Electrochemical Deposition of Copper on TaN

Aleksandar Radisic,[1] Alan C. West,[2]
and Peter C. Searson[1]

[1]Department of Materials Science and Engineering
The Johns Hopkins University
Baltimore, MD 21218

[2]Department of Chemical Engineering
Columbia University
New York, NY 10027

The goal of this work is to explore the possibility of electrochemical deposition of high quality copper films directly on diffusion barrier layers without the use of copper seed layer. In this paper we report on the growth of copper on TaN from sulfate, fluoroborate, methanesulfonate, pyrophosphate, and EDTA based copper solutions.

We show that under appropriate experimental conditions, a high density of copper nuclei can be obtained on unpatterned TaN surface. Furthermore, continuous copper films can be obtained by subsequent growth of the clusters at low overpotentials under kinetic or mixed control.

Figure 1 shows the current-potential curves for copper deposition on TaN from various solutions. The onset of the reduction of copper occurs at much lower overpotentials for acidic than alkaline solutions. The copper deposition peak is immediately followed by the onset of hydrogen evolution. In the case of sulfate solution the copper deposition peak and the onset of hydrogen evolution overlap.

Figure 2 shows current-transients for copper deposition from methanesulfonate bath. The deposition of copper on TaN follows the Volmer-Weber 3-D island growth mechanism, and by applying more negative potentials we were able to obtain nucleus densities as high as 10^{11} cm^{-2} leading to approximately 30 nm thick copper films.

Preliminary results of copper deposition onto TaN patterned structures are shown in Figure 3.

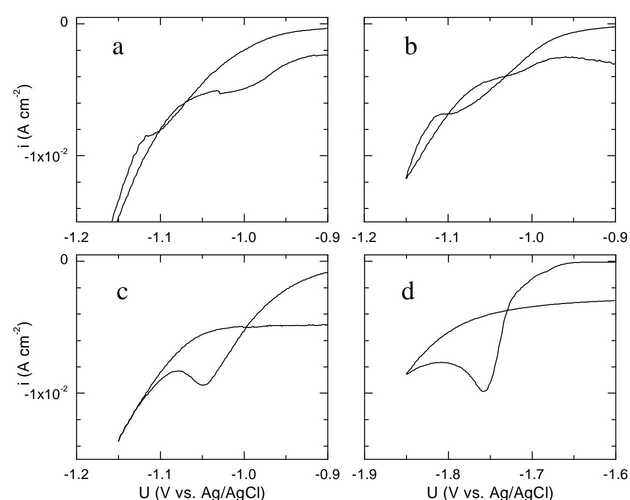
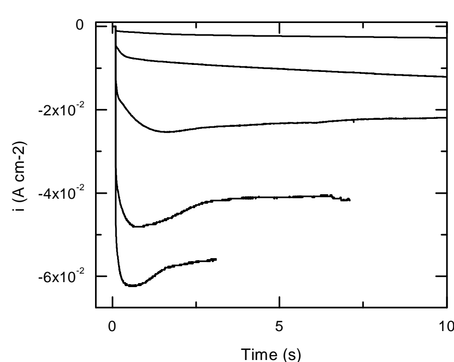


Figure 1. Copper deposition peak region in current potential curves for copper deposition from: a) sulfate (pH≈1), b) sulfate with additives (polyethylene glycol, Cl^- ions and bis(3-sulfopropyl) disulfide) (pH≈1), c) fluoroborate (pH≈1), and d) EDTA based solution (pH≈13.5).



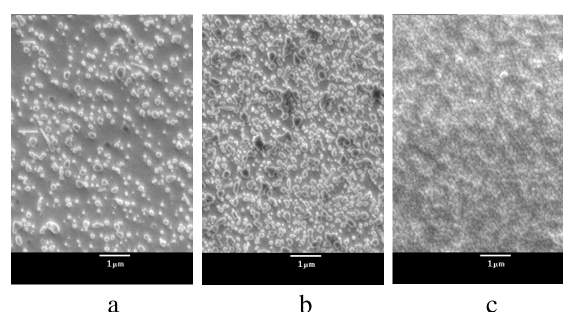


Figure 2. Current transients for copper deposition on TaN from copper-methanesulfonate solution at: -1.0 V, -1.1 V, -1.2 V, -1.3 V and -1.4 V (vs. Ag/AgCl reference electrode). SEM images of copper nuclei deposited at a) –1.0 V, b) -1.2 V, and c) -1.4 V.

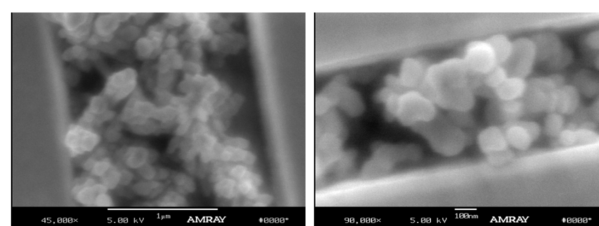


Figure 3. Top view of the copper nuclei deposited into the trenches of the patterned TaN diffusion barrier layer from fluoroborate solution.