LAYER-BY-LAYER OVERPOTENTIAL DEPOSITION OF Ag ON Au(111)

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The ability to carry out precise, layer-by-layer metal deposition, rather than the growth of islands, is important for many nanotechnological applications. STM studies have indicated that layer-by-layer growth can indeed be achieved for Ag thin films (up to 200 monolayer thick) on the Au(111) surface by using Pb as a surfactant[1]. For surface modification studies of catalysts, it is important that ultra thin film deposition can be well controlled on a single monolayer level. Here, we report a procedure for deposition of thin metal layers by using Pb UPD/stripping cycles to mediate 2D growth of Ag on Au(111) at potential far below the Ag bulk deposition potential and to monitor the surface coverage during the process.

As shown in Fig. 1 (dashed line), Ag bulk deposition occurs at potential negative of 0.36 V while two UPD peaks occur at more positive potentials. Overpotential (below 0.36 V) deposition is under diffusion control and results in a 3D growth. By adding Pb^{2+} in the solution, which can be underpotentially deposited between -0.1 and -0.38 V (solid line), a layer-by-layer growth of Ag film can be obtained by cycling potential between –0.3 and –0.1 V, which are well below the Nernst potential for Ag bulk depostion.

It is known that Pb UPD on Au(111) exhibits a small peak at potential positive of the major peak while only a single peak is seen on Ag(111). This feature was used for monitoring the deposition process. As shown in the insert, the current peak at more positive potential decreases with each additional cycle indicating the decrease of uncovered gold surface area. After twelve cycles the feature related to Au(111) surface was gone and the specular reflectivity measurements for this surface (Fig. 2) show a full monolayer of Ag. Doubling the number of potential cycles resulted in a Ag bilayer, which exhibits the characteristic double minima at small *L* in the specular reflectivity profile.

These results demonstrates that the Ag thin films formed by Pb-mediated overpotential deposition are atomically flat. Since UPD of Pb and Tl occur at rather low potentials, this method can be applied for electrodeposition of smooth ultra thin films of noble metals on a metal substrate, which has an oxidation potential lower than the bulk deposition potential of the noble metal., e.g. Pt on Ag. This could be useful for studying and improving bimetallic catalysts.

Acknowledgements
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Reference

1. S.R. Brankovic, N. Dimitrov, and K. Sieradzki, Electrochemical and Solid-State Lett. 2 (1999) 443.

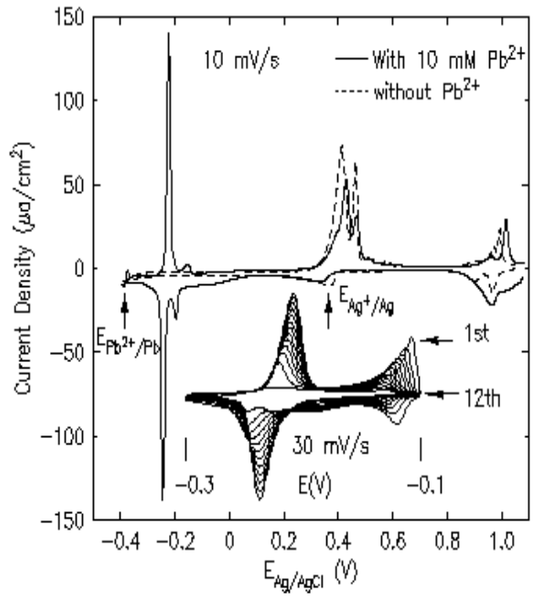

Fig. 1 Linear sweep voltammetry curves for Au(111) in 0.1 M $HClO_4$ containing 0.1 mM Ag^+ . Insert shows the change of Pb UPD feature during the deposition of a Ag monolayer mediated by repeated Pb UPD/stripping cycles.

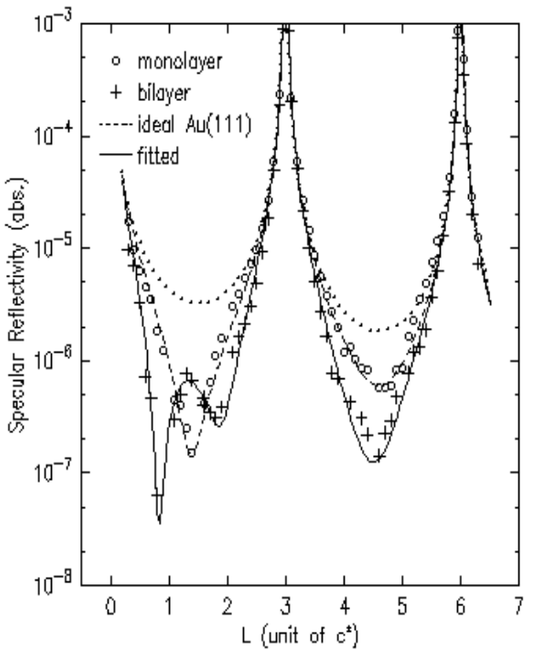

Fig. 2. X-ray specular reflectivity profiles measured for Au(111) after Pb-mediated overpotential deposition of Ag monolayer and bilayer.