

Anions Effects in the Underpotential Deposition of Cd on Au(111), and Formation of the First Monolayers of CdTe, using: AES, XPS, LEED and STM

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The present study investigates Cd UPD on Au (111) from different electrolyte solutions: chloride, sulfate, iodide, acetate and perchlorate. The structure and composition of the atomic layer was analyzed using Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) in an ultrahigh vacuum chamber, as well as in-situ scanning tunneling microscopy (STM). In addition, the structures formed in the first few cycles of alternated deposition of Cd and Te were studied.

Cadmium was deposited from a chloride electrolyte solution, 0.20 mM CdCl₂ and 1 mM HCl (pH 3), Figure 1. Peaks R1 and O1, at -0.30 V, are related to Cd UPD and stripping [1-4], with a Cd coverage of 0.3 ML for peak R1. R2 is related to O2, while R3 is related to O3. R2/R3 are associated with Cd-Au alloy formation and O2/O3 for alloy stripping, shown to occur at potentials more positive than the reversible Cd deposition potential, -0.8 V [4,5,6]. The small peak O4 is related to lifting of Au(111) reconstruction [7,8]. AES spectra showed Cd, Cl and Au peaks, but no oxygen, suggesting Cd monolayers were not oxidized. Cl coverage increased along with Cd coverage as the emersion potential was moved towards more negative potential. LEED patterns changed from a ($\sqrt{7}\times\sqrt{7}$)R 19.1° to ($\sqrt{3}\times\sqrt{3}$)R 30°, as the emersion potential was changed from -0.08 V to -0.80 V.

Cd deposition from sulfate electrolyte, 0.20 mM CdSO₄ and 1 mM H₂SO₄, on Au (111) produced a voltammogram similar to that in Figure 1, but with broader peaks for both Cd UPD and for Cd-Au alloy formation. AES of the surface after Cd UPD, showed S, O, and Cd peaks indicating sulfate coadsorption. XPS spectra of S and O showed binding energies consistent with sulfate. A ($\sqrt{3}\times\sqrt{3}$)R 30° pattern was observed after Cd UPD, while a hexagonal pattern was evident after Cd-Au alloy formation.

The electrodeposition of Cd from an iodide solution, 0.20 mM CdCl₂ and 1 mM HI, was also studied. Voltammetry showed the UPD peak along with a peak for Cd-Au alloy formation and proton reduction. AES showed only I, Au and Cd at all emersed potentials. No chlorine was evident. The binding energy of the iodine peak in the XPS spectrum agrees with published values for CdI [9]. LEED patterns varied from a split ($\sqrt{3}\times\sqrt{3}$)R 30° initially, to a (6X6) after Cd UPD, and a ($\sqrt{3}\times\sqrt{3}$)R 30° at Cd-Au alloy formation. The iodine coverage was almost constant at 0.45 ML over the entire potential range.

Use of an acetate electrolyte solution, 0.20 mM CdSO₄ and 0.40 mM sodium acetate/0.40 mM acetic acid (pH 4.85), resulted in voltammetry similar to that shown Figure 1. Auger spectrum showed Cd and oxygen peaks but the C (272 eV) was difficult to distinguish from the Au (252 eV) and Cd (277 eV) peaks. However, XPS spectra indicated the presence of carbon. The LEED patterns for surface emersed after UPD was again a ($\sqrt{3}\times\sqrt{3}$)R 30°, while alloy formation resulted only in a (1X1). At more negative potential, the Cd/Au ratio increased steeply but no ordered LEED pattern was observed.

From perchlorate, 0.20 mM Cd (ClO₄)₂ in 1 mM HClO₄ (pH 3), the voltammetry in Figure 2 was observed. This was significantly different from previous voltammetry, as there was no separate peak for Cd UPD and Cd-Au alloy formation. Emersion experiments were done at -0.40 V and -0.80 V. AES spectrum showed Cl and O peaks indicating adsorption of perchlorate. LEED experiments showed a faint ($\sqrt{3}\times\sqrt{3}$)R 30° pattern at -0.4 V, which lasted for 10 seconds. AES after LEED showed no change in Cd, Cl and oxygen level, which indicates the surface structure was disordered by exposure to the electron beam, but not desorbed [10].

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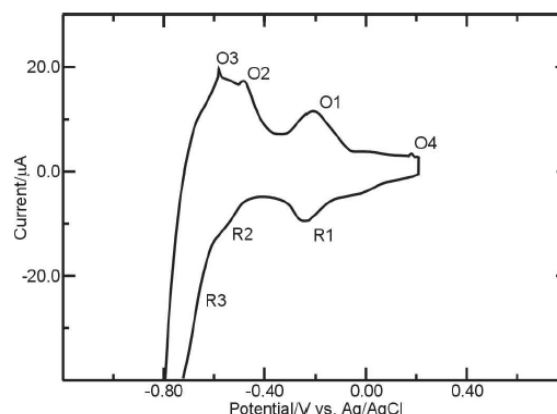


Figure 1. Cyclic voltammogram of Au (111) in 0.20 mM CdCl₂ and 1 mM HCl solution. Scan rate = 5 mV/sec.

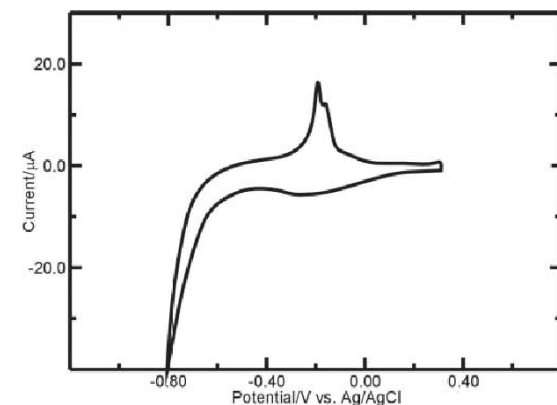


Figure 2. Cyclic voltammogram of Au (111) in 0.20 mM Cd (ClO₄)₂ and 1 mM HClO₄ solution. Scan rate = 5 mV/sec.