

Scanning Tunneling Microscopy Study of Silver upon Au (111) in the Presence of Chloride

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Growth morphologies and atomistic adlayer structures of silver on Au (111) are characterized by in-situ scanning tunneling microscopy (STM) and electrochemical measurements, as chloride anions are present or absent in 0.1 M HClO₄ electrolyte.

In pure perchlorate, Ag is deposited on Au (111) terraces posterior to the first peak of underpotential deposition (upd) and laterally grows at the step edge of predeposited Ag islands or a Au surface near the second peak in a cyclic voltammogram (CV). Also the second adlayer of Ag on the first Ag layer upon Au (111) is ascertained within the upd realm. Atom-resolved STM images reveal a (4×4) Ag adlattice with the surface coverage of 0.56 after the first upd and a close-packed (1×1) Ag structure prior to the bulk deposition of Ag.

On the contrary, in a chloride-containing solution, there are distinct steps of Ag growth and adlayer structures, supplemented by meso-sized STM images, pointing out the enhanced surface mobility due to the adsorption of chloride. The first Ag island is deposited only at the lower part of a Au (111) step which is energetically more favorable than the upper part of the step. As the potential becomes negative values, Ag additionally grows and a complete monolayer of Ag is accomplished. On the other hand, stripping of Ag upon Au (111) causes the formation of AgCl with a particle-shape, which strongly adheres to the Au surface that is responsible for the irreversibility of the whole system in the presence of chloride.

There are four characteristic Ag structures in saturated AgCl and 0.1 M HClO₄ ([Ag⁺] = [Cl⁻] = ca. 10⁻⁵ M) at each potential region, which are substantially matched to the features in a CV, related to the phase transition of a Ag adlayer. Surface coverage of a Ag adlayer structure, based on the atomic STM image, reveals that Ag and Cl almost equally adsorb on a Au (111) substrate during a upd process, suggesting the bilayer structure between silver and chloride.

Conclusively chloride has a significant influence on a Ag adlayer structure and plays a competitive role in a Ag adsorption/desorption process.