Cu Electrodeposition on W: Surface Effects on Film Nucleation and Growth

J. A. Kelber, J. Liu, C. Wang, S. Rudenja , N. Magtoto, and C. Bjelkevig*
Department of Chemistry, University of North Texas, PO Box 305070, Denton, TX 76203

SEM and electrochemical measurements if Cu nucleation on W electrodes indicate that Cu nucleation size varies with deposition potential in a manner consistent with Ostwald ripening. The evolution of Cu microstructure under electrodeposition conditions is of increasing technological interest as microchip interconnect geometries continue to shrink. The electrodeposition of adherent Cu thin films on W surfaces in the absence of a Cu seed layer has been demonstrated[1]. W is therefore a potential candidate for seedless Cu electrodeposition, and control of Cu film microstructure is therefore of interest. Although the surface mobility of adatoms is generally recognized as important to microstructural evolution during film deposition under UHV conditions, such effects are generally neglected in the modeling of electrodeposition processes. Recent in-situ electrochemical STM measurements[2], however, have demonstrated the mobility of Cu ad-atoms on Cu substrates under acidic conditions.

A cyclic voltammogram (CV) for Cu deposition on W from a purged 0.005M $CuSO_4/H_2SO_4$ (pH = 1.0) solution is shown in figure 1. A Cu reduction peak is observed at –98 mV (vs Ag/AgCl) and a stripping peak is observed at +136 mV. Deposition from this solution at pulsed potentials (t= 10 sec, -500mV < V < -200 mV) produced shiny, adherent films of Cu on W foil electrodes[1]. Substantial variation in film microstructure was observed with varying potential, as shown in figure 2. The film deposited at –200 mV (fig. 2, top) consists of large Cu nuclei (diameter > ~ 1 μ), with no observable Cu deposition between nuclei, and an average thickness of 144 Cu monolayers, based on an integration of the net Cu charge passed[1]. (Striations in the figure are a characteristic of the W foil.) In contrast, deposition at –500 mV (fig. 2, bottom: average thickness 190 Cu monolayers) results in the formation of both large and many small nuclei (diameter << 1μ). The absence of small nuclei at more anodic deposition potentials is consistent with Ostwald ripening, where the greater detachment rate of mobile Cu adatoms from smaller clusters results in the growth of large clusters at the expense of smaller ones. The results shown in figure 2 are also consistent with the demonstrated[2] enhanced mobility of Cu adatoms on Cu at more anodic potentials below the dissolution potential.

This talk will discuss electrochemical, SEM and STM data for electrodeposition on W in comparison with corresponding data on other surfaces surfaces. Results are discussed in light of existing understandings of surface mobility/microstructure relationships in both UHV and aqueous environments.

*Permanent address, Department of Chemistry, University of Texas at Austin, Austin, TX

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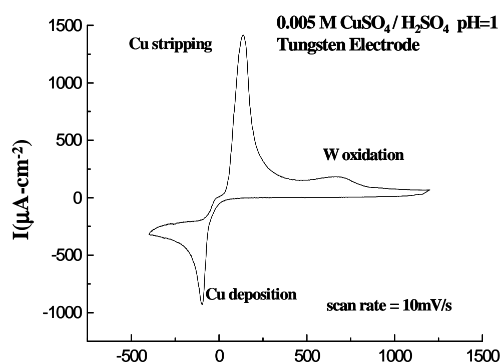

Figure 1; CV data for Cu electrodeposition on clean tungsten

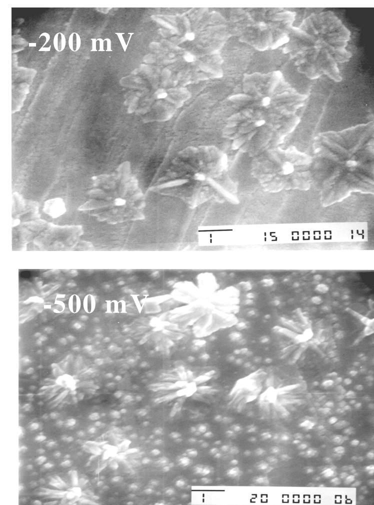

Figure 2: SEM images of Cu films deposited on polycrystalline W from purged 0.05M $CuSO_4/H_2SO_4$ solution (pH = 1) at 10 sec pulses at fixed potentials: (top) film deposited –200 mV vs Ag/AgCl; (bottom) deposited at –500 mV.