Copper Electrodeposition onto Ru Substrates: Effect of Additives

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The potential relevance of Cu electrodeposition onto Ru substrates to future direct metallization of ULSI interconnects is discussed. The impact of additive concentration on the electrochemical nucleation and growth of Cu onto Ru was studied using electrochemical methods as well as scanning electron microscopy. In all cases, Ru was deposited by physical vapor deposition.

Both potentiostatic and galvanostatic electrodeposition was studied, with an emphasis on discerning how the operating conditions affect particle densities during the initial stages of electrodeposition, where three-dimensional island growth appears to be the prevailing mechanism. Furthermore, experimental results are compared with a numerical and several theoretical models[1].

Figure 1 shows the variation of electrical potential during galvanostatic electrodeposition in four different electrolytes. In each case, experiments were carried out at 10 mA cm^{-2}, in a solution of 0.024M $CuSO_4$ and 0.375M H_2SO_4. Additive compositions, when present in the electrolyte are: 50 ppm Cl-, 300 ppm PEG (MW 3350 g/mol), and 1 ppm of SPS.

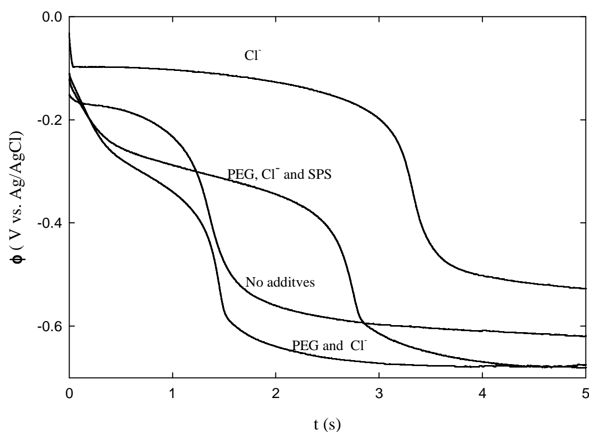

Figure 1. The electrode potential as a function of time for four electrolytes containing no additives, chloride-ions only, PEG and chloride, or PEG, chloride and SPS. The applied current density in all cases was 10 mA cm^{-2}.

In addition to modifying the potential-current relationship, additives affect particle density. The relationship between particle density and additive composition is a primary focus of the presentation.

Figures 2 and 3 show SEM images after 5 sec. of potentiostatic deposition at -0.05V *vs.* Ag/AgCl. In figure 2, results are show for an electrolyte containing 0.024M $CuSO_4$ and 0.375M H_2SO_4, 50 ppm Cl-, and 300 ppm PEG (MW 3350 g/mol). In figure 3, 1 ppm of SPS is also added to the electrolyte. Consistent with previous results on Tantalum surfaces, the addition of SPS results in a decrease in particle density.

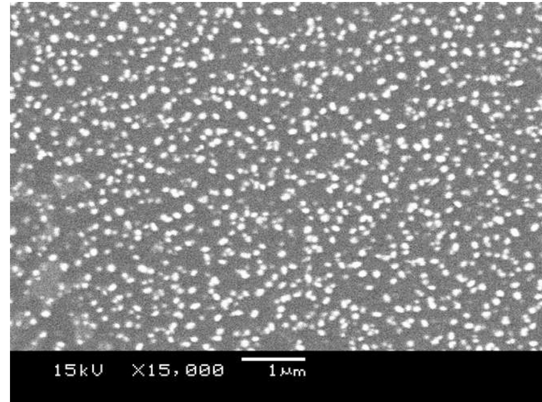

Figure 2 SEM images of Cu particles electrodeposited on a 10-nm thick, PVD Ru substrate. The bath composition was containing 0.024M $CuSO_4$ and 0.375M H_2SO_4, 50 ppm Cl-, and 300 ppm PEG (MW 3350 g/mol). Applied potential was -0.05 V *vs* Ag/AgCl.

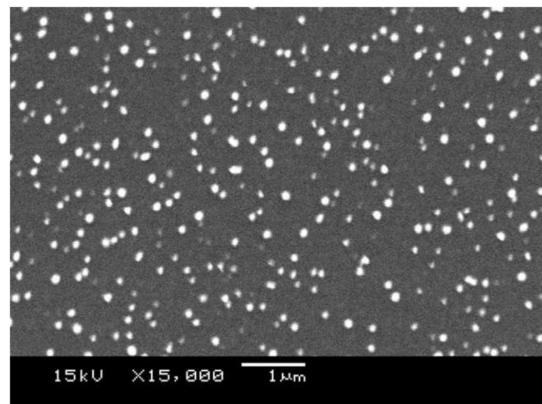

Figure 3 SEM images of Cu particles electrodeposited on a 10-nm thick, PVD Ru substrate. All conditions identical to those used to obtain the results in figure 2, except 1 ppm SPS is added to the electrolyte.

References

1. Y. Cao and A. C. West, *Journal of the Electrochemical Society*, 149(4), C223 (2002).