

Control of Electroless Cobalt(Tungsten) Damascene Plating Baths

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Use of electrolessly deposited Co and Ni as barrier and capping layers for Cu circuitry in the Damascene semiconductor chip process¹ is currently under investigation.^{2,3} Such metals have higher electrical conductivity compared to metal nitride materials, which enables Cu to be electrodeposited directly on the barrier layer without the use of a Cu seed layer. Higher barrier layer conductivity also reduces the overall resistance for circuit traces of a given cross-sectional area. In addition, electroless deposition provides highly conformal coatings, even within ultra-fine trenches and vias, so that the overall coating thickness can be minimized. Electroless Co and Ni baths being investigated for Damascene barrier deposition typically also contain a refractory metal (e.g., W, Mo or Re), which co-deposits with the Co or Ni and increases the maximum temperature at which effective barrier properties are retained.

A typical bath for electroless deposition of Damascene barrier layers contains 0.1 M cobalt chloride or sulfate, 0.2 M sodium hypophosphite, 0.03 M sodium tungstate, 0.5 M sodium citrate, 0.5 M boric acid, and a small amount of a surfactant. Such Co(W,P) baths typically operate at about pH 9 and a temperature of 85° - 95°C. A seed layer of Pd is typically used to initiate electroless deposition on silicon oxide or Cu, but direct deposition of capping layers of Co(W,P) on Damascene copper circuits was recently reported³ for a Co(W,P) bath employing two reducing agents. For both bath types, close control of the bath constituents is essential to obtaining consistently good deposits.

The reducing agent concentration in a Co or Ni electroless plating bath can be determined from the increase in the rate of Cu electrodeposition from an acid Cu electrodeposition solution produced by addition of the reducing agent. The Cu electrodeposition rate is measured by the CVS method.⁴ In practice, the CVS stripping peak area (A_r) is first measured for the Cu electrodeposition solution without reducing agent, termed $A_r(0)$, and then after addition of a plating bath sample (diluted with water or acid) and/or a reducing agent calibration solution. The normalized rate parameter $A_r/A_r(0)$ is used to determine the reducing agent concentration by reference to a calibration curve, or by the linear approximation technique.⁵

The efficacy of this approach was demonstrated via CVS measurements of A_r at a rotating Pt disk electrode in an acid copper sulfate solution (25°C) containing 70 g/L copper sulfate pentahydrate, 175 g/L sulfuric acid, 1 g/L sodium citrate dihydrate, and 50 mg/L chloride ion. CVS measurements were made using a Qualilab QL-10 plating bath analyzer (ECI Technology, Inc.).

Figures 1 and 2 show calibration plots for hypophosphite and DMAB, respectively. Good sensitivity to both reducing agents is evident. Such calibration plots

were also shown to be valid for analysis of proprietary Co-W (citrate) electroless plating baths employing the hypophosphite alone, and those employing both hypophosphite and DMAB reducing agents. In addition, procedures have been developed for analyzing the other constituents of electroless Co(W,P) baths.

References:

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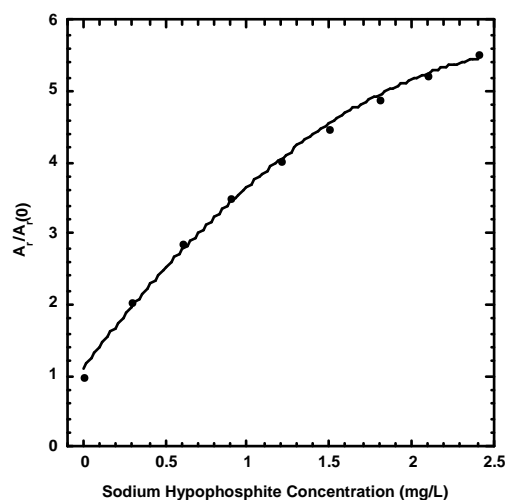


Fig.1 Calibration plot for hypophosphite reducing agent in acid copper electrodeposition solution.

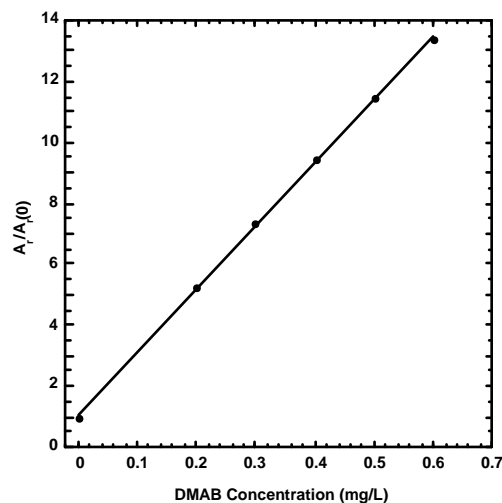


Fig. 2 Calibration plot for DMAB reducing agent in acid copper electrodeposition solution.

