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ACCEPTED MANUSCRIPT

Mechanisms of the initial steps in the Pd electro-deposition onto Au(111)

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Abstract

The growth of the first Pd layers electrochemically deposited in a chloride containing solution onto Au(111) has been investigated by cyclic voltammetry, potential step experiments and time resolved *in situ* surface X-ray diffraction. The underpotential deposition of the first layer is depicted by several processes with different kinetics. A first reaction, characterized by a quite fast kinetics below 1 s, is followed by a slow adsorption process and by instantaneous nucleation-and-growth.

The almost complete layer-by-layer growth up to two pseudomorphic layers has been observed, even if the third and following relaxed layers start growing before the full completion of the second one, forming huge 3D islands. Chloride does not seem to act as a smoothing agent during the Pd film deposition.

Finally, thanks to the detailed structure of the Pd deposit obtained with *in situ* surface X-ray diffraction we could unambiguously assign the peaks observed in the electrochemical characterization of the Pd/Au(111) films in 0.1 M H₂SO₄.

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