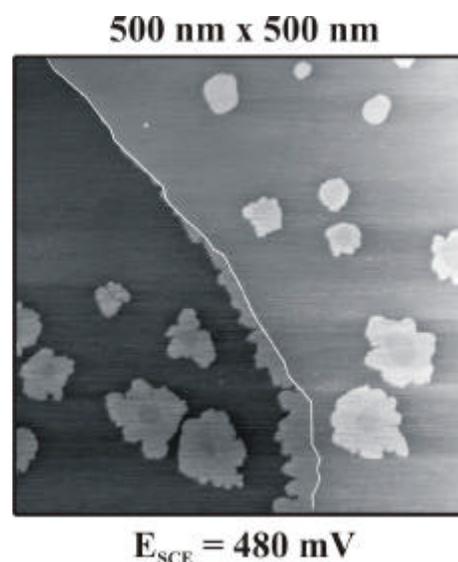


Fig. 1: STM image of Au(111) in 0.1 M H₂SO₄ + 0.1 mM PdCl₄²⁻, showing the initial stages of Pd deposition. Nucleation is seen to occur exclusively at the monoatomic high step (marked by the white line) and at the rims of the gold islands; the growth is two-dimensional. From Ref. [1].

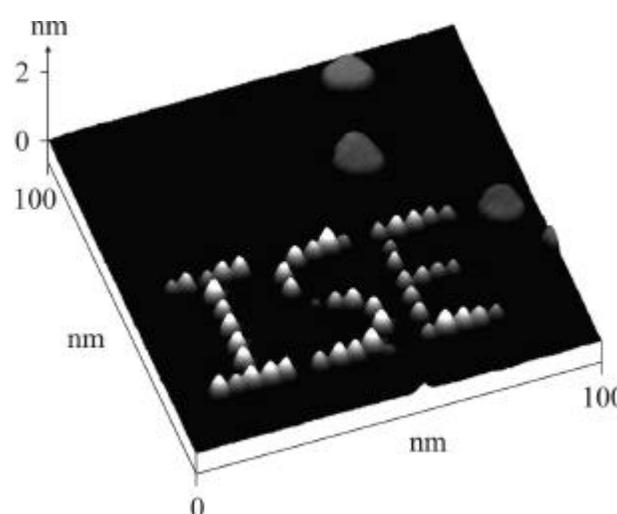


Fig. 2: STM image of Cu clusters on Au(111) in 0.05 M H₂SO₄ + 1 mM CuSO₄ at +10 mV vs. Cu/Cu⁺⁺. The Cu clusters are 0.6 nm high and were generated by the tip of an STM. The 48 Cu clusters are arranged in letters that are 33 nm big. From Ref. [2]