Combined UHV-electrochemistry on Reactive Metal Surfaces: What Can We Learn?

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Combined UHV-electrochemistry (UHV-EC) involves sample transport between the electrochemical cell and the UHV analysis chamber under controlled conditions. Over the past ~25 years, UHV-EC has been used with considerable success to probe chemical and electrochemical reactions at noble and semi-noble metal surfaces, including Ag, Au, Pt and Pd single crystal surfaces. In such cases, the unavoidable exposure of the sample surface to vapor above the electrochemical cell during sample emersion does not significantly obscure chemical information. Technological challenges in areas such as corrosion and ULSI processing, however, require the study of surfaces that are quite reactive towards H_2O vapor, including Fe, Ni, Cu, W and Ta. Uncontrolled sample reaction with H_2O vapor during the emersion process becomes a serious issue, as does the stability of surface oxide/hydroxide layers in UHV.

Data from corrosion/etching studies on Fe[1] and Cu[2] surfaces demonstrate that reactive metal surfaces emersed at different potentials show systematically varied changes in oxide/hydroxide structure. This demonstrates that in spite of sample transfer and exposure to UHV, detailed information regarding electrochemically-induced changes in the surface oxide/hydroxide layer.

Recently, UHV-EC studies of Cu electrodeposition on W, relevant to ULSI applications, have been initiated. A cyclic voltammogram (fig. 1), obtained for a W foil sample cleaned in UHV and then transferred to the electrochemical cell containing a Cu sulfate solution, indicates a Cu reduction peak near –0.24 V (Ag/AgCl), and a broad W oxidation peak near + 0.5 V. XPS data (fig. 2) obtained after sample immersion/emersion under open circuit conditions (OCP = -0.1 V), indicate no substantial W oxidation, but strong sulfate adsorption on the W surface. More detailed spectra (however) demonstrate that the presence of ~ one monolayer of oxygen cannot be discounted. Prospects for detailed UHV-EC studies of Cu electrodeposition on W and other metal surfaces will be discussed.

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References

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Figure 1: Cu E-deposition on clean W ($0.001M\ CuSO_4 + 0.5M\ H_2SO_4$)

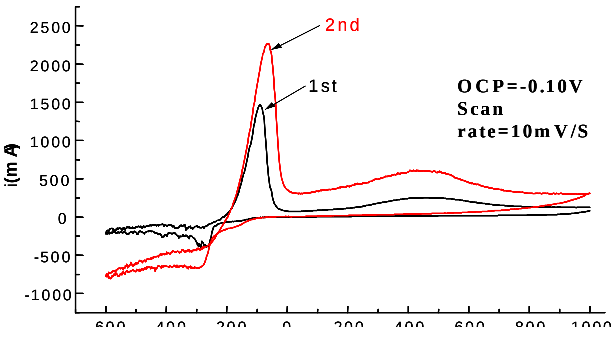

Figure 2: Emersion of W(OCP, -0.1V/Ag/AgCl) (0.001M CuSO4+0.5M H2SO4)