

Detection of Suppressor Breakdown Contaminants in Copper Plating Baths

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Acid copper sulfate baths are employed in the "Damascene" process¹ to electrodeposit Cu within fine trenches and vias in dielectric material on semiconductor chips. Two organic additives are required to provide bottom-up filling of the Damascene features. The "suppressor" additive, which is typically high-molecular-weight (MW) polyethylene glycol (PEG), adsorbs strongly on the Cu cathode surface, in the presence of chloride ion, to form a film that sharply increases the overpotential for Cu deposition. The "anti-suppressor" additive counters the suppressive effect of the suppressor to provide the accelerated deposition within trenches and vias needed for bottom up filling.

Close organic additive control needed for Damascene plating is provided by Cyclic Voltammetric Stripping (CVS) analysis, which involves alternate plating and stripping of Cu at a Pt rotating disk electrode. The additives are detected from the effect that they exert on the electrodeposition rate measured via the Cu stripping peak area (A_r). The suppressor concentration is typically determined by CVS response curve or dilution titration analysis.² During Damascene Cu plating, however, the suppressor polymer chains are cleaved to produce lower-MW species that are less effective as suppressors and interfere with the electrodeposition process. These suppressor breakdown contaminants must also be controlled if high quality Damascene deposits are to be consistently obtained.

The relative concentrations of the active suppressor and the suppressor breakdown contaminants can be determined by performing the CVS dilution titration analysis using two different negative potential limits. The CVS rate parameter (A_r) is first measured in the supporting electrolyte to provide $A_r(0)$, and then after each standard addition of a known volume fraction of the plating bath sample, until an endpoint value of 0.5 for $A_r/A_r(0)$ is reached. The endpoint volume fraction for the more negative potential limit yields a direct measure of the active suppressor additive concentration since the suppressor breakdown contaminants are not effective at suppressing the Cu deposition rate at the more negative potentials. The endpoint volume fraction for the less negative potential limit yields a measure of the concentration of the active suppressor additive plus the suppressor breakdown contaminants. The ratio of the two endpoint volume fractions provides a relative measure of the breakdown contaminant concentration.

The efficacy of this approach was demonstrated via CVS dilution titrations using a rotating Pt disk electrode in a typical acid Cu supporting electrolyte (25°C) containing 75 g/L $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, 175 g/L H_2SO_4 , and 50 ppm chloride ion. PEG's of various MW's were added to simulate typical suppressor additives and breakdown contaminants. CVS measurements were made using a Qualilab QL-10[®] plating bath analyzer (ECI

Technology, Inc.). The working electrode potential was scanned to -0.400 V vs. SSCE to detect high-MW PEG species and -0.225 V to also detect low-MW PEG species.

Dilution titration results for 10 μM PEG solutions demonstrated that PEG species of less than 1000 MW have relatively small effects for the -0.400 V limit (very large endpoint volume fractions), whereas the low-MW PEG species are readily detected with the -0.225 V limit (relatively small endpoint volume fractions). In both cases, the endpoint volume fractions decreased as the MW was increased, indicating that the higher-MW PEG polymers are more effective at suppressing the Cu deposition rate on a per molecule basis. Consequently, cleavage of high-MW polymers during Cu plating tends to decrease the activity of the suppressor additive.

Figure 1 shows a plot of the ratio of the endpoint volume fraction for the -0.400 V potential limit to that for the -0.225 V limit as a function of the weight fraction of the 900 MW PEG species in mixtures of 900 and 10,000 MW species. Good sensitivity of this ratio to the relative concentration of the 900 MW species in the presence of the 10,000 MW species is evident. This plot is analogous to a calibration curve for the low-MW species but such plots usually cannot be used for actual plating baths, which contain PEG species having a wide MW range. In practice, the endpoint volume fraction ratio for two CVS potential limits provides a reliable relative measure of the concentration of the suppressor breakdown contaminants, permitting bleed and feed rates to be appropriately adjusted

References:

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2. W. O. Freitag, C. Ogden, D. Tench and J. White, *Plating Surf. Fin.* **70**(10), 55 (1983)

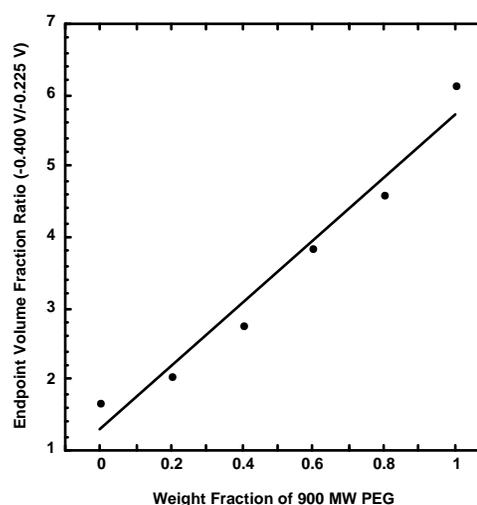


Fig. 1 Ratio of CVS endpoint volume fraction at a -0.400 V potential limit to that at -0.225 V as a function of the weight fraction of 900 MW species in 1.0 g/L PEG solutions also containing 10,000 MW species.

