Epitaxial Electrodeposition of Metals by Defect Mediated Growth and its Application

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Thin films of various materials are deposited onto the surface of bulk materials (substrates) in order to achieve properties unattainable in the substrates alone. [1] Among the various types of thin films, those with single crystal quality and in registry with the crystallographic orientation of the substrate are called epitaxial films. They are crucial in current technologies ranging from microelectronics to catalyst.

Electrodeposition has merits such as the remarkably low cost and the easy handling but typically results in a rough film which is not suitable to application. In their pioneering work, Sieradzki et al. proposed a new and general method to perform metal epitaxy in electrochemical environment, which was named the defect mediated growth (DMG). [2] In their scheme, the metal of interest is co-deposited with a reversibly deposited mediator metal (Pb^{2+} or Cu^{2+}). The mediator is periodically deposited and stripped from the surface by appropriate cycling of the electrode potential, which spawns a high density of metal clusters on a growing layer and leads to layer-by-layer growth. For Ag/Au(111) and Ag/Ag(111) systems with Pb^{2+} or Cu^{2+} as mediators, they could obtain epitaxial films with considerable thickness (250 ML or more).

While the lattice mismatch between Ag(111) (metallic radius 0.288 nm) and Au(111) (0.288 nm) is negligibly small, that between Cu(111) (0.256 nm) and Au(111) is as large as 11 %; thus the electrodeposition of Cu on Au(111) generally results in rough polycrystalline films. Hence we were motivated by the question whether the DMG method would also produce a heteroepitaxial film for the film/substrate system with large lattice mismatch. [3] When Cu is deposited on Au(111) with Pb as mediator, in situ STM images show that the periodically deposited mediator adlayer spawns a myriad of small metal clusters and leads to flat epilayer. The film quality was confirmed by XRD, AES, and Cyclic Voltammetry of Pb UPD. These overall results show that high-quality epilayer was achieved by DMG. The application of deposited metal to electrode with high quality will be discussed, too.

Reference:

[1] D. L. Smith, *Thin-Film Deposition*, McGraw-Hill: New York (1997).
[2] K. Sieradzki, S. R. Brankovic, N. Dimitrov, *Science*, 284, 138 (1999).
[3] S. Hwang, I.Oh, J. Kwak, *J. Am. Chem. Soc.*, 123, 7176 (2001)